Inorganic Chemistry
Article
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Heteroleptic Silver(I) Complexes Prepared from Phenanthroline and Bis-phosphine Ligands

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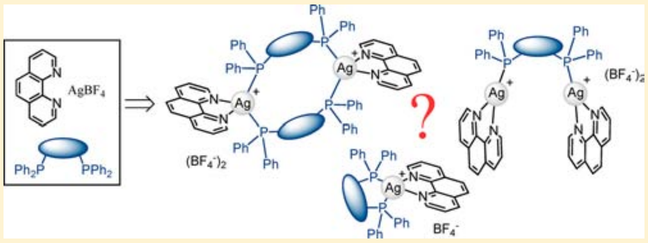
Ⓢ *Supporting Information*



ABSTRACT: The heteroleptic coordination scenario of silver(I) with various phenanthroline ligands (NN) and different bis-phosphine (PP) derivatives has been investigated. In addition to the X-ray crystal structural characterization of the resulting mixed ligand Ag(I) complexes, detailed NMR studies have been performed to disclose the behavior of the prepared silver(I) complexes in solution. The results obtained with silver(I) have been also systematically related to the one obtained for copper(I) with the same combination of PP and NN ligands. Starting from an equimolar mixture of AgBF$_4$, bis[(2-diphenylphosphino)phenyl] ether (POP), and 1,10-phenanthroline (phen), the mononuclear complex [Ag(POP)(phen)]$^+$ has been obtained as the tetrafluoroborate salt. By following the same experimental procedure starting from bis(diphenylphosphino)methane (dppm) or 1,3-bis-(diphenylphosphino)propane (dppp) as the PP ligand, dinuclear complexes with two bridging PP ligands, i.e., [Ag$_2$(NN)$_2$(μ-dppm)$_2$]$^{2+}$ and [Ag$_2$(NN)$_2$(μ-dppp)$_2$]$^{2+}$ with NN = phen or Bphen (bathophenanthroline), have been isolated as the tetrafluoroborate salts. Surprisingly, by using an equimolar ratio of AgBF$_4$, phen or Bphen, and 1,2-bis(diphenylphosphino)ethane (dppe), the corresponding monobridged diphosphine dinuclear complexes [Ag$_2$(NN)$_2$(μ-dppe)]$^{2+}$ have been obtained as the tetrafluoroborate salts. These compounds have been also prepared in excellent yield by using a more appropriate 2:1:2 (phen:dppe:Ag) stoichiometry. These results prompted us to also perform the reactions with dppm and dppp using a 1:2:2 (PP:NN:Ag) stoichiometry. Under these conditions, [Ag$_2$(NN)$_2$(μ-dppm)](BF$_4$)$_2$ (NN = phen or Bphen) and [Ag$_2$(NN)$_2$(μ-dppp)](BF$_4$)$_2$ (NN = phen or Bphen) have been obtained upon crystallization. When compared to their copper(I) analogues, the complexation scenario becomes more complex with silver(I) as the system tolerates also coordinatively frustrated metal ligand assemblies, i.e., with a trigonal coordination geometry. Depending on the stoichiometry or on the nature of the PP partner, silver(I) shows an adaptive capability leading to various complexes with different coordination geometries and composition. However, as in the case of copper(I), their solution behavior is highly dependent on the relative thermodynamic stability of the various possible complexes. In most of the cases, a single Ag(I) complex is observed in solution and the NMR data are in a perfect agreement with their solid state structures. The dppp-containing complexes are the only notable exception; both [Ag$_2$(NN)$_2$(μ-dppp)$_2$](BF$_4$)$_2$ and [Ag$_2$(NN)$_2$(μ-dppp)](BF$_4$)$_2$ are stable in the solid state but a dynamic mixture is observed as soon as these compounds are dissolved. Finally, whereas both dppe and dppp are chelating ligands for copper(I), it is not the case anymore with silver(I) for which a destabilization of species with chelating dppe and dppp ligands is clearly suggested by our results.

■ INTRODUCTION

Because of their potential for applications in the field of light-emitting devices,[1] mixed copper(I) complexes combining bis-phosphines (PP) and aromatic diimine ligands of the phenanthroline family (NN) have been intensively investigated during the past decade.[1−4] As part of this research, we have systematically investigated the preparation of heteroleptic [Cu(PP)(NN)]$^+$ complexes from various 1,10-phenanthroline derivatives and different PP ligands.[4] Whereas the heteroleptic complexes are stable in the solid state, equilibrium between the homoleptic and the heteroleptic complexes is often observed in solution. Detailed analysis revealed that the dynamic equilibrium resulting from ligand exchange reactions is governed by the relative thermodynamic stability of the different possible complexes, namely [Cu(PP)(NN)]$^+$, [Cu(NN)$_2$]$^+$ and [Cu(PP)$_2$]$^+$.[4] Following this systematic studies on [Cu(PP)(NN)]$^+$ compounds, we became naturally interested in extending our investigation to analogous heteroleptic silver(I) complexes. Only a few examples of analogous silver(I) mixed ligand

Received: September 16, 2013
Published: November 27, 2013

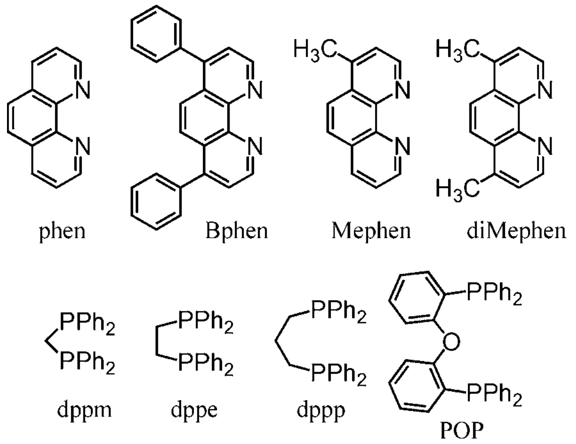
derivatives have been effectively investigated so far.[5−9] For representative examples, 1,1′-bis(diphenylphosphino)ferrocene (dppFc)[5] and bis(diphenylphosphanyl)-o-carborane[6] ligands were successfully used to prepare the corresponding [Ag(PP)(phen)]$^+$ derivatives. The PPh_3 ligand was also used by H. T. Hor et al. to synthesize the [Ag(PPh_3)(phen)](X) compounds,[7] where X = BF_4 or PF_6, and more recently, the bisphosphine derivative [Ag(phen)$(PPh_3)_2^+$][X^-] was structurally characterized using a functionalized acylpyrazolonate anion.[8] It is noteworthy that C. Pettinari et al., studying some families of silver compounds in depth,[9] have reported interesting structural characterizations of dinuclear silver compounds of general formula $[(AgX)_2(PP)(NN)_2]$, where X = ClO_4 or NO_3.[9e]

In this paper, we now report on the synthesis of new silver heteroleptic complexes incorporating both phenanthroline and PP ligands. We were especially interested in varying the length of the spacer in the PP derivatives and the degree of steric hindrance of the phenanthroline ligand to examine their structural effects on the resulting complexes. In addition to their X-ray crystal structural characterization, detailed NMR studies have been performed to disclose the behavior of the prepared silver(I) complexes in solution. The heteroleptic coordination scenario observed with silver(I) is also systematically related to the one observed for copper(I) with the same ligands.[4]

■ RESULTS AND DISCUSSION

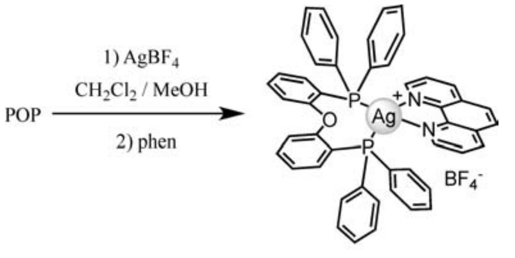
The ligands used in the present studies, namely 1,10-phenanthroline (phen), bathophenanthroline (4,7-diphenyl-1,10-phenanthroline, Bphen), 4,7-dimethyl-1,10-phenanthroline (diMephen), 4-methyl-1,10-phenanthroline (Mephen), bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), and bis[(2-diphenylphosphino)phenyl] ether (POP) are all commercially available. These ligands are depicted in Chart 1.

Chart 1. NN and PP Ligands Used in the Present Studies



[Ag(POP)(phen)](BF_4). The experimental conditions for the preparation of the heteroleptic silver(I) complexes were first adjusted with POP and phen (Scheme 1). Under optimized conditions, a solution of POP (1 equiv.) and $AgBF_4$ (1 equiv.) in CH_2Cl_2/MeOH (5:1) was stirred under Ar at room temperature for 1 h, then phen (1 equiv.) was added. After 1 h, the mixture was evaporated. ^1H and ^{31}P NMR analysis of the crude mixture thus obtained indicated the formation of a single compound. The heteroleptic complex [Ag(POP)(phen)]$^+$ was then isolated in a pure form as its tetrafluoroborate salt by recrystallization in CH_2Cl_2/Et_2O (73% yield). The structural assignment of complex [Ag(POP)(phen)](BF_4) was deduced from both its ^1H NMR and $^{31}P\{H\}$ NMR spectra (see ESI). The $^{31}P\{^1H\}$ NMR spectrum displays two doublets centered at $\delta = -6.75$ ppm in CD_2Cl_2 at room temperature because of the coupling of the equivalent phosphorus atoms with both ^{107}Ag and ^{109}Ag nuclei.[10] The structure of [Ag(POP)(phen)](BF_4) was further confirmed by mass spectrometry. The expected pseudo-molecular ion peak was effectively observed at $m/z = 827.1$ ($[M-BF_4^-]^+$, calcd for $C_{48}H_{36}AgP_2N_2O$: 826.63.

Scheme 1. Preparation of [Ag(phen)(POP)](BF_4) from $AgBF_4$ (1 equiv.), POP (1 equiv.), and phen (1 equiv.)



[Ag(phen)(POP)](BF_4)

X-ray quality crystals were obtained by vapor diffusion of Et_2O into a CH_2Cl_2 solution of [Ag(POP)(phen)](BF_4). As shown in Figure 1, X-ray structural analysis revealed the formation of a mononuclear heteroleptic complex where the silver(I) cation is in an N_2P_2 distorted tetrahedral environment. Both the phenanthroline and the diphosphine moieties are chelating ligands. It can be noted that the POP ligand is bound to the metal only through its pair of P donor atoms, the ether O atom being at a nonbonding distance from the Ag(I) center (Ag(1)−O(1): 3.210(2) Å, see Figure 1). The structure of [Ag(POP)(phen)](BF_4) is indeed very similar to the one reported for the analogous copper(I) complex, [Cu(phen)(POP)](BF_4).[11] However the Ag−P and Ag−N distances are longer (mean values: + 0.19 and +0.26 Å) than those observed for the copper complex: 2.269(2)−2.273(2) and 2.084−2.104(4) Å, respectively. This is in agreement with the fact that the silver atomic radius (1.7 Å) is larger when compared to copper (1.4 Å).[12] Consequently, the value of the phenanthroline bite angle N(1)−Ag−N(2), 71.69(8)° is smaller than the one observed for the corresponding copper complex (80.88(13)°). Close inspection of the crystal packing reveals a pairwise stacking of phen ligands between neighboring cations (Figure 1). The components of this pair are related to one another through a center of inversion located between the phenanthroline rings. The average value for the distance between the two phenanthroline ligands is 3.46 Å, and the $\pi-\pi$ stacking induces a slight deviation of the silver from the phenanthroline plane (ca. 0.45 Å).

$[Ag_2(NN)_2(\mu\text{-dppm})_2](BF_4)_2$ and $[Ag_2(NN)_2(\mu\text{-dppp})_2](BF_4)_2$. The treatment of 1,10-phenanthroline (phen) with an equimolar amount of the appropriate bis-phosphine ligand (dppm or dppp) and $AgBF_4$ in CH_2Cl_2/MeOH (5:1) gave the corresponding binuclear silver(I) complexes (Scheme 2). The $[Ag_2(phen)_2(\mu\text{-PP})_2](BF_4)_2$ derivatives were isolated in a pure form by recrystallization in CH_2Cl_2/Et_2O. By following the

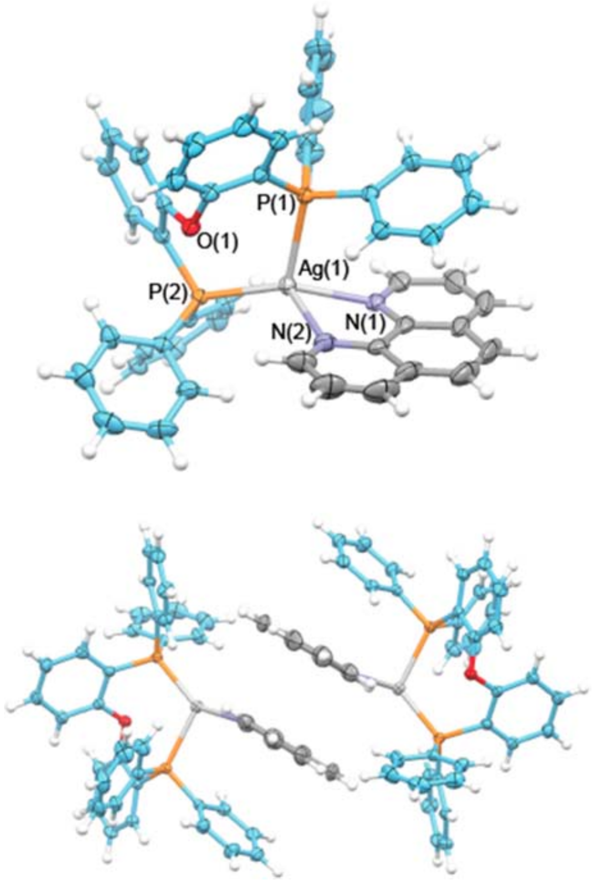
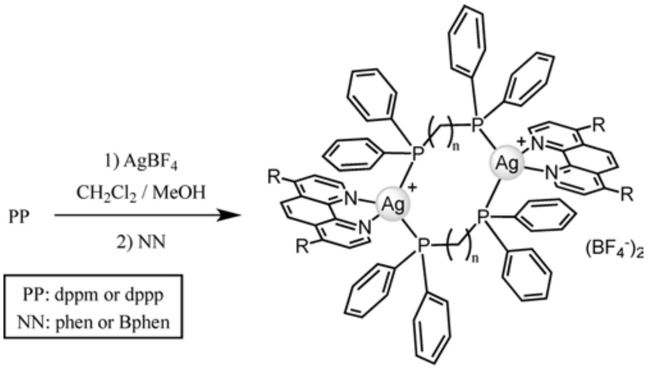


Figure 1. Top: X-ray crystal structure of [Ag(POP)(phen)](BF_4)·CH_2Cl_2 (the BF_4 counteranion and the CH_2Cl_2 molecule are omitted for clarity). Bottom: Representation showing the pairwise stacking of phenanthroline ligands between two neighboring cations. Selected bond lengths (Å): Ag(1)−P(1), 2.5319(7); Ag(1)−P(2), 2.3815(6); Ag(1)−N(1), 2.331(2); Ag(1)−N(2), 2. 378(3). Selected bond angles (deg): P(1)−Ag(1)−P(2), 114.49(3); N(1)−Ag(1)−N(2), 71.69(8); N(1)−Ag(1)−P(1), 95.81(6); N(1)−Ag(1)−P(2), 140.81(6); N(2)−Ag(1)−P(1), 100.74(6); N(2)−Ag(1)−P(2), 122.25(6).

Scheme 2. Preparation of the [Ag_2(NN)$_2$(μ-PP)$_2$](BF_4)$_2$ Derivatives from $AgBF_4$ (1 equiv.) and the Appropriate PP (1 equiv.) and NN (1 equiv.) Ligands



R = H, n = 1: [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$
R = Ph, n = 1: [Ag_2(Bphen)$_2$(μ-dppm)$_2$](BF_4)$_2$
R = H, n = 3: [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$
R = Ph, n = 3: [Ag_2(Bphen)$_2$(μ-dppp)$_2$](BF_4)$_2$

same experimental procedure starting from 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline, Bphen) as the NN ligand, compounds [Ag_2(Bphen)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(diMephen)$_2$(μ-dppp)$_2$](BF_4)$_2$ were obtained in 82 and 97% yield, respectively.

For both [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$, crystals suitable for X-ray crystal structure analysis were obtained by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the dinuclear silver(I) complex. Perspective views of these molecules are shown in Figure 2 and selected bond lengths and angles are listed in Table 1. Compounds [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$ exhibit a similar structure in which two [Ag(phen)]$^+$ moieties are bridged by two diphosphine units. This kind of (μ-dppx)$_2$ arrays has been well-studied concerning the coordination chemistry of diphosphinoalkane ligands.[13] It is noteworthy that in the binuclear Ag_2(μ-dppx)$_2$ compounds previously reported in the literature, solvent molecules as CH_3CN or coordinating anions such as $CF_3CO_2^-$ or ClO_4^- usually complete the coordination sphere of the silver(I) atoms.[9,14] In the case of [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$, the two silver atoms adopt a distorded tetrahedral coordination geometry, and both dinuclear complexes possess a center of inversion located, midway between the two Ag atoms, in the heart of the [Ag_2(μ-PP)$_2$]$^{2+}$ metallacycle which adopts a chair conformation. The phenanthroline behaves as a chelating ligand and the value of the dihedral angle formed by the P−Ag−P and the N−Ag−N planes is 86.64 and 85.46° for [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$, respectively. In the solid state, as indicated by the P−Ag−P angle, the Ag_2P_4 metallacycle is more open for compound [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$ when compared to [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$. In both cases, the Ag−P and P−Ag−P angle are similar to those reported for related compounds such as [Ag_2(NO_2)$_2$(μ-dppm)$_2$][9a] or [Ag_2(η^2-O_2CCH_3)$_2$(μ-dppm)$_2$].[15] Because of the length and to the flexibility of the dppp ligand, the interatomic metal−metal distance is significantly more important in [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$ than in [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$; however, in both cases, the existence of a metal−metal bond is ruled out. As highlighted in Figure 2 for compound [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$, two intramolecular $\pi-\pi$ interactions are clearly observed: one between two phenyl rings of each dppm ligand (denoted as *a* in Figure 2), and one between one phenyl group of each dppm ligand and the phenanthroline group coordinated to the same silver atom (denoted as *b* in Figure 2). In contrast, for compound [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$, no particular intramolecular $\pi-\pi$ interactions can be observed.

Compounds [Ag_2(NN)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(NN)$_2$(μ-dppp)$_2$](BF_4)$_2$ (NN = phen or Bphen) were also characterized in solution by ^1H and ^{31}P NMR spectroscopy. Their NMR behavior was examined in CD_2Cl_2 over a broad range of temperatures (180 to 293 K). The ^1H NMR spectra were consistent with the solid state structures obtained for [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$ (see ESI). Analysis of the integration of the ^1H NMR spectra revealed that, in all the cases, both PP and NN ligands are present in a 1:1 ratio. Additionally, only a single set of signals can be distinguished for both PP and NN ligands. Low temperature ^1H NMR experiments brought no additional information as no significant changes could be observed. For both dppm derivatives, no clear signals could be observed in the

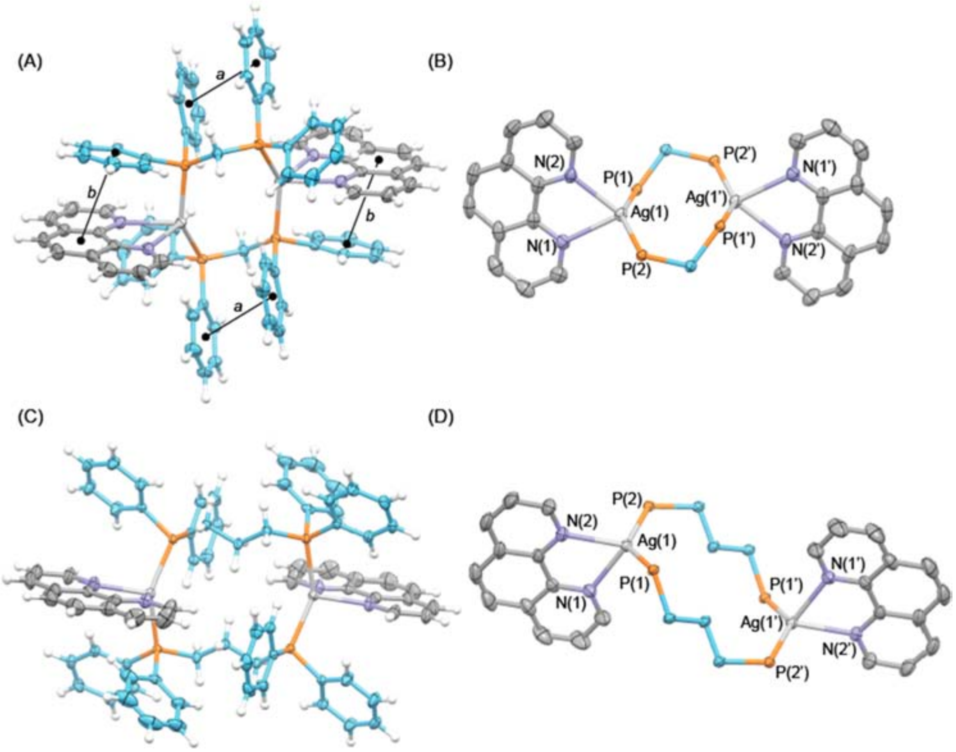


Figure 2. (A) Structure of $[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2.Et_2O$ (the counteranions and the Et_2O molecule are omitted for clarity, thermal ellipsoids drawn at the 50% probability level); the intramolecular $\pi-\pi$ interactions (*a* and *b*) are highlighted. (B) Details of the coordination sphere around the Ag(I) cations in the structure of $[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2.Et_2O$ (C) Structure of $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2.CH_2Cl_2$ (the counteranions and the CH_2Cl_2 molecule are omitted for clarity, thermal ellipsoids drawn at the 50% probability level). (D) Details of the coordination sphere around the Ag(I) cations in the structure of $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2 \cdot CH_2Cl_2$.

Table 1. Bond Distances (Å) and Bond Angles (deg) within the Coordination Sphere of $[Ag_2(phen)_2(\mu\text{-dppm})_2]^{2+}$ (A) and $[Ag_2(phen)_2(\mu\text{-dppp})_2]^{2+}$ (B) (see Figure 2 for the numbering)

bond lengths (Å)			angles (deg)		
	(A)	(B)		(A)	(B)
Ag(1)−P(1)	2.4559(8)	2.4321(5)	P(1)−Ag(1)−P(2)	142.35(3)	134.49(1)
Ag(1)−P(2)	2.4123(8)	2.4208(5)	N(1)−Ag(1)−N(2)	68.46(11)	70.16(7)
Ag(1)−N(1)	2.450(3)	2.390(2)	N(1)−Ag(1)−P(1)	98.14(7)	104.20(5)
Ag(1)−N(2)	2.421(3)	2.403(2)	N(1)−Ag(1)−P(2)	101.34(7)	110.91(6)
			N(2)−Ag(1)−P(1)	99.44(7)	110.94(5)
			N(2)−Ag(1)−P(2)	117.61(7)	107.67(5)

^{31}P NMR spectra recorded at room temperature. This is likely related with a fast dynamic exchange between different possible conformations of their 8-membered ring metallacycles. At low temperature, the ^{31}P NMR spectra revealed however their characteristic resonances. As a typical example, the ^{31}P NMR spectrum recorded for $[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2$ in CD_2Cl_2 at 213 K is depicted in Figure 3. This spectrum can be explained as resulting from the superposition of three different spectra due to the existence of the $^{107}Ag\text{-}^{107}Ag$, $^{109}Ag\text{-}^{109}Ag$, and $^{107}Ag\text{-}^{109}Ag$ species in solution (Figure 3).[16] There is effectively a perfect match between the simulated and the experimental ^{31}P NMR spectra. Importantly, no other resonances could be detected in the ^{31}P NMR spectrum recorded at low temperature, showing that $[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2$ remains intact in solution. This was also the case for the corresponding Cu(I) dinuclear complex, $[Cu_2(phen)_2(\mu\text{-dppm})_2]^{2+}$.[4]

The ^{31}P NMR spectra of $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2$ and $[Ag_2(Bphen)_2(\mu\text{-dppp})_2](BF_4)_2$ recorded under the same conditions are much simpler. This is shown for compound $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2$ in Figure 4. Indeed, a system of two doublets [$\delta = 4.52$, $^1J_{Ag-P} = 457$ (^{109}Ag) and 395 (^{107}Ag) Hz] is observed. This is in agreement with the fact that low values are expected for the $^4J_{P-P}$ and $^5J_{Ag-P}$ coupling constants in this case. Consequently, the shape of the spectra is only influenced by the $^1J_{Ag-P}$ coupling constants. Careful inspection of the ^{31}P NMR spectrum recorded at 213 K also reveals the presence of a minor signal at $\delta = -2.8$ ppm constituted by a system of two doublets [$^1J_{Ag-P} = 378$ (^{109}Ag) and 320 (^{107}Ag) Hz] (Figure 4). This signal is attributed to the presence of mononuclear complex $[Ag(dppp)(phen)]^+$, in which the dppp ligand chelates the silver atom in a tetrahedral AgP_2N_2 environment as in the case of $[Ag(POP)(phen)](BF_4)$. Thus, in this case, a partial decomplexation/recomplexation of the labile dppp ligand induces an equilibrium process between the bi- and mononuclear silver(I) complexes. In the literature, the existence of intramolecular exchanges involving the migration (shift) of the phosphorus atom of a diphosphine from a

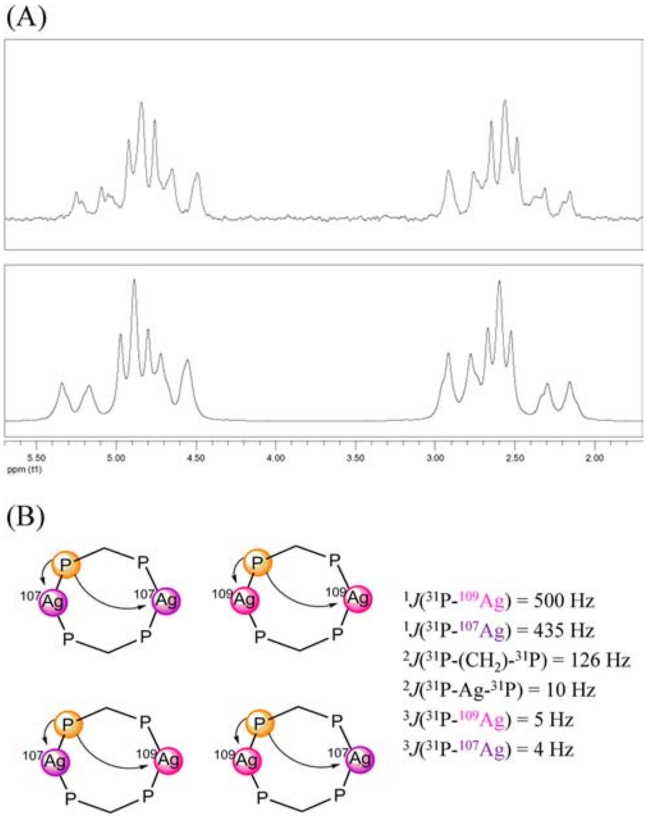


Figure 3. (A) Experimental (top, CD_2Cl_2, 202 MHz, 213 K) and simulated (bottom) $^{31}P\{^1H\}$NMR spectra of $[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2$. (B) For complexes with two silver atoms, the isotopic ratio is close to 1:1 for the two spin isotopes ^{107}Ag and ^{109}Ag (natural abundance 48.2 and 51.8%, respectively) leading to a distribution of isotopomers close to 1:2:1 ($^{107}Ag\text{-}^{107}Ag$, $^{107}Ag\text{-}^{109}Ag$, and $^{109}Ag\text{-}^{109}Ag$), the ^{31}P spectra consist of subspectra for each isotopomer (the *J* values used to obtain the simulated spectrum are indicated).

bridging position to a chelating one (or the opposite) has been already considered for $[Ag_2(\mu\text{-dppx})_3]$ derivatives.[17] It is worth noting that in the case of copper(I), $[Cu(dppp)(phen)](BF_4)$ is the only detectable compound and no traces of a dinuclear complex with two bridging dppp ligands could be detected. The chelating tendency of the $Ph_2P(CH_2)_nPPh_2$ ligands observed for $n = 3$ in the particular case of these Cu(I) complexes decreases however when increasing further the chain length. Effectively, dinuclear complexes have been reported for 1,4-bis(diphenylphosphino)butane ($n = 4$).[2d] In the case of silver, it appears that the dinuclear complexes are preferred. This may result from the larger size of the Ag(I) cation preventing a favorable orbital overlap for a chelating dppp ligand. In this way, the mononuclear Ag(I) complex is destabilized thus contributing to displace the equilibrium toward the dinuclear Ag(I) system despite an entropic penalty. The latter must be therefore compensated by an enthalpic effect resulting most probably from the more favorable coordination geometry within the dinuclear complexes.

$[Ag_2(NN)_2(\mu\text{-PP})](BF_4)_2$. By adding 1 equiv. of the phen ligand to a 1:1 mixture of $AgBF_4$ and dppe, the mono bridged diphosphine dinuclear complex $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$ was obtained whatever the crystallization conditions (Scheme 3). This compound was also prepared using a more appropriate 2:1:2 (phen:dppe:Ag) stoichiometry. $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$ was thus obtained in 96% yield by recrystallization. Similar results were obtained when Bphen, Mephen and diMephen were used as NN ligands. Effectively, in all the cases, the corresponding $[Ag_2(NN)_2(\mu\text{-dppe})](BF_4)_2$ compounds were obtained in excellent yields (82−98%).

Crystals suitable for X-ray crystal structure analysis were obtained for $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$ and $[Ag_2(diMephen)_2(\mu\text{-dppe})](BF_4)_2$. For both compounds, two $[Ag(NN)]^+$ moieties are connected by one bridging diphosphine group and each silver atom is tricoordinated (Figure 5, Table 2). The two structures are similar and the functionalization of the phenanthroline ligand with methyl groups has only a minor impact on the molecular skeleton. In these compounds, the Ag−P and Ag−N bonds are shorter than in $[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2$ and $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2$ (mean values: −0.09 and −0.13 Å). Consequently, the N−Ag−N angles are more important (ca. + 4°) than the ones observed in the case of tetracoordinated silver compounds. The intermetallic distances are also drastically shorter and the P−Ag bonds are nearly perpendicular to the Ag−Ag axis. The values of the intermetallic separation, 3.0658(11) and 3.101(2) Å, for $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$ and $[Ag_2(diMephen)_2(\mu\text{-dppe})](BF_4)_2$, respectively, suggest the existence of intramolecular argentophilic interactions.[18] It is noteworthy that examples of mono bridged diphosphine silver phenanthroline compounds were until recently unknown and that, the perchlorate counterpart of $[Ag_2(diMephen)_2(\mu\text{-dppe})](BF_4)_2$[9e] adopts a quite different dinuclear structure. In this case, the two silver cations include a CH_3CN molecule in their coordination sphere and are tetracoordinated. Moreover, the relative orientation of the two diphenylphosphino groups of dppe ligand is antiperiplanar and not staggered; as a result, the intermetallic distance is much larger and there are no intramolecular $\pi-\pi$ interactions between the two diMephen ligands.

Compounds $[Ag_2(NN)_2(\mu\text{-dppe})](BF_4)_2$ were also characterized in solution and the most interesting features concern their ^{31}P NMR spectra. For these (μ-dppe) arrays, a doublet of multiplets reminiscent of the signal already discussed for the $(\mu\text{-dppx})_2$ array is detected. However, two important differences must be noted: (i) the chemical shift of the signals is now in the 12.2−17.8 ppm range, and (ii) the values of the $^1J_{Ag-P}$ constants are significantly increased in agreement with the fact that the silver atoms are coordinated to three and not to four heteroatoms.[19] To corroborate our assignment, we performed simulation of the ^{31}P NMR spectra of compounds $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$ and $[Ag_2(Bphen)_2(\mu\text{-dppe})](BF_4)_2$. Again, they well-match the experimental spectra as illustrated in Figure 6 for the former compound. It must be also added that no other species could be detected by performing low temperature ^1H or ^{31}P NMR measurements for compounds $[Ag_2(NN)_2(\mu\text{-dppe})](BF_4)_2$ thus showing their good stability in solution. In the solid state structures of $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$ and $[Ag_2(diMephen)_2(\mu\text{-dppe})](BF_4)_2$, silver−silver interactions were observed. In an attempt to demonstrate the existence of such argentophilic interactions in solution, derivative $[Ag_2(Mephen)_2(\mu\text{-dppe})](BF_4)_2$ was carefully analyzed. For this compound, assuming a hypothetical silver−silver interaction, two isomers are in principle possible depending on the relative orientation of the methyl groups of the two phenanthroline ligands (syn or anti). However, whatever the temperature, only one signal was detected for the methyl groups in ^1H NMR spectrum of $[Ag_2(Mephen)_2(\mu\text{-dppe})](BF_4)_2$ suggesting that they are equivalent. Consequently, neither the existence of the two isomers nor a possible metal−

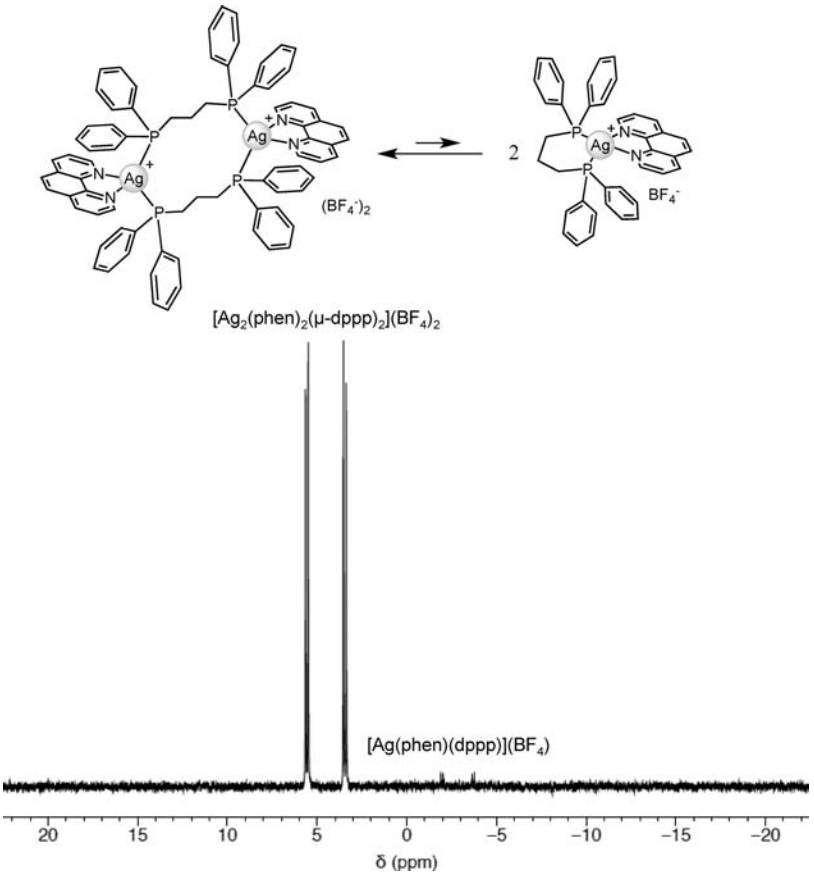
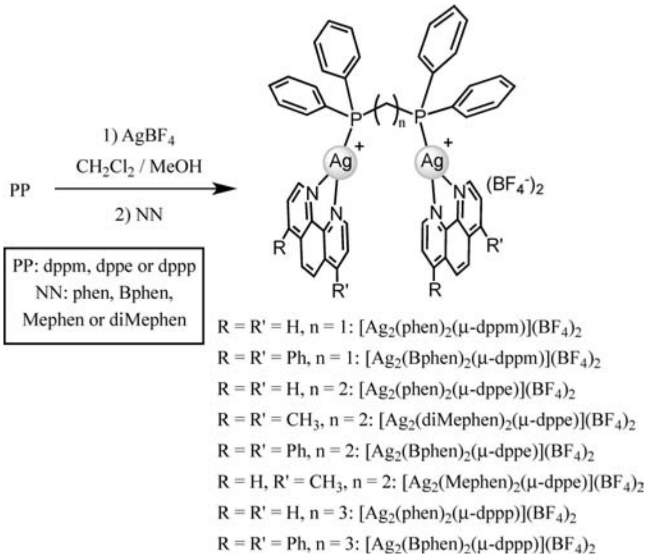


Figure 4. ^{31}P{^{1}H} NMR spectra (202 MHz, CD_2Cl_2) recorded at 213 K upon dissolution of recrystallized [Ag_2(phen)$_2$(*μ*-dppp)$_2$](BF_4)$_2$ and proposed equilibrium between mono- and dinuclear complexes.

Scheme 3. Preparation of the [Ag_2(NN)$_2$(*μ*-PP)](BF_4)$_2$ derivatives from $AgBF_4$ (2 equiv.) and the Appropriate PP (1 equiv.) and NN (2 equiv.) Ligands



metal interaction could be evidenced. It is likely that the argentophilic interactions results from a solid-state effect and contribute to stabilize the supramolecular arrangement in the crystal lattice.

In contrast to the previous PP ligands (POP, dppm, and dppp), the heteroleptic coordination scenario observed for dppe with phen and silver(I) can be hardly related to what was observed in the case of copper(I).[4] Actually, compound [Cu(dppe)(phen)](BF_4) was obtained exclusively from an equimolar mixture of dppe, phen and Cu(CH_3CN)$_4$(BF_4).[4] In contrast, [Ag_2(phen)$_2$(*μ*-dppe)](BF_4)$_2$ was the only isolable product when the reaction was performed from $AgBF_4$ under similar stoichiometric conditions. As already discussed in the case of dppp, chelation of the silver(I) cation appears to be unfavorable despite the well-known tendency of dppe to behave as a chelating ligand.[2d,4] Even in the presence of an excess of dppe, the formation of [Ag_2(phen)$_2$(*μ*-dppe)](BF_4)$_2$ with two unsaturated Ag(I) cation is preferred to a metallacylic structure with two bridging dppe ligands and two saturated metals as observed for dppm and dppp. This suggests a strong destabilization of the dinuclear metallacycle in the case of the dppe ligand, most probably as a result of steric constraints. Importantly, when the reaction dppe with phen and silver(I) was performed under appropriate stoichiometric conditions, [Ag_2(phen)$_2$(*μ*-dppe)](BF_4)$_2$ is exclusively obtained. In contrast, by mixing dppe, phen, and Cu(CH_3CN)$_4$(BF_4) in a 1:2:2 stoichiometry, a mixture of complexes was obtained (mainly [Cu(dppe)(phen)](BF_4) and [Cu (phen)$_2$](BF_4) based on the ^{1}H NMR of the crude mixture). Even if unsaturated species such as [Cu_2(phen)$_2$(*μ*-dppe)](BF_4)$_2$ may be present to a minor extent, the copper(I) is poorly stabilized in the mixture and partial oxidation is rapidly observed under normal laboratory conditions.

The results obtained when dppe was used as the PP ligand prompted us to also perform the reactions with dppm and dppp

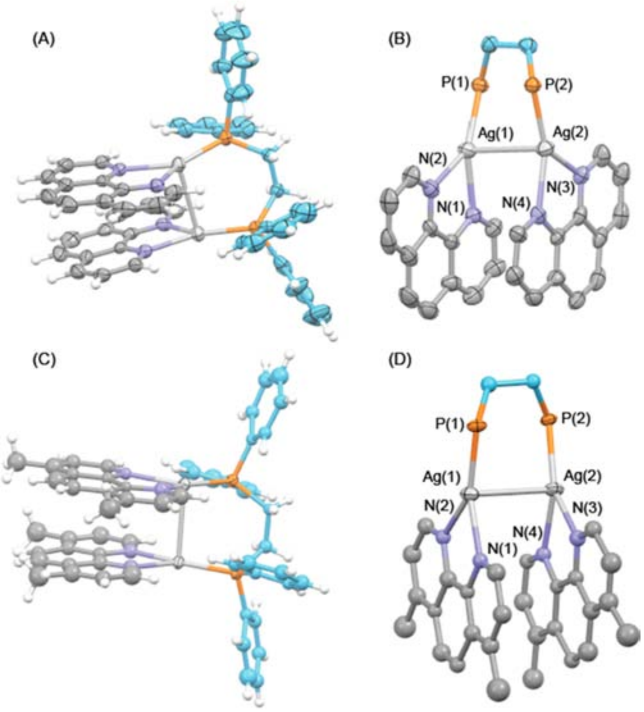


Figure 5. (A) Structure of $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2.CH_2Cl_2{\cdot}H_2O$ (the counteranions and the solvent molecules are omitted for clarity, thermal ellipsoids drawn at the 50% probability level). (B) Details of the coordination sphere around the Ag(I) cations in the structure of $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2{\cdot}CH_2Cl_2{\cdot}H_2O$. (C) Structure of $[Ag_2(diMephen)_2(\mu\text{-dppe})](BF_4)_2{\cdot}(H_2O)_{3.8}$ (the counteranions and the H_2O molecules are omitted for clarity, thermal ellipsoids drawn at the 50% probability level). (D) Details of the coordination sphere around the Ag(I) cations in the structure of $[Ag_2(diMephen)_2(\mu\text{-dppe})](BF_4)_2{\cdot}(H_2O)_{3.8}$.

using a 1:2:2 (PP:NN:Ag) stoichiometry. Under these conditions, $[Ag_2(NN)_2(\mu\text{-dppm})](BF_4)_2$ (NN = phen or Bphen) and $[Ag_2(NN)_2(\mu\text{-dppp})](BF_4)_2$ (NN = phen or Bphen) were obtained upon crystallization (Scheme 3). Consequently, we have shown that, for both dppm and dppp, it is possible to control the nature of the final product, i.e., the mono versus the doubly bridged dinuclear silver species, by adjustment of the initial stoichiometry. In contrast, in the particular case of dppe, the mono bridged diphosphine dinuclear Ag(I) complex is always obtained whatever the initial stoichiometry.

The X-ray crystal structure obtained for compound $[Ag_2(Bphen)_2(\mu\text{-dppm})](BF_4)_2$ is depicted in Figure 7. The

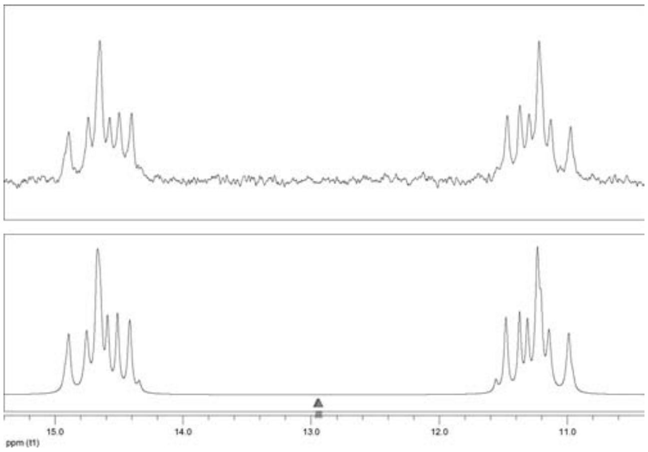


Figure 6. Experimental (top, CD_2Cl_2, 202 MHz, 213 K) and simulated (bottom) $^{31}P\{^1H\}$NMR spectra of $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$.

structure is similar to those described in the previous section for $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2$ and $[Ag_2(Bphen)_2(\mu\text{-dppe})](BF_4)_2$. This is clear by the comparison of their bond lengths and bond angles (Tables 2-3). However, the Ag−Ag distance (3.126(2) Å) is slightly longer for $[Ag_2(Bphen)_2(\mu\text{-dppm})](BF_4)_2$ when compared to that observed for the dppe derivatives (mean value: 3.08 Å) having a longer diphosphinoalkane chain. It is noteworthy that the phenyl groups of the Bphen ligands do not prevent the occurrence of phenanthroline−phenanthroline interactions. Moreover intramolecular C−H/π-interactions are observed between the phenyl groups of adjacent Bphen ligands.

Crystals suitable for X-ray crystal structure analysis were also obtained for compound $[Ag_2(phen)_2(\mu\text{-dppp})](BF_4)_2$ (Figure 8, Table 3). As expected, each phen ligand chelates the silver atom in a trigonal geometry. However, in contrast to what was observed for dppm and dppe, the mono bridged structure of $[Ag_2(phen)_2(\mu\text{-dppp})](BF_4)_2$ shows no intramolecular phenanthroline−phenanthroline interactions. Indeed, the complex adopts an extended conformation in the solid state and the phen ligands are oriented in opposite directions. The dihedral angle between the Ag(1)−P(1)−P(2) and Ag(2)−P(1)−P(2) planes has a value of 110.1° and is markedly different from that observed for example for $[Ag_2(phen)_2(\mu\text{-dppm})](BF_4)_2$ (16.9°). As a result, the Ag−Ag distance (7.026(2) Å) has also the highest value found for the bimetallic compounds reported herein.

The NMR spectra recorded for compounds $[Ag_2(NN)_2(\mu\text{-dppm})](BF_4)_2$ (NN = phen or Bphen) are very similar to the

Table 2. Bond Distances (Å) and Bond Angles (deg) within the Coordination Sphere of $[Ag_2(phen)_2(\mu\text{-dppe})]^{2+}$ (A) and $[Ag_2(diMephen)_2(\mu\text{-dppe})]^{2+}$ (B) (see Figure 5 for the numbering)

bond lengths (Å)			angles (deg)		
	(A)	(B)		(A)	(B)
Ag(1)−P(1)	2.357(2)	2.345(4)	P(1)−Ag(1)−Ag(2)	90.20(7)	91.97(13)
Ag(2)−P(2)	2.330(2)	2.340(4)	P(2)−Ag(2)−Ag(1)	93.07(7)	96.36(12)
Ag(1)−N(1)	2.322(7)	2.303(13)	N(1)−Ag(1)−N(2)	73.9(3)	73.9(4)
Ag(1)−N(2)	2.267(8)	2.257(12)	N(3)−Ag(2)−N(4)	74.3(3)	72.4(4)
Ag(2)−N(3)	2.298(8)	2.261(13)	N(1)−Ag(1)−P(1)	137.96(19)	137.7(3)
Ag(2)−N(4)	2.252(8)	2.325(13)	N(3)−Ag(2)−P(2))	136.7(2)	149.5(3)
Ag(1)−Ag(2)	3.0658(11)	3.101(2)	N(2)−Ag(1)−P(1)	146.2(2)	147.7(3)
			N(4)−Ag(2)−P(2)	148.9(2)	137.4(3)

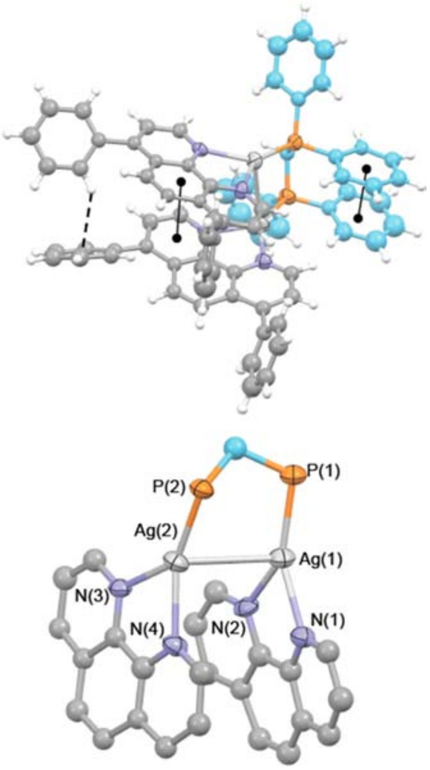


Figure 7. Top: structure of $[Ag_2(Bphen)_2(\mu\text{-dppm})](BF_4)_2\cdot(CH_2Cl_2)_{0.75}\cdot(Et_2O)_{0.5}$ (the counteranions and the solvent molecules are omitted for clarity, thermal ellipsoids drawn at the 50% probability level); the intramolecular $\pi-\pi$ (full line) and CH-π (dashed line) interactions are highlighted. Bottom: details of the coordination sphere around the Ag(I) cations.

one described for the corresponding dppe derivatives in the previous section. The doublet of multiplets observed in their ^{31}P NMR spectra were also explained by a distribution of isotopomers close to 1: 2: 1 (^{107}Ag-^{107}Ag, ^{107}Ag-^{109}Ag, and ^{109}Ag-^{109}Ag) and a perfect match is observed between the simulated and the experimental ^{31}P NMR spectra (see the Supporting Information). It must be added that no other species or ligand exchange processes could be evidenced by performing low temperature ^1H or ^{31}P experiments with compounds $[Ag_2(NN)_2(\mu\text{-dppm})](BF_4)_2$, showing that they remain intact in solution. Remarkably, the heteroleptic Ag(I) coordination scenario can be controlled by the stoichiometry of the various components, i.e., 2:2:2 or 2:2:1 (Ag(I):phen:dppm). In both cases, all ligands and metal binding sites are utilized to generate either exclusively trigonal or tetrahedral complexes. This particular system shows therefore a remarkable adaptability, suggesting a high thermodynamic stability for both $[Ag_2(NN)_2(\mu\text{-dppm})](BF_4)_2$ and $[Ag_2(NN)_2(\mu\text{-dppm})_2](BF_4)_2$ preventing ligand exchange reactions in solution. Such adaptability is not observed in the case of copper(I). Effectively, only the $[Cu_2(NN)_2(\mu\text{-dppm})_2](BF_4)_2$ compound is stable and if the match is not perfect by stoichiometry, poorly stabilized Cu(I) cations are present in the mixture and a partial oxidation is observed.

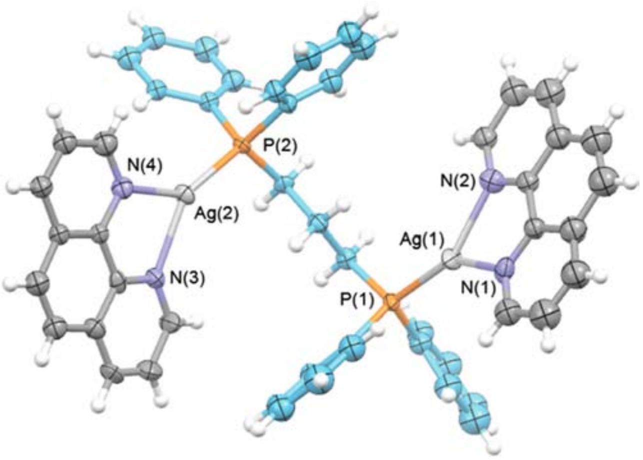


Figure 8. Structure of $[Ag_2(phen)_2(\mu\text{-dppp})](BF_4)_2\cdot(CH_2Cl_2)_{0.5}\cdot(H_2O)_{2.25}$ (the counteranions and the solvent molecules are omitted for clarity, thermal ellipsoids drawn at the 50% probability level).

The behavior of $[Ag_2(phen)_2(\mu\text{-dppp})](BF_4)_2$ was found to be completely different. When crystals of this compound are dissolved in CD_2Cl_2, several complexes can be detected in solution. In the ^{31}P NMR spectra recorded at low temperatures (see the Supporting Information), the characteristic features of $[Ag_2(phen)_2(\mu\text{-dppp})](BF_4)_2$ (a broad doublet of multiplets at $\delta = 13.23$ ppm) are clearly observed at 193 K together with two others signals situated at $\delta = 4.5$ and -2.9 ppm assigned to the doubly bridged compound $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2$ and to the mononuclear compound $[Ag(phen)(\mu\text{-dppp})](BF_4)$, respectively. The dynamic equilibrium involving at least these three identified silver species is governed by the relative thermodynamic stability of these compounds. In this particular case, it appears clearly that coordinatively saturated complexes are preferred in solution as in the case of copper(I).[2−4]

■ CONCLUSIONS

In conclusion, an efficient procedure allowing the preparation of mixed phenanthroline/diphosphine silver(I) compounds has been developed. In contrast with reported results of the

Table 3. Bond Distances (Å) and Bond Angles (deg) within the Coordination Sphere of $[Ag_2(Bphen)_2(\mu\text{-dppm})]^{2+}$ (A) and $[Ag_2(phen)_2(\mu\text{-dppp})]^{2+}$ (B) (see Figures 7 and 8 for the numbering)

bond lengths (Å)			bond angles (deg)		
	(A)	(B)		(A)	(B)
Ag(1)−P(1)	2.357(3)	2.327(3)	N(1)−Ag(1)−N(2)	72.2(4)	73.6(4)
Ag(2)−P(2)	2.357(3)	2.344(3)	N(3)−Ag(2)−N(4)	72.2(3)	72.3(3)
Ag(1)−N(1)	2.296(10)	2.275(10)	N(1)−Ag(1)−P(1)	146.3(3)	142.8(3)
Ag(1)−N(2)	2.303(11)	2.267(10)	N(3)−Ag(2)−P(2)	139.4(2)	145.0(3)
Ag(2)−N(3)	2.319(10)	2.312(9)	N(2)−Ag(1)−P(1)	141.1(3)	143.6(3)
Ag(2)−N(4)	2.296(10)	2.286(9)	N(4)−Ag(2)−P(2)	147.6(3)	142.7(3)
Ag(1)−Ag(2)	3.126(2)				

literature, we have demonstrated that, under our experimental conditions, it is possible to selectively control the number of bridging bis(diphenylphosphino)alkyl ligands into the resulting molecular frameworks. Moreover, six dinuclear silver(I) compounds have been characterized by X-ray diffraction studies, verifying that no anion or solvent molecule coordinates the silver atoms. Although the silver cation may adopt a tetrahedral or trigonal geometry, the intermetallic distance varies from 3.066 to 7.026 Å. These properties are due, on one hand, to the capability of the silver atom of adopting different geometries and bite angles, and on the other hand, to the well-known flexibility and versatility of the coordination properties of the diphosphine ligands.

When compared to their copper(I) analogues, the situation is more complicated with silver(I). Indeed, for copper(I), maximum site occupancy[20] is the key principle for the dynamic heteroleptic complexation scenario, in this case all the ligands and metals are utilized to generate coordinatively saturated complexes.[4] In the case of silver(I), the complexation scenario becomes more complex as the system tolerates also coordinatively frustrated metal ligand assemblies, i.e., with a trigonal coordination geometry. Depending on the stoichiometry or on the nature of the PP partner, silver(I) shows an adaptive capability leading to various complexes with different coordination geometries and composition. Indeed, silver(I) derivatives are less prone to oxidation when compared to copper(I) complexes and the stabilization of the silver(I) cation is not necessarily associated with a tetrahedral coordination geometry. However, as in the case of copper(I), their solution behavior is highly dependent on the relative thermodynamic stability of the various possible complexes. In most of the cases, a single compound is observed in solution and the NMR data are in a perfect agreement with their solid state structures. The dppp-containing complexes are the only notable exception; both $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2$ and $[Ag_2(phen)_2(\mu\text{-dppp})](BF_4)_2$ are stable in the solid state but a dynamic mixture is observed as soon as these compounds are dissolved. Finally, whereas both dppe and dppp are chelating ligands for copper(I),[2d,4] it is not the case anymore with silver(I) for which a destabilization of species with chelating dppe and dppp ligands is clearly suggested by our results.

■ EXPERIMENTAL SECTION

General Procedures. Reagents were purchased as reagent grade and used without further purification. Et_2O was distilled over Na/benzophenone under Ar. Dichloromethane (CH_2Cl_2) was distilled over CaH_2 under Ar. All reactions were performed in standard glassware under an argon atmosphere using Schlenk and vacuum-line techniques. Evaporation and concentration were done using a water aspirator and drying in vacuo at 10^{-2} Torr. NMR spectra were recorded on Bruker ARX 250, DPX 300 and on an Avance 300, and Avance 500 spectrometers equipped with a 5 mm triple resonance inverse probe with dedicated ^{31}P channel operating at 500.33 for ^1H NMR. Chemical shifts δ are in ppm, with positive values to high frequency relative to external tetramethylsilane reference for ^1H and ^{13}C, to 85% H_3PO_4 for ^{31}P, and to $AgNO_3$ for ^{109}Ag, respectively; coupling constants J are in Hz. Temperature calibration was determined using a methanol chemical shift thermometer. ^{109}Ag resonances were obtained using 2D ^{31}P-^{109}Ag HMQC-{^1H}. NMR simulations were run with MesTReC 4.9.9.3 software. For complexes with two silver atoms, the isotopic ratio is close to 1:1 for the two spin isotopes ^{107}Ag and ^{109}Ag (natural abundance 48.2 and 51.8%, respectively) leading to a distribution of isotopomers close to 1: 2: 1 (^{107}Ag-^{107}Ag, ^{107}Ag-^{109}Ag, and ^{109}Ag-^{109}Ag). The ^{31}P spectra consist of subspectra for each isotopomer with either a AA′XX′, a AA′XY, a AA′XX′A″A‴, or a AA′XYA″A‴ (A = ^{31}P, X = ^{107}Ag, Y = ^{109}Ag) pattern depending on the $^2J_{(P-P)}$ and $^3J_{(P-P)}$ values. In most of the cases, the two phosphorus atoms of the PP ligands are magnetically nonequivalent. Elemental analysis were carried out on a Perkin−Elmer 2400 B analyzer (Flash combustion and detection by catharometry) at the L.C.C. Microanalytical Laboratory in Toulouse. Mass spectra were obtained at the *Service Commun de Spectrométrie de Masse* (Université Paul Sabatier and CNRS, Toulouse, France). Spectra were performed on a triple quadrupole mass spectrometer (Perkin−ElmerSciex API 365) using electrospray as the ionization mode.

General Procedure for the Preparation of $[Ag(phen)(POP)](BF_4)$ and $[Ag_2(NN)_2(\mu\text{-PP})_2](BF_4)_2$. A solution of the appropriate bis-phosphine ligand (1 equiv.) and $AgBF_4$ (1 equiv.) in a 5:1 CH_2Cl_2/MeOH mixture was stirred for 1 h, then phen or Bphen (1 equiv.) was added. After 1 h, the solvents were evaporated. The heteroleptic complexes were then obtained pure as crystalline solids by slow diffusion of Et_2O into a CH_2Cl_2 solution of the crude product.

$[Ag(phen)(POP)](BF_4)$. This compound was thus obtained in 73% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 300 MHz, 298 K): δ = 6.83−6.89 (m, 4H), 7.03 (t, J = 7 Hz, 2H), 7.13−7.21 (m, 16H), 7.25−7.34 (m, 6H), 7.70 (dd, J = 5 and 8 Hz), 7.99 (s, 2H), 8.47 (dd, J = 8 and 1.5 Hz, 2H), 8.77 (dd, J = 5 and 1.5 Hz, 2H) ppm. $^{31}P\{^1H\}$ RMN (CD_2Cl_2, 121.5 MHz, 298 K): δ = −6.75 (2d, J_{Ag-P} = 423 and 366 Hz) ppm. ESI-MS (+): m/z = 827.2 ($[M\text{-}BF_4]^+$, calcd. for $C_{48}H_{36}AgP_2N_2O$: 826.6). $C_{48}H_{36}AgP_2N_2OBF_4\cdot CH_2Cl_2$: calcd. C 58.95, H 3.84, N 2.81; found C 59.01, H 3.89, N 2.68.

$[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2$. This compound was thus obtained in 80% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 500 MHz, 293 K): δ = 3.74 (br s, 4H), 6.93 (m, J = 8 Hz, 16H), 7.06−7.12 (m, 24H), 7.66 (dd, J = 8 and 4.5 Hz, 4H), 7.69 (s, 4H), 8.20 (dd, J = 8 and 1.5 Hz, 4H), 8.72 (dd, J = 4.5 and 1.5 Hz, 4H) ppm. $^{31}P\{^1H\}$NMR (CD_2Cl_2, 202 MHz, 213 K): δ = 3.71 (dm, $^1J_{P-Ag}$ = 500 and 435 Hz, $^2J_{P-P}$ = 126 Hz, $^2J_{P-Ag}$ = 10 Hz, $^3J_{P-Ag}$ = −5 Hz and −4 Hz) ppm. $^{13}C\{^{31}P\}\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 298K): δ = 26.14, 124.19, 126.64, 128.52, 129.06, 130.21, 131.58, 132.60, 137.05, 143.25, 151.07 ppm. ^{109}Ag NMR (CD_2Cl_2, 23 MHz, 213 K): δ = 1020 ppm. $C_{74}H_{60}Ag_2B_2F_8N_4P_4$ (1518.54): calcd. C 58.53, H 3.98, N 3.69; found C 58.51, H 3.83, N 3.62.

$[Ag_2(Bphen)_2(\mu\text{-dppm})_2](BF_4)_2$. This compound was thus obtained in 82% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 300 MHz, 298 K): δ = 3.85 (br s, 4H), 7.01 (m, J = 7.5 Hz, 16H), 7.13 (t, J = 7 Hz, 8H), 7.23−7.25 (m, 16H), 7.45−7.48 (m, 8H), 7.54−7.57 (m, 12H), 7.60 (d, J = 5 Hz, 4H), 7.71 (s, 4H), 8.82 (d, J = 5 Hz, 4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 213 K): δ = 3.95 (dm) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz, 298 K): δ = 25.20, 124.12, 124.81, 126.48, 128.48, 128.94, 129.51, 129.87, 130.17, 131.66, 132.63, 136.93, 143.51, 148.98, 150.32 ppm. $C_{98}H_{76}Ag_2B_2F_8N_4P_4$ 0.5CH_2Cl_2: calcd. C 63.42, H 4.16, N 3.00; found C 62.87, H 4.00, N 3.11.

$[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2$. This compound was thus obtained in 77% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 500 MHz, 213 K): δ = 1.94 (br s, 4H), 2.36 (br s, 8H), 7.10 (m, J = 7.5 Hz), 7.16−7.19 (m, 16H), 7.31 (m, J = 7 Hz, 8H), 7.53 (dd, J = 8 and 4 Hz, 4H), 7.79 (s, 4H), 8.02 (d, J = 4 Hz, 4H), 8.32 (dd, J = 8 and 1 Hz, 4H,) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 213 K): δ = 4.52 (2d, $^1J_{P-Ag}$ = 457 and 397 Hz) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (CD_2Cl_2, 125.8 MHz, 221 K): δ = 23.80, 28.37, 124.61, 127.29, 129.08, 129.50, 130.80, 131.74, 132.17, 138.00, 143.18, 149.78 ppm. ^{109}Ag NMR (CD_2Cl_2, 23 MHz, 213 K): δ = 1055 ppm. ESI-MS (+): m/z = 1487.5 ($[M\text{-}BF_4]^+$, calcd. for $C_{78}H_{68}Ag_2BF_4N_4P_4$: 1487.25). $C_{78}H_{68}Ag_2B_2F_8N_4P_4\cdot CH_2Cl_2$: calcd. C 57.17, H 4.25, N 3.38; found C 57.74, H 4.20. N 3.40.

$[Ag_2(Bphen)_2(\mu\text{-dppp})_2](BF_4)_2$. This compound was thus obtained in 97% yield as a colorless crystalline solid (due to its poor solubility, this compound was only characterized by ^1H NMR). ^1H NMR (CD_2Cl_2, 300 MHz, 293 K): δ = 2.11 (br s, 4H), 2.65 (br s, 8H), 7.10−7.40 (br m, 40H), 7.35−7.64 (m, 24H), 7.87 (s, 4H), 8.79 (br s, 4H) ppm. $C_{102}H_{84}Ag_2B_2F_8N_4P_4\cdot H_2O$ (1897.39): calcd. C 64.58, H 4.57, N 2.95; found C 64.80, H 4.41, N 2.95.

General Procedure for the Preparation of $[Ag_2(NN)_2(\mu\text{-PP})](BF_4)_2$. A solution of the appropriate bis-phosphine ligand (1

Table 4. Crystallographic Data, Data Collection, and Refinement Parameters for $[Ag(POP)(phen)](BF_4)\cdot CH_2Cl_2$ (A), $[Ag_2(phen)_2(\mu\text{-dppm})_2](BF_4)_2\cdot Et_2O$ (B), $[Ag_2(phen)_2(\mu\text{-dppp})_2](BF_4)_2\cdot Et_2O$ (C), $[Ag_2(phen)_2(\mu\text{-dppe})](BF_4)_2\cdot CH_2Cl_2\cdot H_2O$ (D), $[Ag_2(diMephen)_2(\mu\text{-dppe})](BF_4)_2\cdot (H_2O)_{3.8}$ (E), $[Ag_2(Bphen)_2(\mu\text{-dppm})](BF_4)_2\cdot (CH_2Cl_2)_{0.75}.(Et_2O)_{0.5}$ (F), and $[Ag_2(phen)_2(\mu\text{-dppp})](BF_4)_2.(CH_2Cl_2)_{0.5}.(H_2O)_{2.25}$ (G)

	(A)	(B)	(C)	(D)	(E)	(F)	(G)
chem. form.	$C_{49}H_{38}Ag_1B_1Cl_2F_4N_2O_1P_2$	$C_{82}H_{80}Ag_2B_2F_8N_4O_2P_4$	$C_{80}H_{72}Ag_2B_2Cl_4F_8N_4P_4$	$C_{51}H_{44}Ag_2B_2Cl_2F_8N_4OP_2$	$C_{54}H_{55.67}\ Ag_2B_2F_8N_4O_{3.83}P_2$	$C_{75.75}\ H_{61.50}\ Ag_2\ B_2\ Cl_{1.50}\ F_8\ N_4O_1P_2$	$C_{51.50}H_{47.5}\ Ag_2B_2Cl_1F_8N_4O_{2.25}P_2$
fw	998.38	1666.80	1744.53	1251.13	1273.35	1548.32	1245.21
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$\mathrm{P}\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/\mathrm{n}$	$P\bar{1}$
a (Å)	11.9918(5)	15.4142(7)	11.2573(5)	11.9880(10)	37.9967(16)	14.7910(10)	11.2083(6)
b (Å)	12.8882(6)	13.1813(8)	13.7792(6)	31.809(2)	32.2079(13)	21.016(2)	12.6121(6)
c (Å)	14.8827(7)	20.2680(10)	14.4971(6)	13.9080(10)	14.0707(6)	24.5521(18)	20.8920(10)
α (deg)	77.871(4)	90	104.345(4)	90	90	90	100.343(4)
β (deg)	80.596(5)	112.022(5)	98.500(5)	102.568(9)	94.628(3)	98.344(8)	92,211(4)
χ (deg)	89.471(4)	90	112.360(4)	90	90	90	113.308(5)
V (Å^3)	2217.84(18)	3817.6(4)	1939.90(18)	5176.4(7)	17163.5(12)	7551.2(11)	2648.5(3)
Z	2	2	1	4	12	4	2
D_{calcd} (g cm^{-3})	1.495	1.450	1.493	1.605	1.469	1.361	1.56
μ (Mo Kα), mm^{-1}	0,704	0.666	0.791	0.993	0.812	0.678	0.922
T (K)	180	180	180	180	180	180	160
θ range (deg)	3.19–29.00	2.66–29.07	3.01–29.06	1.97–26.01	2.68–29.02	2.11–26.02	2.78–29.10
data collected	20802	34807	18200	49539	155144	75514	25370
unique data/ R_{int}	11753/0.028	10145/0.050	10255/0.023	9814/0.060	45818/0.072	13886/0.100	14046/0.036
no. of params/ restraints	559/0	444/0	469/0	649/0	987/30	442/3	357/12
data used, [I > nσ(I)]	7982, n = 3	5246, n = 3	7401, n = 3	6560, n = 1.2	10882, n = 3	4444, n = 3	6528, n = 3
R-factor	0.0323	0.0351	0.0303	0.0764	0.0916	0.0779	0.1035
weighted R-factor	0.0380	0.0410	0.0344	0.0785	0.0902	0.0876	0.1580
GOF	1.107	1.112	1.100	1.706	1.100	1.087	0.951
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.73/−0.79	0.83/−0.61	0.91/−0.62	1.46/−1.33	2.25/−1.97	1.76/−0.65	2.52/−2.13

equiv.) and $AgBF_4$ (2 equiv.) in a 5:1 CH_2Cl_2/MeOH mixture was stirred for 1 h, then the appropriate phenanthroline ligand (2 equiv.) was added. After 1 h, the solvents were evaporated. The heteroleptic complexes were then obtained pure as crystalline solids by slow diffusion of Et_2O into a CH_2Cl_2 solution of the crude product.

$[Ag_2(phen)_2(\mu\text{-}dppe)](BF_4)_2$. This compound was thus obtained in 96% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 500 MHz, 293 K): δ = 2.87 (br s, 4H), 7.50 (m, J = 7.5 Hz, 8H), 7.56 (t, J = 7 Hz, 4H), 7.62 (m, 8H), 7.82 (dd, J = 8 and 4.5 Hz, 4H), 7.93 (s, 4H), 8.47 (dd, J = 8 and 1.5 Hz, 4H), 8.95 (dd, J = 4.5 and 1.5 Hz, 4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 213 K): δ = 12.94 (dm, $^1J_{P-Ag}$ = 725 and 627 Hz, $^3J_{P-P}$ = 50 and 44 Hz, $^4J_{P-Ag}$ = −5 Hz and −4 Hz) ppm. $^{13}C\{^{31}P\}\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 298 K): δ = 24.09, 125.04, 127.24, 129.38, 129.55, 130.77, 131.46, 132.93, 138.83, 142.54, 151.63 ppm. ^{109}Ag NMR (CD_2Cl_2, 23 MHz, 213 K): δ = 1077 ppm. $C_{50}H_{40}Ag_2B_2F_8N_4P_2$ (1148.17): calcd. C 52.30, H 3.51, N 4.88; found C 52.38, H 3.21, N 4.84.

$[Ag_2(Bphen)_2(\mu\text{-}dppe)](BF_4)_2$. This compound was thus obtained in 82% yield as a colorless crystalline solid. NMR ^1H (CD_2Cl_2, 250 MHz, 293 K): δ = 2.98 (br s, 4H), 7.54–7.64 (m, 32H), 7.71–7.78 (m, 8H), 7.86 (d, J = 5 Hz, 4H), 8.02 (s, 4H), 9.19 (d, J = 5 Hz, 4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101 MHz, 293 K): δ = 14.09 (dm) ppm. $^{13}C\{^{31}P\}\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 298 K): δ = 24.19, 124.76, 125.34, 127.20, 128.94, 129.40, 129.59, 129.62, 130.74, 131.51, 133.04, 136.36, 143.23, 151.26, 151.38 ppm. $C_{74}H_{56}Ag_2B_2F_8N_4P_2$ (1452.56): calcd. C 61.19, H 3.89, N 3.86; found C 61.37, H 3.67, N 3.83.

$[Ag_2(Mephen)_2(\mu\text{-}dppe)](BF_4)_2$. This compound was thus obtained in 99% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 250 MHz, 298 K): δ = 2.88 (s, 6H), 2.96 (m, 4H), 7.54–7.73 (m, 22H), 7.84 (dd, J = 8 and 4.5 Hz, 2H), 7.98 (AB, J = 9 Hz, 4H), 8.51 (dd, J = 8 and 1 Hz, 2H), 8.82 (d, J_3 = 5 Hz, 2H), 9.19 (dd, J = 4.5 and 1 Hz, 2H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 213 K): δ = 12.19 (br dm) ppm.

$[Ag_2(diMephen)_2(\mu\text{-}dppe)](BF_4)_2$. This compound was thus obtained in 89% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 300 MHz, 298 K): δ = 2.81 (s, 12H), 2.95 (m, 4H), 7.53–7.60 (m, 16H), 7.64–7.71 (m, 8H), 7.86 (d, J = 5 Hz, 4H), 8.01 (s, 4H), 8.64 (d, J = 5 Hz, 4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81 MHz, 298 K): δ = 16.14 (dm) ppm. $C_{54}H_{48}Ag_2B_2F_8N_4P_2\cdot 2CH_2Cl_2$: calcd. C 48.95, H 3.81, N 4.08; found C 49.39, H 3.77, N 4.16.

$[Ag_2(phen)_2(\mu\text{-}dppm)](BF_4)_2$. This compound was thus obtained in 42% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 300 MHz, 298 K): δ = 4.04 (m, 2H), 7.43–7.46 (m, 12H), 7.60–7.72 (m, 16H), 8.11 (d, J = 8 Hz, 4H), 9.02 (dd, J = 5 and 1.5 Hz, 4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101 MHz, 298 K): δ = 16.60 (br d) ppm. $C_{49}H_{38}Ag_2B_2F_8N_4P_2\cdot H_2O$ (1152.16): calcd. C 51.08, H 3.50, N 4.86; found C 51.20, H 3.07, N 4.89.

$[Ag_2(Bphen)_2(\mu\text{-}dppm)](BF_4)_2$. This compound was thus obtained in 71% yield as a colorless crystalline solid. ^1H NMR (CD_2Cl_2, 300 MHz, 298 K): δ = 4.13 (m, 2H), 7.18–7.20 (m, 8H), 7.40–7.55 (m, 24H), 7.65 (t, J = 2 Hz, 8H), 7.72–7.79 (m, 8H), 9.28 (d, J = 5 Hz, 4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 213 K): δ = 17.75 ppm (dm, $^1J_{P-Ag}$ = 735 and 636 Hz, $^2J_{P-P}$ = 150 Hz, $^3J_{\ P-Ag}$ = −6 Hz and -5 Hz).$^{13}C\{^{31}P\}\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 298 K): δ = 27.88, 124.10, 125.41, 125.97, 128.86, 129.44, 129.61, 129.66, 131.62, 133.24, 135.58, 141.80, 150.77, 152.30 ppm. $C_{73}H_{54}Ag_2B_2F_8N_4P_2$ (1438.53): calcd. C 60.95, H 3.78, N 3.89; found C 60.50, H 3.59, N 3.74.

$[Ag_2(phen)_2(\mu\text{-}dppp)](BF_4)_2$. This compound was thus obtained in 80% yield as a colorless crystalline solid. $C_{51}H_{42}Ag_2B_2F_8N_4P_2$ (1162.20): calcd. C 52.71, H 3.64, N 4.82; Found C 52.84, H 3.53, N 4.66. As soon as dissolved in CH_2Cl_2, ligand exchange took place

and analysis of the NMR spectra revealed the presence of different species in solution.

[Ag_2(Bphen)$_2$(μ-dppp)](BF_4)$_2$. This compound was thus obtained in 97% yield as a colorless crystalline solid. $C_{75}H_{58}Ag_2B_2F_8N_4P_2$ (1466.58): calcd. C 61.42, H 3.99, N 3.82; found C 61.15, H 3.76, N 3.69. As soon as dissolved in CH_2Cl_2, ligand exchange took place and analysis of the NMR spectrum revealed the presence of different species in solution.

X-ray Crystal Structures. Data were collected at low temperature on an Excalibur Oxford diffractometer or on a IPDS STOE, using a graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by Direct Methods using SIR92,[21] and refined by full-matrix least-squares procedures using the programs of the PC version of CRYSTALS.[22] Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[23] For complexes [Ag(POP)(phen)](BF_4), [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$ and [Ag_2(phen)$_2$(μ-dppe)](BF_4)$_2$ all non-hydrogen atoms were refined anisotropically. Solvent molecules were refined isotropically for complexes [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$ and [Ag_2(phen)$_2$(μ-dppp)](BF_4)$_2$. For complex [Ag_2(Bphen)$_2$(μ-dppm)](BF_4)$_2$ and [Ag_2(diMephen)$_2$(μ-dppe)](BF_4)$_2$, only the heaviest atoms were refined anisotropically, because of the lack of data and high number of parameters. Hydrogen atoms were refined by using a riding model. Absorption corrections were introduced by using the MULTISCAN program.[24] For compound [Ag_2(Bphen)$_2$(μ-dppm)](BF_4)$_2$, the structure displays the presence of three crystallographically independent "C54 H48 Ag2 P2 N4" entities, only one has been depicted in Figure 5. The crystallographic data and refinement parameters are reported in Table 4 for all the compounds.

ASSOCIATED CONTENT

Supporting Information

Representative ^{1}H and ^{31}P NMR spectra of the new compounds are given in the ESI. Crystallographic (CIF) files for [Ag(POP)(phen)](BF_4).CH_2Cl_2, [Ag_2(phen)$_2$(μ-dppm)$_2$](BF_4)$_2$.Et_2O, [Ag_2(phen)$_2$(μ-dppp)$_2$](BF_4)$_2$.Et_2O, [Ag_2(phen)$_2$(μ-dppe)](BF_4)$_2$.CH_2Cl_2.H_2O, [Ag_2(diMephen)$_2$(μ-dppe)](BF_4)$_2$.(H_2O)$_{3.8}$, [Ag_2(Bphen)$_2$(μ-dppm)](BF_4)$_2$.(CH_2Cl_2)$_{0.75}$.(Et_2O)$_{0.5}$ and [Ag_2(phen)$_2$(μ-dppp)](BF_4)$_2$.(CH_2Cl_2)$_{0.5}$.(H_2O)$_{2.25}$. This material is available free of charge via the Internet at http://pubs.acs.org. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre and were allocated the deposition numbers CCDC 958165, CCDC 958166, CCDC 958167, CCDC 958168, CCDC 958169, CCDC 958170 and CCDC 958171, respectively.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the CNRS and the EC (contract PITN-GA-2008-215399 - FINELUMEN). We further thank Dr. O. Moudam for the initial preparation of compound [Ag(POP)(phen)](BF_4) and Dr. P. Braunstein for helpful discussions.

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