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The Cyclic "Silver-Diphos" Motif $[Ag_2(\mu\text{-diphosphine})_2]^{2+}$ as a Synthon for Building up Larger Structures

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The dinuclear, cyclic structural motif $[Ag_2(\text{diphosphine})_2]^{2+}$, here termed the "silver-diphos" motif, previously observed in many diphosphine−silver complexes, has been investigated as a synthon for building up larger structures such as coordination cages and polymers. A series of ligands containing one to four meta-substituted diphosphine groups, attached via a central core, has been synthesized from the corresponding fluoroarenes by reaction with $KPPh_2$. Upon reaction with silver salts, the target synthon is adopted by meta-substituted diphosphines 1,3-bis(diphenylphosphino)benzene (**L1**), 2,6-bis(diphenylphosphino)benzonitrile (**L2**), and 3,5-bis(diphenylphosphino)benzamide (**L3**), each of which gives a single species in solution consistent with the expected dimeric complexes $[Ag_2L_2(\text{anion})_2]$. X-ray crystal structures of $[Ag_2(\mathbf{L1})_2(OTf)_2]$ and $[Ag_2(\mathbf{L2})_2(SbF_6)_2]$ confirm the adoption of the silver-diphos motif in the solid state. Amide-functionalized diphosphine **L3** forms a hydrogen-bonded chain structure in the solid state via the amide group. A discrete boxlike cage $[Ag_4(\mathbf{L4})_2][SbF_6]_4$ based on two silver-diphos synthons is formed when the tetraphosphine $Ph_2Sn\{3,5\text{-bis(diphenylphosphino)benzene}\}_2$ (**L4**) reacts with silver(I). Its single-crystal X-ray structure reveals a central cavity of minimum diameter, ca. 5.0 Å, which contains a single SbF_6^- counterion disordered over two sites. In contrast to the highly selective behavior of the di- and tetra-phosphines **L1**−**L4**, the heptaphosphine $P\{3,5\text{-bis(diphenylphosphino)benzene}\}_3$ **L5** and the hexaphosphine $PhSn\{3,5\text{-bis(diphenylphosphino)benzene}\}_3$ **L6** give dynamic mixtures upon reaction with silver salts in solution. This nonspecific behavior is rationalized by the fact that their diphosphine groups are not appropriately disposed to form stable discrete structures based on the silver-diphos synthon. By contrast, the octaphosphine $Sn\{3,5\text{-bis(diphenylphosphino)benzene}\}_4$ **L7** does selectively form a single, discrete, highly symmetrical product in solution, $[Ag_4(\mathbf{L7})(OTf)_4]$. In this case, the ligand unexpectedly adopts an interarm tetra-chelating coordination mode, resulting in a continuous 24-membered ring around the periphery of the molecule. To understand the adoption of this unusual coordination mode, the alternative diphosphine $Ph_2Sn(3\text{-diphenylphosphinobenzene})_2$ **L8**, which models a single interarm chelating site of **L7**, was also investigated. By contrast to **L7**, its coordination was nonspecific, giving mixtures of silver complexes upon reaction with AgOTf. The selective interarm chelation by **L7** may therefore be stabilized by the continuous coordination ring in $[Ag_4(\mathbf{L7})(OTf)_4]$; that is, the four chelating sites can be thought of as acting in a cooperative manner. Alternatively, interarm steric repulsions between phenyl groups may favor interarm chelation. Overall, we conclude that, if the diphosphine groups are appropriately articulated to act independently (i. e., they are adequately separated and oriented), the silver-diphos synthon can be a useful tool for the coordination-based self-assembly of larger structures.

Introduction

Studying the coordination behaviors of multidentate ligands is important for expanding our knowledge and understanding of coordination-based self-assembly. It is valuable to identify examples of unusual self-assembly, as well as synthons which may reliably be employed for the design of new discrete or polymeric coordination structures.[1–3]

While *N*- and *O*-donor ligands have been extensively studied in coordination self-assembly,[1,2] tertiary phosphines have been less explored.[3] Despite this, several unique

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structures and insights have resulted from the study of these ligands in this context. These include the selective assembly of unsaturated partial polyhedral structures,[3a] polar mixed-ligand cages,[3a,b] cages with external calixarene-like binding sites,[3c] exohedral anion templation,[3d] nanoporous phases,[3e] and the identification ring-opening polymerization relationships between discrete and polymeric structures.[3f] This rich diversity of behavior results in part from the relatively bulky and irregular shapes of these building blocks, as well as their flexibilities in adopting both divergent and convergent bridging conformations. In addition, their amenability to ^{31}P NMR spectroscopy aids greatly in gaining insight into behavior in solution.

Here, we describe an investigation into the utility of the cyclic [Ag$_2$(diphosphine)$_2$]$^{2+}$ (here termed "silver-diphos") structural motif for building up larger structures in a rational way. This structural motif (Figure 1a) has previously been found to be adopted by silver complexes of a wide range of flexible diphosphines with oligomethylene backbones[4] but has not, to our knowledge, been probed as a usable "synthon" for building up larger structures. It is topologically closely related to the widespread classical carboxylic acid dimer (Figure 1b)[5] as well as the silver carboxylate synthon recently described by Brammer et al.[6] (Figure 1c). Larger structures could be built up by making further connections on diametrically opposite points on the backbones of the two diphosphines. A promising backbone type in this regard would be 1,3,5-trisubstituted aryl rings, with the two phosphino groups in mutually meta positions, as well as being meta to the backbone functionality (X in Figure 1d). We describe here an investigation into a series of ligands which contain from one to four such diphosphine groups (specifically 3,5-bis(diphenylphosphino)benzenetri-yl) attached to a central core via this position, as shown in Figure 2.

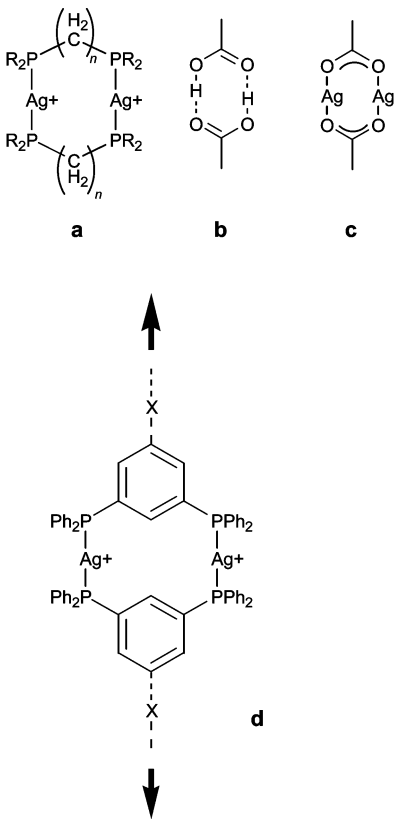

Figure 1. Cyclic silver-diphosphine structures (**a**), topologically related synthons based on carboxylic acids (**b**) and silver carboxylates (**c**), and proposed use of meta-substituted diphosphines to build up larger structures investigated in this paper (**d**).

Results and Discussion

Synthesis and Characterization of Ligands Containing *meta*-Diphosphine Groups. All phosphines were synthesized from their corresponding fluoroarenes by reaction

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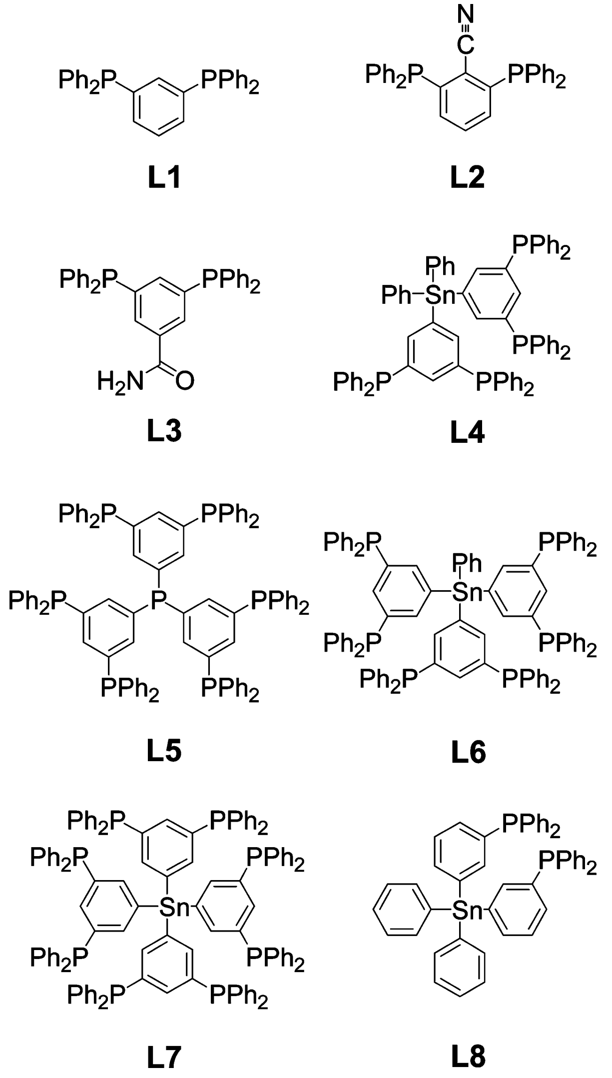


Figure 2. Multidentate ligands **L1**−**L7** bearing *meta*-diphosphine units and diphosphine **L8** which models a single interarm chelate coordination site of **L7**.

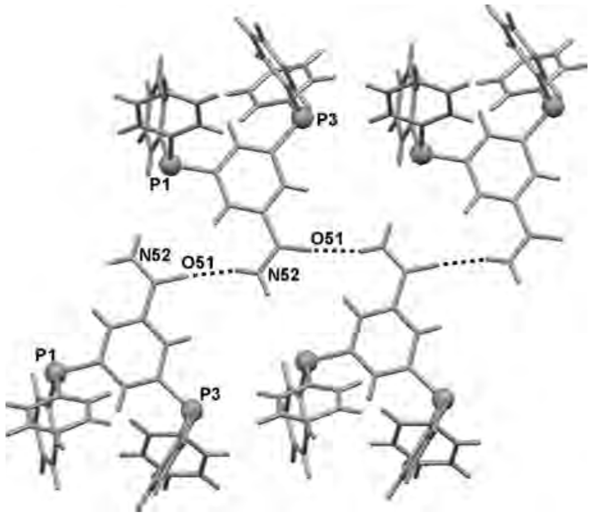
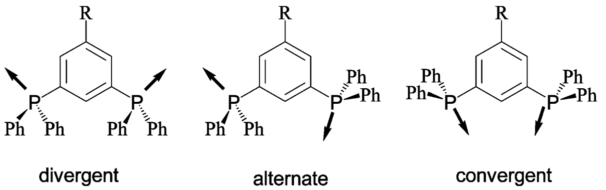


Figure 3. X-ray crystal structure of **L3** showing the H-bonded chain formed by the amide groups.



divergent alternate convergent

Figure 4. Formal representations of the possible orientations of the lone pairs for *meta*-diphosphine groups.

with potassium diphenylphosphide in THF. For 1,3-bis(diphenylphosphino)benzene ligand **L1**, this is different from the previously reported method.[7] **L1** was isolated in 90% yield as a viscous liquid, similar to its description in the previous report. 2,6-Bis(diphenylphosphino)benzonitrile **L2** was prepared according to the literature procedure,[8] starting from the corresponding difluoride. 3,5-Bis(diphenylphosphino)benzamide **L3** was obtained as a white crystalline solid in 82% yield following recrystallization from methanol. Single crystals suitable for X-ray diffraction were obtained by the slow cooling of a methanolic solution of **L3**. The X-ray crystal structure (Figure 3) displays H-bonding between amide groups on adjacent molecules to give a chain with one NH···O hydrogen bond per molecule (with a N···O distance of 2.879(12) Å and a N−H···O angle 166.2(7)°). The most common amide packing mode, the cyclic H-bonded dimer (analogous to the carboxylic acid dimer), is not adopted; however, this type of chain has also been recognized as a recurring packing motif for amides.[9] Rotation about the bond between phosphorus and the central aryl ring can lead to a variety of lone pair orientations, which in their extreme manifestations can be termed divergent, alternate, or convergent, as illustrated in Figure 4. The convergent conformation is necessary to form the silver-diphos motif, but it is interesting that the divergent conformation is also possible for noncoordinated meta-substituted diphosphines, as seen in this crystal structure. The packing mode adopted is likely to be a tradeoff between the amide H bonding and the packing of the phenyl rings. It is possible that both the conformation (divergent lone pairs) and the extended packing (linear versus dimeric H-bonding motif) will have been influenced by the preferred packing modes of the bulky aryl substituents in the lattice.

The tetraphosphine bis-3,5{bis(diphenylphosphino)benzenetri-yl}diphenylstannane **L4** was prepared by reaction of the corresponding tetrafluoride with four equivalents of potassium diphenylphosphide, to yield an analytically pure white solid in 69% yield. The ^{31}P NMR spectrum showed a single resonance at −4.8 ppm. The new heptaphosphine with one central and six peripheral phosphine groups, tris{3,5-bis(diphenylphosphino)benzenetri-yl}phenyl phosphine **L5**, was prepared by reaction of the corresponding hexafluoride precursor, tris(3,5-difluorophenyl)phosphine, with six equivalents of potassium diphenylphosphide and was obtained as a white powder in 84% yield following workup from methanol. The fast atom bombardment mass spectrometry (FAB-MS) spectrum of the product showed a signal at 1367

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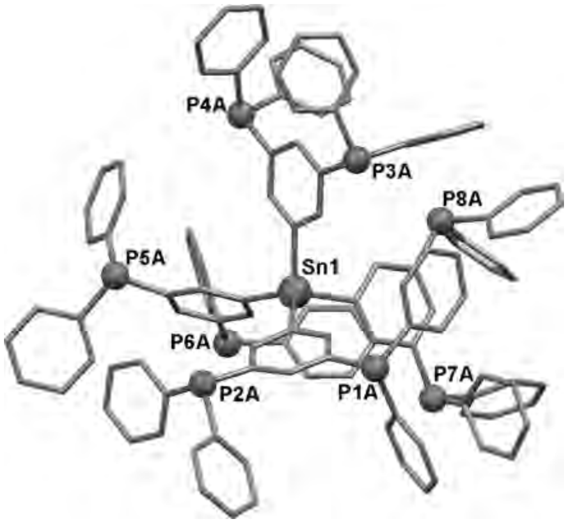

Figure 5. View of one of the independent octaphosphine molecules in the crystal structure of **L7**. H atoms have been omitted for clarity.

m/*z*, indicating the molecular ion. The ^{31}P NMR spectrum showed a signal at −2.3 ppm for the central phosphorus atom and a more intense signal at −3.6 ppm for the six equivalent peripheral phosphine groups. The ^{1}H NMR spectrum showed complex overlapping multiplets of 69 aromatic hydrogen atoms from 7.23 to 7.06 ppm. The ^{13}C NMR spectrum showed a number of unresolved peaks from 139.3 to 138.9 ppm due to overlapped multiplets, which account for the carbon atoms in the three phenyl rings attached to the central phosphorus atom. The carbon signals of the exterior phenyl groups are assignable from their multiplicities and the magnitudes of their ^{31}P,^{13}C coupling constants.

The hexaphosphine tris{3,5-bis(diphenylphosphino)benzenetri-yl}phenyl stannane **L6** was prepared from tris{3,5-bis(difluorophenyl)phenylstannane. A workup with methanol and column chromatography yielded **L6** as a cream-colored solid in 71% yield. The octaphosphine tetrakis{3,5-bis(diphenylphosphino}benzetriyl)stannane **L7** was prepared by the phosphination of tetrakis(3,5-difluorophenyl)stannane and obtained as a white powder in 81% yield following a workup from methanol. The FAB-MS spectrum showed a peak at 1900 *m*/*z*, which corresponds to the molecular ion. The ^{31}P NMR spectrum showed a single resonance at −5.2 ppm. Single crystals of **L7** suitable for X-ray diffraction were obtained by slow diffusion from an acetone solution.

Two independent molecules were found in the crystal, one of which is shown in Figure 5. The ligand displays the expected tetrahedral geometry at the central tin atom, albeit distored, with with C···Sn···C bond angles ranging from 102.32(15)° to 114.35(15)°. There are eight independent *meta*-diphosphine units in the crystal, four of which adopt divergent conformations, three of which adopt alternate conformations, and one adopting a convergent conformation.

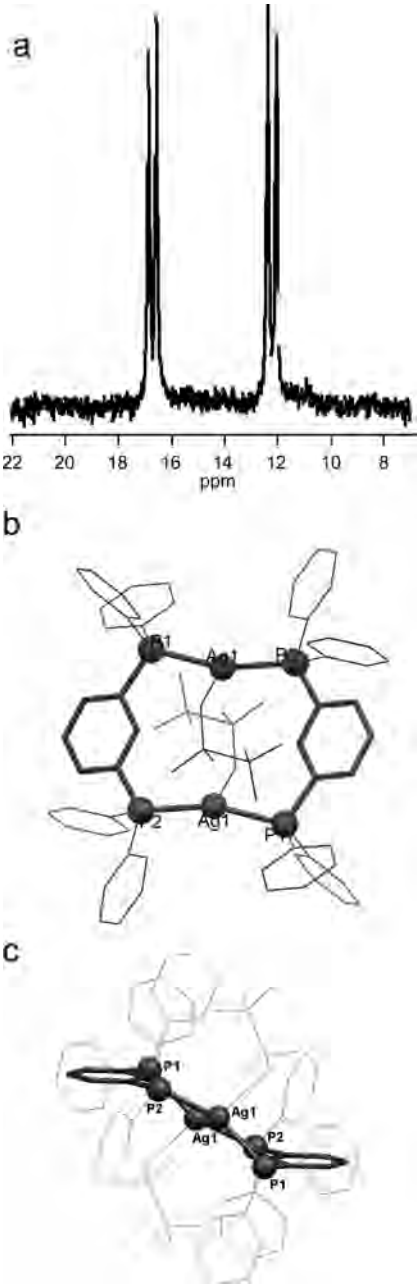

Figure 6. (a) ^{31}P NMR spectrum of $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$ in $CDCl_3$/CH_3NO_2 (4:1). (b) X-ray crystal structure of $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$. (c) View to emphasize the stepped conformation of the central rings.

Coordination to Silver(I). Dimeric Complexes with Diphosphines L1, L2, and L3. 1,3-Bis(diphenylphosphino)benzene **L1** has previously been demonstrated to form dimeric dimetallic rings with platinum(II) and palladium(II) via the M_2(diphos)$_2$ bridging coordination mode. These structures are clearly analogous to the silver-diphos motif.[10] A $CDCl_3$/CH_3NO_2 (4:1) solution containing equimolar amounts of **L1** and AgO_3SCF_3 gave a ^{31}P NMR spectrum with characteristic one-bond couplings to the spin 1/2 silver isotopes ^{107}Ag and ^{109}Ag (Figure 6).

The complex exhibited a distinctive downfield chemical shift (14.5 ppm), relative to that of the free ligand. The magnitude of the coupling constant $^{1}J(^{109}\mathrm{Ag},^{31}\mathrm{P}) = 587$ Hz indicates that two phosphorus atoms coordinate at each silver

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center.[11] **L1** reacted also with other silver(I) salts in a mixture of $CDCl_3/CH_3NO_2$ (4:1), again to give characteristic one-bond coupling to ^{107}Ag and ^{109}Ag in ^{31}P NMR spectra at room temperature. However, use of the more strongly coordinating solvent mixture $CDCl_3/CH_3CN$ (4:1) gave ^{31}P NMR spectra which were broader, in which $^{107/109}Ag,^{31}P$ coupling was unresolved at room temperature. This suggests that acetonitrile in excess can compete with the phosphine for coordination at the silver(I) centers causing some Ag−P dissociation. Chemical shift and coupling constant data are summarized in the experimental section. Crystals suitable for X-ray diffraction studies were grown by the slow diffusion of diethyl ether into a 0.044 M solution of $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$ in $CDCl_3/CH_3NO_2$.

The X-ray crystal structure (Figure 6) confirms the expected cyclic dimeric structure. Two diphosphine ligands bridge the two silver ions, with an inversion center at the center of the molecule. The H···H distance between the two central rings of the ligands is 3.85(2) Å, and the Ag···Ag distance is 4.99(3) Å, both of which are too large for any significant interaction.[12] However, there is a short O···H contact of 2.38(2) Å between each of these H atoms and O atoms of the triflate anions, which may help to stabilize the structure. The central phenyl rings do not point directly toward each other, but adopt a "stepped" conformation (Figure 6c). This is similar to that seen in the platinum complex $[(PtCl_2)(\mathbf{L1})_2]$[10] and the nanoporous silver polymer based on 1,3,5-tris(diphenylphosphino)benzene.[3e] The coordination at silver is not linear, but slightly bent with a P−Ag−P angle of 155.80(5)°. The two triflate anions each coordinate to different silver centers, in terminal monodentate fashion, with Ag−O distances of 2.586(4) Å.

Although the nitrile-diphosphine **L2** has been previously reported,[6] its coordination chemistry has not been investigated, to our knowledge. It provides an interesting test of the silver-diphos synthon since the nitrile group could potentially interfere sterically or via coordination to silver. When **L2** was reacted with AgO_3SCF_3, in a 1:1 ratio in $CDCl_3/CH_3NO_2$ (4:1), characteristic one-bond coupling to ^{107}Ag and ^{109}Ag is seen in the ^{31}P NMR spectrum. Relative to the free ligand, the complex exhibited a downfield chemical shift of 9.7 ppm with $^1J(^{109}Ag,^{31}P) = 587$ Hz, again, indicating the coordination of two phosphorus atoms to each silver center. The FT-IR spectrum of the complex showed two absorptions due to nitrile groups, one at 2211 cm^{-1} due to the ligand itself and another at 2267 cm^{-1} most likely due to residual acetonitrile used in the crystallization coordinated to the Ag centers (see below).

Crystals suitable for X-ray diffration were obtained by the slow diffusion of diethyl ether into a solution of $[Ag_2(\mathbf{L2})_2][SbF_6]_2$ in $CHCl_3/CH_3CN$. The X-ray crystal structure showed three independent dimeric structures (Figure 7a). The silver-diphos motif is present in all three individual dimeric molecules, with two silver ions bridged by two diphosphine ligands. The main difference between the dimers relates to additional coordination of acetonitrile. Two of the dimers contain centers of symmetry with one molecule of acetonitrile coordinated at each silver(I) center. In one of the dimers, the coordination is approximately linear; that is, the C≡N−Ag angle is 178(3)°. In the other, the acetonitrile coordination is angled; that is, the C≡N−Ag angle is 132(3)°. The third dimer is noncentrosymmetric, with two acetonitrile molecules coordinated to one silver(I) center and none to the other. Despite the asymmetry of the acetonitrile coordination in this dimer, the ring structure is not greatly distorted, with P−Ag distances of 2.408(7) and 2.399(7) Å for the two-coordinate AgP_2 center, being similar than the 2.446(7) and 2.439(7) Å P−Ag distances at the AgP_2N_2 center. The P−Ag−P angles differ more notably, however, at 165.3(3) Å for the AgP_2 center and 145.3(3) Å for the AgP_2N_2 center. Each dimer adopts the same type of stepped conformation as observed for $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$. This conformation is in fact imposed by the need to accommodate the two nitrile groups (Figure 7b). The interligand N···C distances of the nitrile groups are 3.28(10), 3.26(10) and 3.04(10) Å for each of the three dimers which are similar to the combined van der Waals radii (1.70 for C, 1.55 for N gives 3.25 Å).[13]

The three dimers differ only slightly in their P−Ag bond lengths, which range from 2.399(7) to 2.448(7) Å and are comparable to those in $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$. The P−Ag−P angles in the three dimers range from 141.7(2) to 165.3(3)°. These angles are also comparable to those of $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$. The Ag···Ag distances within the three dimers, however, are 5.88(15), 6.12(15), and 5.57(15) Å, which are on average almost 1 Å larger than that in $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$ (Ag···Ag = 4.99(3) Å). This may be attributed to the steric bulk of the nitrile groups at the center of these dimers or the coordination of acetonitrile at the silver centers.

Ligand **L3** is of interest since it can potentially exhibit crystal packing which is directed both by the silver-diphos synthon and by hydrogen bonding via the amide group. $[Ag_2(\mathbf{L3})_2(O_3SCF_3)_2]$ was prepared by reaction of **L3** with one equivalent of silver triflate in pure acetonitrile. The use of this coordinating solvent was necessary because of the lower solubility of **L3**. The ^{31}P NMR spectrum showed two broad signals at room temperature without resolved phosphorus−silver coupling, indicating P−Ag dissociation on the NMR time scale. This is expected due to the large excess of coordinating solvent present. However, on cooling to −30 °C, a single phosphorus environment with characteristic, sharp one-bond coupling to ^{107}Ag and ^{109}Ag was observed, with $^1J(^{109}Ag,^{31}P) = 496$ Hz, which indicates the coordination of two phosphorus atoms to each of the silver centers. It is likely therefore that the silver-diphos motif is adopted by this complex in solution, in common with **L1** and **L2**. The complex was isolated as a white powder by the addition of excess diethyl ether to an acetonitrile solution. The FAB-MS spectra showed peaks at 1343 and 596 *m/z*, which correspond to $[Ag_2(\mathbf{L3})_2(O_3SCF_3)]^+$ and $[Ag_2(\mathbf{L3})_2]^{2+}$, re-

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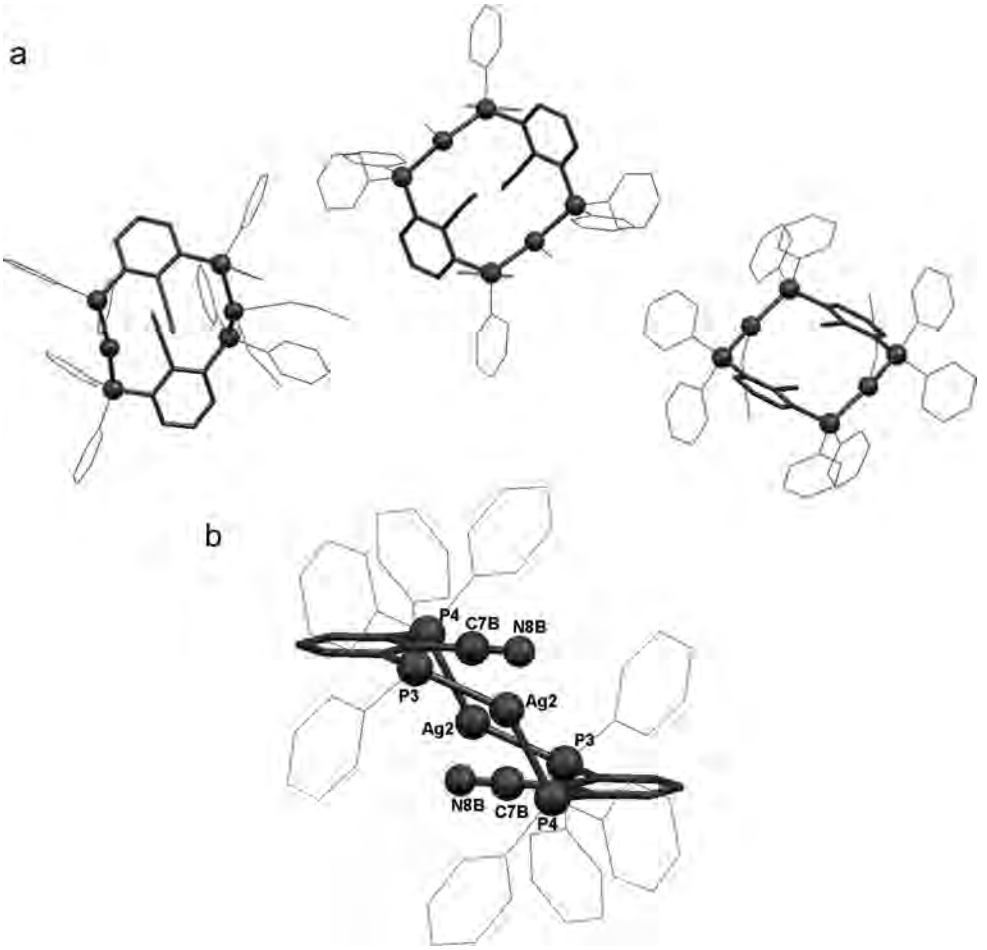


Figure 7. (a) The molecular structures of the three independent dimers found in the crystal of $[Ag_2(\mathbf{L2})_2(SbF_6)_2]$. (b) View to emphasize the stepped conformation enforced by the presence of the nitrile functions. Hydrogen atoms, SbF_6 counterions, and solvent molecules have been omitted for clarity.

spectively. Unfortunately, crystals of the complex suitable for X-ray diffraction could not be obtained.

Cage Complex Based on Tetraphosphine L4. The tetraphosphine **L4** has two *meta*-diphosphine arms connected through a diphenyl tin group. The arrangement of the diphosphine groups should allow for the bridging coordination mode as seen for **L1**, **L2**, and **L3**, between two or more **L4** ligands. This could lead to either discrete or polymeric structures, as shown in Figure 8a.

The reaction of **L4** with two equivalents of silver triflate in $CDCl_3/CH_3NO_2$ (4:1) gave a solution exhibiting a sharp ^{31}P NMR spectrum, indicating a single phosphorus environment, with well-resolved $^{107}Ag,^{31}P$ and $^{109}Ag,^{31}P$ coupling. The $^{109}Ag,^{31}P$ coupling constant of 574 Hz indicates that two phosphorus atoms bond to each silver center. The FAB-MS spectrum for the silver hexafluoroantimonate complex showed a peak at 1615 *m*/*z* which corresponds to the $[Ag_4(\mathbf{L4})_2(SbF_6)_2]^{2+}$ dication. Crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether into a $CHCl_3/CH_3NO_2$ (4:1) solution of **L4** and $AgSbF_6$. A crystal structure determination revealed the discrete boxlike cage structure shown in Figure 8b, consistent with the solution state ^{31}P NMR and FAB-MS spectra. The bridging coordination mode of each diphosphine arm is analogous to that seen in the disphosphine complexes described above. However, the conformation of these motifs is necessarily "arched" rather than "stepped", in order to form a discrete rather than polymeric structure, which indicates a significant aspect of the flexibility of the silver-diphos motif. The interior C−Sn−C angle of 110.2(2)° is, within error, the same as the exterior C−Sn−C angle of 109.8(3)° between the phenyl groups, suggesting very little strain about the tin centers. The silver centers are almost linear, with P−Ag−P bond angles of 169.72(6)° and 166.21(6)°. One of the coordinating SbF_6 anions was located inside the cage, disordered over two sites, and weakly bridging between two silver centers with Ag•••F distances of 2.975(16) and 3.192(17) Å. A pair of weakly coordinating SbF_6 anions, related by crystallographic symmetry and disordered over two sites, are located outside the cage with a Ag•••F distance of 2.949(16) Å, and the fourth anion was found to be noncoordinating. The exterior dimensions of the cage are approximately 18 × 20 × 14 Å between the furthest H atoms of the phenyl rings. The interior of the cage is an open cavity with a Sn•••Sn distance of ca. 10.4 Å, two long Ag•••Ag distances (ca. 8.7 Å), and two shorter Ag•••Ag distances (ca. 5.9 Å). Taking into account the van der Waals radii of the framework atoms, the cavity can accommodate a sphere of diameter 5.0 Å. The cavity has two large access windows which could permit anions and solvent to diffuse in and out of the cage. The ^{19}F NMR spectrum of the cage prepared from $AgBF_4$, $[Ag_4(\mathbf{L4})(BF_4)_4]$ showed only one chemical environment for the BF_4 anions,

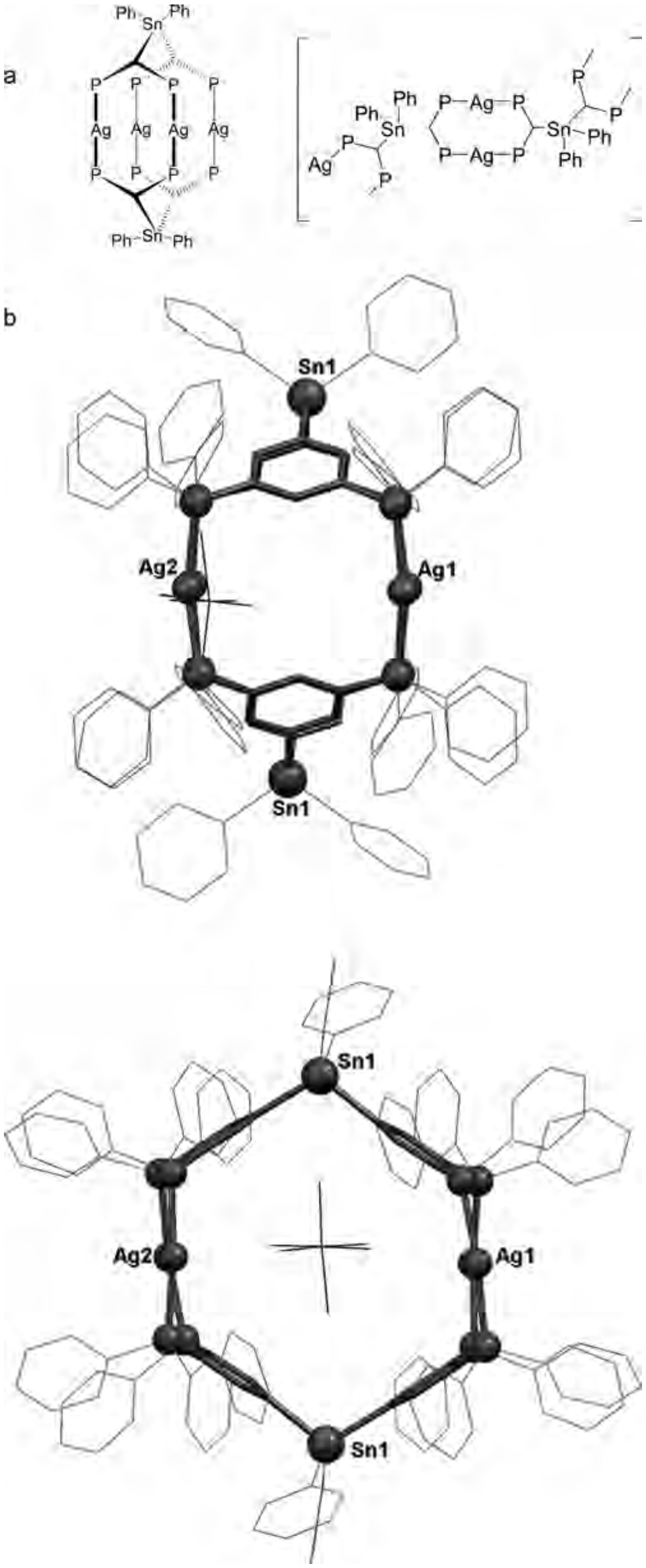
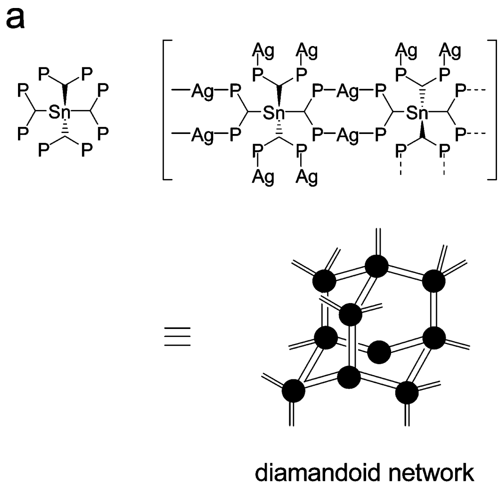
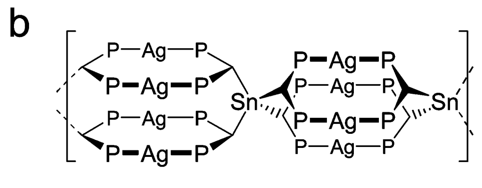


Figure 8. (a) Schematic representations of a discrete $Ag_4(\mathbf{L4})_2$ cage versus a linear polymer, both based on the silver-diphos motif, that can be expected on the reaction of **L4** with silver(I). (b) Side-on and end-on views of the X-ray crystal structure of the discrete cage $[Ag_4(\mathbf{L4})_2(SbF_6)_2]^{2+}$ showing the boxlike structure and the included SbF_6 anion, which is disordered over two sites. H atoms are omitted for clarity. The necessarily arched conformation of the silver-diphos connections can be seen in the side-on view.



diamandoid network



linear chain of cages

Figure 9. Diamandoid network (a) and linear chain of cages (b), both based on silver-diphos motifs which could be expected to form using octaphosphine **L7**.

suggesting that they are able to diffuse freely in and out of the structure at room temperature on the NMR time scale. There was no apparent difference between the included SbF_6^- and BF_4^- counterions with regard to templation of the cage, that is, the stability of the cage or its rate of formation (in all of our NMR studies of silver-phosphine assemblies to date, NMR spectra show that equilibrium is already achieved by the time the NMR spectrum is run).

Dynamic Mixtures Formed by L5 and L6. Heptaphosphine **L5** and hexaphosphine ligand **L6** might be expected to form either extended coordination polymers or discrete structures. However, construction of simple models reveals that, in contrast to **L4**, the disposition of the three diphosphine arms of each of these ligands is not appropriate for the formation of stable discrete cages. Solutions of mixtures of **L5** or **L6** with three equivalents of silver(I) salts gave ^{31}P NMR spectra which were broad with no resolved $^{107/109}Ag,^{31}P$ coupling. This suggests dynamic exchange at the silver centers on the NMR time scale, consistent with the formation of dynamic mixtures of oligomers. At −60 °C, ^{31}P spectra were sharp and showed evidence of coupling to silver; however, a large number of P environments was present in each case, confirming the nonselective coordination of these ligands. Repeated attempts to obtain single crystals resulted only in the formation of amorphous powders.

Chelate Coordination of Four Metal Ions by Octaphosphine L7. L7 has four diphosphine arms emanating from a central tetrahedral Sn center. If it were to adopt the silver-diphos motif upon reaction with silver(I), a three-dimensional diamondoid network polymer could be expected (Figure 9a). Alternatively, a one-dimensional polymer could be expected on the basis of catenated cages analogous to that formed by the tetraphosphine **L4** (Figure 9b). Simple models show that it is not possible to form a stable discrete structure based on the silver-diphos motif. When a solution of **L7** in $CDCl_3$ was added to a solution of silver(I) salts in CH_3CN at a ligand-to-metal ratio of 1:4, sharp signals showing well-resolved ^{107}Ag,^{31}P and ^{109}Ag,^{31}P coupling were observed, suggesting that a stable discrete structure had in fact formed (Figure 10). The sharp spectrum obtained for these complexes and the magnitude of the ^{109}Ag,^{31}P coupling (in the range 546−545 Hz) indicate the formation of a single highly symmetrical species in solution with AgP_2 coordination centers. This was surprising because of the expected formation of oligomeric or polymeric species, as described above. The spectrum could however be explained if there was chelation of silver ions between the diphos arms. Crystals of [Ag_4(**L7**)(O_3SCF_3)$_4$] were obtained by the slow diffusion of diethyl ether into a $CHCl_3$/CH_3NO_2 solution of the complex. An X-ray structure determination confirmed the formation of this tetra-chelate structure (Figure 10).

Four 10-membered chelate rings are formed by the coordination of silver ions between the diphenylphosphino arms of **L7**. This results in a continuous 24-membered coordination ring around the periphery of the molecule. The *meta*-diphosphine arms necessarily adopt the divergent conformation indicated in Figure 4. Ag−P bond distances range from 2.4211(17) to 2.4680(18) Å. The silver centers are nonlinear, with P−Ag−P angles ranging from 145.42(6) to 151.22(6)°. Three of the silver centers have monodentate triflate anions coordinated with Ag···O distances ranging from 2.452(8) to 2.733(7) Å. The fourth has a bidentate triflate anion with Ag···O distances of 2.616(5) and 2.705(5) Å and an expectedly acute O−Ag−O angle of 53.70(16)°.

This chelate coordination mode was not observed for **L4**−**L6**, and therefore it appears to be uniquely stabilized in the case of **L7**. It is possible that it becomes favored for **L7** due to the formation of the continuous large ring. This behavior can alternatively be described in terms of cooperativity between the four interarm sites. In particular, since coordination of silver between the arms reduces the rotational freedom about the Sn−C bonds, decoordination of a single silver ion from the saturated complex [Ag_4(**L7**)(OTf)$_4$] leaves a free coordination site which remains preorganized for chelation due to silver chelation of the sites to either side. In other words, neighboring coordination sites may act in a mutually cooperative manner to favor the chelate coordination mode. Cooperative binding of metal ions by oligodentate ligands has previously been described in terms of positive homotropic allosteric effects.[14] However, this has previously referred to the *strength* of binding rather than the *mode* of binding.

The diphosphine bis(3-diphenylphosphinophenyl)diphenylstannane **L8** was prepared as a model compound to test this aspect. Diphosphine **L8** has two diphenylphosphine groups in the meta positions of two independent phenyl groups and therefore has the potential to form a single chelate ring in an analogous fashion to a single coordination site of [Ag_4(**L7**)(O_3SCF_3)$_4$]. Since **L8** has only one chelating site available, it would be less predisposed to chelation than **L7** if the latter does exhibit cooperative chelate binding between its four sites.

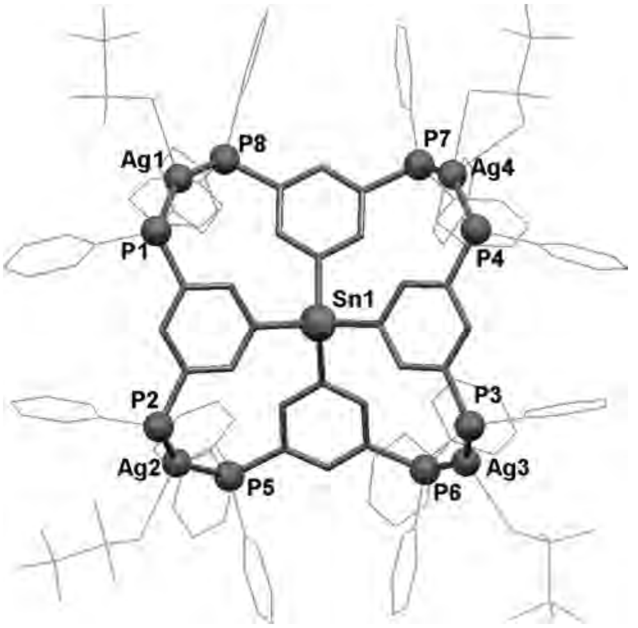


Figure 10. ^{31}P NMR spectrum of [Ag_4(**L7**)(O_3SCF_3)$_4$] in $CDCl_3$/CH_3CN (4:1) and X-ray crystal structure of [Ag_4(**L7**)(O_3SCF_3)$_4$] showing the interarm tetra-chelate coordination mode adopted.

When a solution of **L8** in $CDCl_3$ was added to solution of AgO_3SCF_3 in CH_3CN in a 1:1 molar ratio, the ^{31}P NMR spectrum revealed a broad signal at 12.6 ppm (Figure 11), in contrast to the sharp signals with $^{107/109}$Ag,^{31}P coupling observed for [Ag_4(**L7**)(O_3SCF_3)$_4$] (Figure 10), and indicative of dynamic behavior. On cooling to −30 °C, the ^{31}P NMR spectrum displayed two main sets of ^{107}Ag,^{31}P and ^{109}Ag,^{31}P doublets. The $^1J(^{109}\text{Ag},^{31}\text{P})$ coupling constants for these species were 533 and 500 Hz, indicating that both were based on AgP_2 coordination centers. Of the two complexes formed, one could potentially be the chelate complex, but at least one of them must be based on bridging coordination, for example, the dimer formed through a silver-diphos motif, [Ag_2(**L8**)$_2$(OTf)$_2$] (Figure 11). Therefore, diphosphine **L8**, unlike octaphosphine **L7**, does not selectively form a chelate complex with silver(I). This supports the idea that the selective chelation at the four sites of **L7** arises from cooperative behavior. However, since **L7** and **L8** are not isosteric, it remains possible that the selective chelation by **L7** is a result of steric repulsions between the phenyl groups on adjacent arms, which would be expected to favor divergent conformations and so interarm chelation.

Conclusions

Diphosphines based on meta-substitution at an aryl ring adopt the target dimeric silver-diphos synthon upon reaction with silver salts. In extending this principle to ligands containing up to four such diphosphine groups attached to a central core, it is clear that, if the diphosphine groups are appropriately articulated, as in **L4**, larger stuctures, such as cages, based on the silver-diphos synthon can form selectively. Where the ligand structure does not permit simultaneous adoption of the silver-diphos synthon at all diphosphine sites to form a discrete structure, a mixture of oligomeric

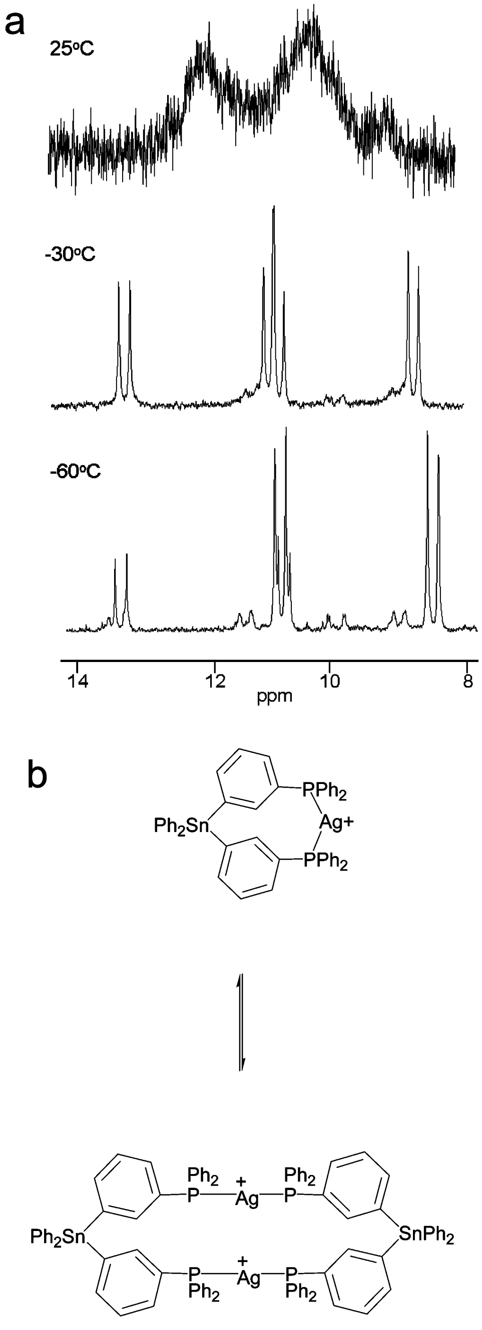


Figure 11. (a) Variable-temperature ^{31}P NMR spectra of diphosphine **L8** and AgO_3SCF_3 (1:1) in $CDCl_3/CH_3CN$ (4:1) showing the nonselective coordinating behavior and a proposed equilibrium based on AgP_2 centers, which would explain the two main species observed.

structures was observed in solution (**L5** and **L6**). An interesting exception to this was the discrete complex formed by octaphosphine **L7**, which is based on the alternative coordination mode of interarm chelation. This complex provides an interesting case in which cooperativity between the coordination sites and the build up of interarm steric congestion leads to selective interarm chelation. Extending this work further, by ensuring that the diphosphine groups in an oligo(diphosphine) ligand are sufficiently well-separated to act independently, it should be possible to generate further polymeric and cage structures in a rational way based on the silver-diphos synthon.

Experimental Section

General. All chemicals purchased from commercial sources were of reagent grade and used without further purification. All reactions involving air-sensitive reagents were carried out under an inert atmosphere of nitrogen using predried solvents. 2,6-Bis(diphenylphosphino)benzonitrile (**L3**) was prepared according to the literature procedure.[8] NMR spectra were recorded on Bruker AM 300 MHz or AM 500 MHz spectrometers. ^{31}P and ^{13}C NMR spectra are proton-decoupled. ^{1}H NMR spectra were referenced to the protio residue in the solvent, ^{31}P NMR spectra to external 85% H_3PO_4 (aq), and ^{19}F NMR spectra to $CFCl_3$. Melting points were determined using an Electrothermal 9100 melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 983G spectrophotometer equipped with a Perkin-Elmer 3700 data station. Solid samples were recorded as KBr pressed discs. Mass spectra were recorded on a VG Autospec.

Synthesis of Fluoroaryl Precursors. Tris(3,5-difluorophenyl)phosphine (Precursor to L4). The following method differs from that reported in the literature.[15] To magnesium turnings (0.5 g, 20 mmol) was added a crystal of iodine and a solution of bromo-3,5-difluorobenzene (1.00 g, 5.2 mmol) in diethyl ether (15 mL). The reaction was left to stand for approximately 15 min, after which time it proceeded with no external heating. A further solution of bromo-3,5-difluorobenzene (2.35 g, 12.2 mmol) in diethyl ether (35 mL) was added dropwise to bring the reaction to a steady reflux. Upon complete addition of the bromo-3,5-difluorobenzene solution, the reaction was brought back to reflux for 1 h, forming a light brown/orange solution. The reaction was then allowed to cool to room temperature and phosphorus trichloride (0.58 g, 4.3 mmol) added gradually. A precipitate forms almost instantaneously, and the reaction was slightly exothermic. After addition of the phosphorus trichloride was complete, the reaction was brought to reflux for a further 2 h. The reaction was then placed in an ice bath, the excess Grignard reagent hydrolyzed using HCl (10%, 50 mL), and the resulting aqueous phase extracted with diethyl ether (4 × 50 mL). The combined fractions were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the solvent removed in vacuo to yield a viscous brown oil that was sublimed under reduced pressure (0.01 mmHg, 100 °C) to give an analytically pure white crystalline solid (0.88 g, 56%). Elem anal. calcd (%): C, 58.39; H, 2.45. Found: C, 58.32; H, 2.37. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.86 (tt, 3 H), $^{3}J(^{19}F,^{1}H) = 8.7$ Hz, $^{4}J(^{1}H,^{1}H) = 2.1$ Hz, 6.82−6.74 (m, 6 H).^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2 (ddd, CF_{ar}), $^{1}J(^{19}F,^{13}C) = 253.5$ Hz, $^{3}J(^{19}F,^{13}C) = 11.2$ Hz, $^{3}J(^{31}P,^{13}C) = 11.2$ Hz, 139.2 (dt, CP), $^{1}J(^{31}P,^{13}C) = 16.2$ Hz, $^{3}J(^{19}F,^{13}C) = 6.6$ Hz, 116.1 (m, CH_{ar}), 105.6 (t, CH_{ar}), $^{2}J(^{19}F,^{13}C) = 25.1$ Hz).^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$): δ −108.2 (s). ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ −0.5 (s). EI-MS *m*/*z* (%): 370 (100) [M^{+}].

Bis(3,5-difluorophenyl)diphenylstannane (Precursor to L5). 3,5-Difluorophenyl-magnesium-bromide (0.54 M, 54 mmol) was prepared analogously to that of tris(3,5-difluorophenyl)phosphine

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(**1**). To this was added a solution of diphenyl-tin-dichloride (7.37 g, 21.4 mmol) dissolved in diethyl ether (30 mL). The reaction was brought to reflux for 2 h, after which the excess Grignard reagent was hydrolyzed using HCl (10%, 50 mL). The resulting aqueous phase was extracted with diethyl ether (4 × 50 mL). The combined fractions were dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered off and the solvent removed *in vacuo* to yield a crude yellow solid (9.2 g) that was recrystallized from ethanol to give an off-white crystalline solid (6.4 g, 62%). Elem anal. calcd (%): C, 57.76; H, 3.23. Found: C, 57.76; H, 3.10. M.p.: 135−136 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.58−7.51 (m, 4 H$_{ar}$), 7.47−7.40 (m 6 H$_{ar}$), 7.10−7.04 (m, 4 H$_{ar}$), 6.84 (tt, 2 H$_{ar}$), $^{2}J(^{19}\mathrm{F},^{1}\mathrm{H}) = 9.2$ Hz, $^{4}J(^{1}\mathrm{H},^{1}\mathrm{H}) = 2.3$ Hz.^{13}C NMR (75 MHz, CDCl$_3$): δ 163.2 (dd, CF$_{ar}$), $^{1}J(^{19}\mathrm{F}, ^{13}\mathrm{C}) = 255.0$ Hz, $^{3}\mathrm{J}(^{19}\mathrm{F},^{13}\mathrm{C}) = 10.0$ Hz, 141.2 (s, CSn$_{ar}$), 137.0 (s, CH$_{ar}$), 135.4 (s, CH$_{ar}$), 129.2 (s, CH$_{ar}$), 119.0 (m, CH$_{ar}$), 105.1 (t, CH$_{ar}$), $^{2}\mathrm{J}(^{19}\mathrm{F},^{13}\mathrm{C}) = 24.9$ Hz. ^{19}F-{^{1}H} NMR (282 MHz, CDCl$_3$): δ −109.7 (s). EI-MS *m/z* (%): 500 (100) [M$^+$].

Tris(3,5-difluorophenyl)phenylstannane (Precursor to L6). 3,5-Difluorophenyl-magnesium-bromide (0.64 M, 32 mmol) was prepared analogously to tris(3,5-difluorophenyl)phosphine (**1**). To this was added trichloro phenyltin (1.5 mL, 2.76 g, 9.1 mmol) dropwise at 0 °C with stirring. A white precipitate formed almost immediately. The reaction was brought to reflux for 2 h, after which the excess Grignard reagent was hydrolyzed using HCl (10%, 50 mL). The resulting aqueous phase was extracted with diethyl ether (4 × 50 mL). The combined fractions were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the solvent removed *in vacuo* to yield a crude yellow solid that was recrystallized from diethyl ether to give a white crystalline solid (3.20 g, 65%). Elem anal. calcd (%): C, 53.87; H, 2.64. Found: C, 54.34; H, 2.55. M.p.: 161−162 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.30−7.15 (m, 14 H$_{ar}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 173.0 (s, CH$_{ar}$), 162.7 (dd, CF$_{ar}$), $^{1}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 246.2$ Hz, $^{3}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 15.3$ Hz, 152.9 (t, CSn$_{ar}$), $^{3}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 14.6$ Hz, 106.72−106.3 (m, CH$_{ar}$), 102.5 (t, CH$_{ar}$), $^{2}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 26.3$ Hz. ^{19}F-{^{1}H} NMR (282 MHz, CDCl$_3$): δ −109.0 (s). EI-MS *m/z* (%): 536 (15) [M$^+$], 459 (100).

Tetrakis(3,5-difluorophenyl)stannane (Precursor to L7). 3,5-Difluorophenyl-magnesium-bromide (0.7 M, 104 mmol) was prepared analogously to tris(3,5-difluorophenyl)phosphine (**1**), and to this was added tin tetrachloride (2.43 mL, 5.42 g, 21 mmol) dropwise at 0 °C with stirring. A white precipitate formed almost immediately. The reaction was brought to reflux for 2 h, after which the excess Grignard reagent was hydrolyzed using HCl (10%, 50 mL). The resulting aqueous phase was extracted with diethyl ether (4 × 50 mL). The combined fractions were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the solvent removed *in vacuo* to yield a crude yellow/brown solid (10.02 g) that was recrystallized from dichloromethane to give a white crystalline solid (3.32 g, 28%). Elem anal. calcd (%): C, 50.48; H, 2.12. Found: C, 50.08; H, 1.92. M.p.: 208−209 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.17−6.89 (m). ^{13}C NMR (75 MHz, CDCl$_3$): δ 163.4 (dd, CF$_{ar}$), $^{1}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 256.3$ Hz, $^{3}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 10.2$ Hz, 138.3 (t, CSn$_{ar}$), $^{3}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 4.5$ Hz, 119.39−118.55 (m, CH$_{ar}$), 106.4 (t, CH$_{ar}$), $^{2}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 24.7$ Hz. ^{19}F-{^{1}H} NMR (282 MHz, CDCl$_3$): δ −108.2 (s). EI-MS *m/z* (%): 572 (50) [M$^+$].

Bis(3-fluoro-phenyl)diphenyl-stannane (Precursor to L8). The Grignard reagent 3-fluorobenzene magnesium bromide was prepared by a method similar to that of tris(3,5-difluoro-phenyl)phosphine (**1**). 1-Bromo-3-fluorobenzene (2.0 mL, 18.2 mmol) was added to magnesium turnings (0.5 g, 21 mmol) in diethyl ether (50 mL) and brought to reflux for 2 h. The reaction was allowed to cool, and a solution of diphenyl-tin-dichloride (2.5 g, 7.3 mmol) in diethyl ether (10 mL) was added dropwise. A white precipitate formed almost immediately. The reaction was heated to reflux for a further 4 h, after which it was allowed to cool, and HCl (10%, 100 mL) added. The aqueous layer was extracted with diethyl ether (5 × 50 mL) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the solvent removed *in vacuo*. A white crystalline solid was obtained upon recrystallization from diethyl ether (2.30 g, 68%). Elem anal. calcd (%): C, 62.24; H, 3.92. Found: C, 62.12; H, 3.84. M.p.: 180−181 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.66−7.02 (m, 24 H$_{ar}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 163.0 (d, CF$_{ar}$), $^{1}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 251.3$ Hz, 140.1 (s, CSn$_{ar}$), 137.1 (s, CH$_{meta}$), 136.7 (s, CSn$_{ar}$), 132.7 (d, CH$_{ortho}$), $^{4}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 3.2$ Hz, 130.2 (d, CH$_{meta}$), $^{3}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 6.6$ Hz, 129.6 (s, CH$_{para}$), 128.9 (s, CH$_{ortho}$), 123.4 (d, CH$_{para}$), $^{2}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 18.5$ Hz, 116.4 (d, CH$_{ortho}$), $^{2}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 20.9$ Hz. DEPT 45 ^{13}C NMR (75 MHz, CDCl$_3$): δ 137.1 (s, CH$_{meta}$), 132.7 (d, CH$_{ortho}$), $^{4}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 3.2$ Hz, 130.2 (d, CH$_{meta}$), $^{3}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 6.6$ Hz, 129.6 (s, CH$_{para}$), 128.9 (s, CH$_{ortho}$), 123.4 (d, CH$_{para}$), $^{2}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 18.5$ Hz, 116.4 (d, CH$_{ortho}$), $^{2}J(^{19}\mathrm{F},^{13}\mathrm{C}) = 20.9$ Hz. ^{19}F-{^{1}H} NMR (121 MHz, CDCl$_3$): δ −112.7. EI-MS *m/z* (%): 405 (100), 464 (65) [M$^+$].

Synthesis of Phosphine Ligands. 1,3-Bis(diphenylphosphino)-Benzene (L1). This procedure differs from that reported in the literature.[8] To potassium diphenylphosphide (20 mL, 0.5 M THF, 11.2 mmol) was added 1,3-difluorobenzene (0.44 mL, 4.5 mmol), dropwise. The mixture was allowed to stir for 1 h and then was brought to reflux overnight. THF was removed under reduced pressure, and methanol (100 mL) was added. The mixture was then heated to reflux for 4 h, after which the methanol was decanted off, yielding a white sticky product that was dried *in vacuo* (1.79 g, 89%). Elem anal. calcd (%): C, 80.71; H, 5.42. Found: C, 80.01; H, 5.49. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.20−7.49 (m, 24 H). ^{31}P-{^{1}H} NMR (121 MHz, CDCl$_3$): δ −4.9 (s); −39.9 (s) (HPPh$_2$, contaminant). EI-MS *m/z* (%): 108 (100), 446 (5) [M$^+$].

3,5-Bis(diphenylphosphino)benzamide (L3). To 3,5-difluorobenzamide (1.50 g, 9.55 mmol) was added potassium diphenylphosphide (40 mL, 0.5 M THF, 20 mmol), and the mixture was refluxed overnight. THF was removed under reduced pressure. Methanol (100 mL) was then added, which resulted in the formation of a white crystalline solid. The crystalline solid was filtered off and washed with methanol (3 × 50 mL) and dried in the air (3.82 g, 82%). Elem anal. calcd (%): C, 76.07; H, 5.15; N, 2.86. Found: C, 75.93; H, 5.02; N, 2.54. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.74 (d, 2 CH), $^{1}J(^{31}\mathrm{P},^{1}\mathrm{H}) = 5.0$ Hz, 7.30−7.18 (m, 21 CH), 6.00 (s, −NH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.8 (s, C$_{carbonyl}$), 141.5 (t, CH$_{ar}$), $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 13.8$ Hz, 139.0 (dd, CP$_{ar}$), $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 19.0$ Hz, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 4.0$ Hz, 136.1 (d, CP$_{ar}$), $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 11.0$ Hz, 133.6 (d, CH$_{ortho}$), $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 20.0$ Hz, 133.6 (s, C$_{ar}$), 132.7 (d, CH$_{ar}$), $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 25.0$ Hz, 129.0 (s, CH$_{para}$), 128.6 (d, CH$_{meta}$), $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 7.5$ Hz. ^{31}P-{^{1}H} NMR (121 MHz, CDCl$_3$): δ −4.7 (s). EI-MS *m/z* (%): 491 (100), 488 (55) [M$^+$].

Bis{bis-3,5(diphenylphosphino)benzenetriyl}diphenyl Stannane (L4). To bis(3,5-difluorophenyl)diphenylstannane (2.0 g, 4.0 mmol) was added potassium diphenylphosphide (36 mL, 0.5 M in THF, 18.0 mmol). The reaction was slightly exothermic and was left to stir at ambient temperature for 1 h and then brought to reflux overnight. The workup procedure was analogous to that of (**L4**) and yielded a white powder (3.20 g, 69%). Elem anal. calcd (%): C, 74.30; H, 4.85. Found: C, 74.12; H, 4.97. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.49−7.14 (m, 56 H$_{ar}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.7 (d, CH$_{ar}$), $^{2}J(^{31}\mathrm{P}, ^{13}\mathrm{C}) = 22.4$ Hz, 139.7 (t, CH$_{ar}$), $^{2}J(^{31}\mathrm{P}, ^{13}\mathrm{C}) = 15.8$ Hz, 138.8

(t, CP_{ar}), $^{3}J(^{31}P, ^{13}C) = 5.9$ Hz, 138.3 (dd, CP_{ar}), $^{1}J(^{31}P, ^{13}C) = 15.2$ Hz, $^{3}J(^{31}P,^{13}C) = 4.2$ Hz, 137.5 (s, CP_{ar}), 137.3 (s, CH_{ortho}), 137.2 (d, CP_{ar}), $^{1}J(^{31}P,^{13}C) = 9.8$ Hz, 134.0 (d, CH_{ortho}), $^{2}J(^{31}P,^{13}C) = 19.7$ Hz, 129.43 (s, CH_{para}), 129.1 (s, CH_{para}), 129.0 (s, CH_{meta}), 128.8 (d, CH_{meta}), $^{3}J(^{31}P,^{13}C) = 11.5$ Hz. ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ −4.8 (s). FAB-MS *m/z*(%): 1164 (100) [M^+].

Tris{3,5-bis(diphenylphosphino)benzenetriyl}phosphine (L5). To tris(3,5-difluorophenyl)phosphine (1.5 g, 4.05 mmol) was added potassium diphenylphosphide (53 mL, 0.5 M in THF, 27.0 mmol). The reaction was slightly exothermic and was left to stir at ambient temperature for 1 h and then brought to reflux overnight. The solvent was removed under reduced pressure to yield a thick, red oil. The excess phosphide was hydrolyzed using methanol (3 × 40 mL), which resulted in a sticky white substance. The product was then refluxed for 4 h in methanol, and upon cooling, an off-white solid formed (4.55 g, 82%). Elem anal. calcd (%): C, 79.06; H, 5.09. Found: C, 78.82; H, 5.14. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23−7.06 (m, 69 H_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0−138.4 (m), 138.2 (dt, CP_{ar}), $^{1}J(^{31}P,^{13}C) = 10.9$ Hz, $^{3}J(^{31}P,^{13}C) = 4.8$ Hz, 136.6 (d, CP_{ar}), $^{1}J(^{31}P,^{13}C) = 11.5$ Hz, 133.4 (d, CH_{ortho}) $^{2}J(^{31}P,^{13}C) = 19.8$ Hz, 128.5 (s, CH_{para}), 128.4 (d, CH_{meta}), $^{3}J(^{31}P,^{13}C) = 7.0$ Hz. ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ −2.3 (s, 1 P), −3.6 (s, 6 P). FAB-MS *m/z* (%): 1367 (100) [M^+].

Tris(3,5-bis(diphenylphosphino)benzenetriyl)phenyl-stannane (L6). **L6** was prepared analogously to **L5** from tris(3,5-difluorophenyl)phenylstannane. A sticky cream-colored product was obtain, which was further purified by silica gel column chromatography using dichloromethane as the mobile phase. Yield: 71%. Elem anal. calcd (%): C, 75.25; H, 4.87. Found: C, 73.14; H, 5.08. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.03 (m, 74 H_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.9 (d, CH_{ar}), $^{2}J(^{31}P, ^{13}C) = 25.6$ Hz, 139.8 (t, CH_{ar}), $^{2}J(^{31}P, ^{13}C) = 12.4$ Hz, 138.3 (t, CP_{ar}), $^{3}J(^{31}P, ^{13}C) = 6.7$ Hz, 138.4 (dd, CP_{ar}), $^{1}J(^{31}P, ^{13}C) = 15.5$ Hz, $^{3}J(^{31}P,^{13}C) = 3.4$ Hz, 137.3 (d, CP_{ar}), $^{1}J(^{31}P,^{13}C) = 11.4$ Hz, 137.0 (s, CH_{ortho}), 137.0 (s, CSn_{ar}), 133.9 (d, CH_{ortho}), $^{2}J(^{31}P,^{13}C) = 19.5$ Hz, 129.4 (s, CH_{para}), 129.2 (s, CH_{meta}), 129.1 (s, CH_{para}), 128.9 (d, CH_{meta}), $^{3}J(^{31}P,^{13}C) = 7.0$ Hz. ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ −5.2 (s) and −39.8 ($HPPh_2$). FAB-MS *m/z* (%): 1531 (100) [M^+].

Tetrakis{bis(3,5-diphenylphosphino)benzenetriyl} Stannane (L7). **L7** was prepared analogously to **L5** from tetrakis(3,5-difluorophenyl)stannane. An analytically pure sample was obtained by recrystallization from acetone. Yield: 84%. Elem anal. calcd (%): C, 75.84; H, 4.88. Found: C, 75.89; H, 5.02. M.p.: 142−143 °C (acetone). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.59−7.05$ (m, 92 H_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.1 (d, CH_{ar}), $^{2}J(^{31}P, ^{13}C) = 28.6$ Hz, 140.0 (t, CH_{ar}), $^{2}J(^{31}P, ^{13}C) = 10.3$ Hz, 138.4 (dd, CP_{ar}), $^{1}J(^{31}P, ^{13}C) = 15.9$ Hz, $^{3}J(^{31}P,^{13}C) = 2.8$ Hz, 137.9 (t, CP_{ar}), $^{3}J(^{31}P, ^{13}C) = 7.5$ Hz, 137.4 (d, CP_{ar}), $^{1}J(^{31}P,^{13}C) = 11.6$ Hz, 133.9 (d, CH_{ortho}), $^{2}J(^{31}P,^{13}C) = 19.4$ Hz, 129.0 (s, CH_{para}), 128.9 (d, CH_{meta}), $^{3}J(^{31}P,^{13}C) = 6.9$ Hz. ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ −5.2 (s). FAB-MS *m/z* (%): 1900 (100) [M^+].

Complexation with Silver. Complexes with Diphosphines L1, L2, and L3. In a typical preparation, a solution of ligand (**L1**, **L2**, or **L3**; 100 mg, 0.224 mmol) in chloroform (4 mL) was added to a solution of silver(I) salt AgX (X = NO_3, O_3SCF_3, ClO_4, SbF_6, BF_4, or PF_6; 0.224 mmol) in acetonitrile (1 mL) or nitromethane (1 mL). NMR data for complexes with various anions are available in the Supporting Information.

$[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]$. Needlelike crystals were obtained by slow diffusion of diethyl ether into a 0.044 M complex solution in $CDCl_3$/CH_3NO_2 over a period of 1 week. Yield: 53%. Elem anal. calcd (%): $[Ag_2(\mathbf{L1})_2(O_3SCF_3)_2]\cdot 0.25(CHCl_3)$: C, 52.93; H, 3.44. Found: C, 53.14; H, 3.46. M.p.: 285 °C (dec.). ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3\backslash CH_3NO_2$): δ 14.5 (d,d), $^{1}J(^{109}Ag,^{31}P) = 587$ Hz. FAB-MS *m/z* (%): 154 (100), 1259 (20) $[Ag_2(L1)_2(O_3SCF_3)]^+$.

$[Ag_2(\mathbf{L2})_2(SbF_6)_2]$. Needlelike crystals were obtained by slow diffusion of diethyl ether into a 0.044 M complex solution in $CDCl_3$/CH_3CN over a period of 1 week. Yield: 45%. Elem anal. calcd (%): C, 45.68; H, 2.84; N, 1.72. Found: C, 45.53; H, 2.91; N, 1.92. M.p.: >300 °C (dec.). ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$/CH_3CN): δ 12.5 and 9.1 (b), $^{1}J(^{109}Ag,^{31}P)$ = unresolved. FT-IR (cm^{-1}): 471.2, 493.8, 505.6, 557.6, 597.8, 659.1, 695.1, 747.6, 796.2, 849.8, 926.0, 998.6, 1026.5, 1072.9, 1097.9, 1162.1, 1187.1, 1215.3, 1269.7, 1312.0, 1331.3, 1398.0, 1437.4, 1481.0, 1560.4, 1585.8, 16.17.1, 2210.8, 2267.2, 3056.2. FAB-MS *m/z* (%): 1392 (100), 1394 (95) $[Ag_2(\mathbf{L2})_2(SbF_6)]^+$.

$[Ag_2(\mathbf{L2})_2(O_3SCF_3)_2]$. ^{31}P-{H} NMR (121 MHz, $CDCl_3\backslash CH_3CN$): δ 9.7 (d,d), $^{1}J(^{109}Ag,^{31}P) = 587$ Hz.

$[Ag_2(\mathbf{L3})_2(O_3SCF_3)_2]$. A solution of 3,5-bis(diphenylphosphino) benzamide (**L3**; 100 mg, 0.21 mmol) in acetonitrile (5 mL) was added to a solution of silver triflate (54 mg, 0.21 mmol) in acetonitrile (2 mL). A white precipitate was obtained by the addition of diethyl ether to the solution in 90% yield. Elem anal. calcd (%): C, 51.49; H, 3.38; N, 1.88. Found: C, 50.96; H, 3.30; N, 1.85. M.p.: >300 °C (dec.). (300 K) ^{31}P-{^{1}H} NMR (121 MHz, CD_3CN): δ broad signals at 12.1 and 8.4, coupling unresolved. (273 K) ^{31}P-{^{1}H} NMR (202 MHz, CD_3CN): δ broad signals at 11.7 and 9.5, coupling unresolved. (243 K) ^{31}P-{^{1}H} NMR (202 MHz, CD_3CN): δ 10.1 (d), $^{1}J(^{109}Ag,^{31}P) = 496$ Hz. FT-IR (cm^{-1}): 469.4, 515.9, 557.8, 573.8, 636.8, 693.0, 743.7, 800.5, 850.5, 895.3, 998.8, 1026.8, 1096.5, 1168.7, 1234.9, 1289.2, 1376.8, 1436.5, 1457.0, 1481.1, 1540.3, 1560.0, 1605.0, 1664.6, 3056.3, 3345.1, 3430.4. FAB-MS *m/z* (%): 596 (100) $[Ag_2(\mathbf{L3})_2]^{2+}$, 1343 (34) $[Ag_2(\mathbf{L3})_2(O_3SCF_3)]^+$.

Complexation with Tetraphosphine L4. In a typical preparation, a solution of tetraphos (**L4**) (100 mg, 0.086 mmol) in chloroform (4 mL) was added to a solution of silver(I) salt (0.172 mmol) AgX (X = NO_3, O_3SCF_3, ClO_4, SbF_6, BF_4, or PF_6) in nitromethane (1 mL). ^{31}P NMR spectra were run in a mixture of $CDCl_3\backslash CH_3NO_2$ (4:1). NMR data for complexes with various anions are available in the Supporting Information.

$[Ag_4(\mathbf{L4})_2(SbF_6)_4]$. Needlelike crystals suitable for X-ray diffraction were obtained by the slow diffusion of diethyl ether into a solution of $[Ag_4(\mathbf{L4})_2(SbF_6)_4]$ in $CHCl_3$/CH_3NO_2 (4:1; 0.0172 M) over a period of 1 week. Yield: 53%. Elem anal. calcd (%): C, 46.72; H, 3.05. Found: C, 46.44; H, 2.80. ^{31}P-{^{1}H} NMR (121 MHz): δ 14.9 (d,d), $^{1}J(^{109}Ag,^{31}P) = 595$ Hz. FAB-MS *m/z* (%): 1615 (100) $[Ag_4(\mathbf{L4})_2(SbF_6)_2]^{2+}$.

Complexation with Octaphosphine L7. In a typical preparation, a solution of **L7** (152 mg, 0.08 mmol) in chloroform (4 mL) was added to a solution of silver(I) salt (0.32 mmol) AgX (X = NO_3, O_3SCF_3, ClO_4, SbF_6, BF_4, or PF_6) in acetonitrile (1 mL). ^{31}P NMR spectra were run in a mixture of $CDCl_3\backslash CH_3CN$ (4:1). NMR data for complexes with various anions are available in the Supporting Information.

$[Ag_4(\mathbf{L7})(O_3SCF_3)_4]$. Crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether into a solution of $[Ag_4(\mathbf{L7})(O_3SCF_3)_4]$ in $CHCl_3$/CH_3CN (4:1; 0.016 M) over a period of 1 week. Yield: 85%. Elem anal. calcd (%): C, 50.86; H, 3.17. Found: C, 47.41; H, 3.08. M.p.: 280 °C (dec.). ^{31}P-{^{1}H} NMR (121 MHz): δ 12.9 (d,d), $^{1}J(^{109}Ag,^{31}P) = 542$ Hz. FAB-MS *m/z* (%): 2780 (100) $[Ag_4(\mathbf{L7})(O_3SCF_3)_3]^+$, 1316 (10) $[Ag_4(\mathbf{L7})(O_3SCF_3)_2]^{2+}$.

X-Ray Crystallographic Section. Crystal data for each structure are given in Table 1. A crystal was mounted onto the diffractometer

Table 1. Crystallographic Data for all Structures

	L3	**L7**	[Ag_2(**L1**)$_2$(O_3SCF_3)$_2$]	[Ag_2(**L2**)$_2$($NCCH_3$)$_2$(SbF_6)$_2$]	[Ag_4(**L**$_4$)$_2$][SbF_6] $2CHCl_3\cdot 4CH_3NO_2$	[Ag_4(**L7**)(O_3SCF_3)$_4$] $4CHCl_3\cdot CH_3NO_2$
formula	$C_{31}H_{25}P_2N_2O$	$C_{122}H_{95.75}P_8Sn_2O_{0.75}$	$C_{31}H_{24}P_2SAgF_3O_3$	$C_{136}H_{109}P_8Sb_4Ag_4Cl_6F_{24}N_9$	$C_{150}H_{126}Ag_4Cl_6F_{24}$ $N_4O_8P_8Sb_4Sn_2$	$C_{129}H_{99}Ag_4Cl_{12}F_{12}$ $NO_{14}P_8S_4Sn$
M	489.46	1940.19	703.37	3704.26	4184.87	3466.66
2θ/deg min−max	3−58	5−50	4−58	4−58	5.30−140.22	4.14−140.30
cryst syst	monoclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
a/Å	14.447 (5)	16.871 (3)	11.874 (2)	16.302 (4)	19.2226(19)	21.3377(10)
b/Å	18.389 (7)	22.880 (4)	12.055 (2)	18.209 (5)	19.3230(16)	20.4212(12)
c/Å	9.880 (4)	28.654 (5)	12.337 (2)	26.457 (7)	23.2909(15)	32.4782(15)
α/deg	90	111.612 (3)	61.696 (3)	80.133 (4)	90	90
β/deg	92.074 (4)	90.887 (4)	81.547 (4)	72.213 (6)	105.845(6)	92.920(3)
γ/deg	90	101.688 (3)	69.754 (4)	77.734 (6)	90	90
V/Å^3	2623.1 (17)	10021 (3)	1458.5 (5)	7260 (3)	8322.4(12)	14133.7(12)
T/K	298	298	153	213	100	100
space group	$P2_1$/c	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z	4	4	2	2	2	4
reflns (measured/unique/observed)[a]	29742/6090/2185	114597/44347/24156	17192/6607/3840	83089/32237/16729	51174/15390/13167	108137/25179/18668
μ	0.190 mm^{-1}	0.434 mm^{-1}	0.924 mm^{-1}	1.540 mm^{-1}	13.388 mm^{-1}	9.885 mm^{-1}
R_{int}	10.73%	6.20%	6.61%	6.61%	7.2%	6.1%
R_1(observed reflections)	5.91%	5.61%	4.92%	4.92%	6.5%	6.6%
wR_2 (all reflections)	14.17%	15.72%	15.53%	15.53%	18.9%	19.8%

[a] Observation criterion $I > 2\sigma(I)$.

Table 2. Comparison of Key Bond Lengths and Angles in Crystal Structures of [Ag_2(**L1**)$_2$(OTf)$_2$] and [Ag_2(**L2**)$_2$(SbF_6)$_2$]

		[Ag_2(**L2**)$_2$(SbF_6)$_2$]		
	[Ag_2(**L1**)$_2$(OTf)$_2$]	**1**	**2**	**3**
Ag···Ag (Å)	4.99(3)	5.88(15)	6.12(15)	5.57(15)
Ag−P (Å)	2.4225(15) 2.4027(15)	2.433(7) 2.448(7)	2.422(7) 2.445(7)	2.439(7) 2.446(7) 2.399(7) 2.408(7)
Ag−O (Å)	2.586(4)			
Ag−N		2.32(3)	2.52(3)	2.38(4) 2.53(6)
P−Ag−P (deg)	155.80 (5)	141.7(2)	156.4(3)	165.3(3) 145.3(3)
Ag−N−C (deg)		178(3)	132(3)	160(4) 158(6)

at room temperature for 3,5-bis(diphenylphosphino)benzamide, **L3**, and tetrakis{3,5-bis(diphenylphosphino}benzenetriyl)stannane, **L7**, and at low temperature under nitrogen at 153 K for [Ag_2(**L1**)$_2$(O_3SCF_3)$_2$] and 213 K for [Ag_2(**L2**)$_2$(SbF_6)$_2$]. The structures were solved using direct methods and refined with the SHELXTL version 5 software, and the non-hydrogen atoms were refined with anisotropic thermal parameters, except for disordered atoms, which are isotropic. Hydrogen-atom positions were added at idealized positions with a riding model and fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded). The function minimized was $\sum[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max|F_o|^2 + 2|F_c|^2]/3$. Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters.

For tetrakis{3,5-bis(diphenylphosphino}benzetriyl)stannane, **L7**, the atomic displacement parameters of the ring C97a−C102 shows evidence of probable disorder; however, this could not be modeled. In [Ag_2(**L2**)$_2$(SbF_6)$_2$], the anions are severely disordered, and it was not possible to model all of the orientations separately. We have attempted to account for this by modeling two main positions and distributing the electron density uniformly over the fluorine atoms for both orientations of all of the anions. The atomic displacement parameters of some atoms in some phenyl rings and the solvent moieties show evidence of possible disorder; however, this could not be modeled.

For [Ag_4(**L4**)$_2$][SbF_6]$\cdot 2CHCl_3\cdot 4CH_3NO_2$ and [Ag_4(**L7**)(O_3SCF_3)$_4$], single crystals were coated in perfluoropolyether oil and mounted on glass fibers. X-ray measurements were made using a Bruker Proteum CCD area-detector diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å).[16] Intensities were integrated[17] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being almost a sphere. Absorption corrections were applied, on the basis of multiple and symmetry-equivalent measurements.[18] The structures were solved by direct methods and refined by least-squares on weighted F^2 values for all reflections.[19] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. The positions of the methyl hydrogen atoms were assigned by a rotating group refinement with fixed, idealized C−H distances. All other hydrogen atoms were constrained to ideal geometries. All hydrogen atoms

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(16) *SMART diffractometer control software*, version 5.625; Bruker AXS Inc.: Madison, WI, 1997−2002.

(17) *SAINT integration software*, version 7.06A; Bruker AXS Inc.: Madison,WI, 1997−2003.

(18) Sheldrick G. M. *SADABS*, version 2.05; University of Göttingen: Göttingen, Germany, 2003.

(19) *SHELXTL program system*, version 6.14; Bruker-AXS Inc.: Madison, WI, 2000−2003.

were assigned isotropic displacement parameters equal to 1.5 times (methyl hydrogen atoms) or 1.2 times (all other hydrogen atoms) that of their parent atom.

The tetracation in [Ag$_4$(**L4**)$_2$][SbF$_6$]·2CHCl$_3$·4CH$_3$NO$_2$ sits on a crystallographic inversion center. Stoichiometry thus demands that the asymmetric unit contain two counterions. One of these shows disorder in the position of four of its fluorine atoms, and distance restraints between the fluorine atoms of the second component of this disorder have been used in order to produce sensible geometry. The second anion is disordered over two sites. One of these sites is close to the inversion center at the center of the cation cage, thus dictating the disorder over the nonsymmetry related sites to be exactly 50:50. The asymmetric unit also contains one molecule of chloroform that is disordered over two sites in an 80:20 ratio. This situation is again complicated by these sites being close to an inversion center. Two molecules of nitromethane complete the contents of the asymmetric unit.

An area of residual electron density was found in the final electron density difference map of [Ag$_4$(**L7**)(O$_3$SCF$_3$)$_4$]. All attempts to model the two disordered molecules of chloroform thought to be present in this space using discrete atoms failed. This area of the structure has been modeled by applying a diffuse solvent model correction to the X-ray intensity data using the Squeeze program of the Platon software suite.[20]

Refinement proceeded smoothly to give the residuals shown in Table 2. Complex neutral-atom scattering factors were used.[21]

Supporting Information Available: Additional figures and a CIF crystallographic file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(21) *International Tables for Crystallography*; Kluwer, Dordrecht, The Netherlands, 1992; Vol. *C*.