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# New Ag(I)−Iminophosphorane Coordination Polymers as Efficient Catalysts Precursors for the MW-Assisted Meyer−Schuster Rearrangement of Propargylic Alcohols in Water

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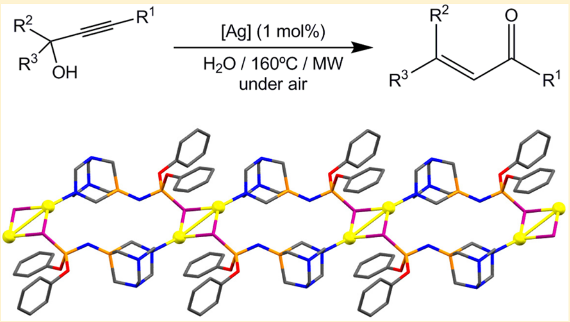
*Supporting Information*

**ABSTRACT:** Treatment of the *N*-thiophosphorylated iminophosphorane ligands $(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2$ [PTA = 1,3,5-triaza-7-phosphaadamantane, **3a** and **3b**] and $(\mathrm{DAPTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2$ [DAPTA = 3,7-diacetyl-1,3,7-triaza-5-bicyclo[3.3.1]nonane, **4a** and **4b**] with an equimolecular amount of $\mathrm{AgSbF_6}$ leads to high-yield formation of the new one-dimensional coordination polymers $[\mathrm{Ag}\{\mu^2\text{-}N,S\text{-}(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2\}]_x[\mathrm{SbF}_6]_x$ (**5a** and **5b**) and $[\mathrm{Ag}\{\mu^2\text{-}O,S\text{-}(\mathrm{DAPTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2\}]_x[\mathrm{SbF}_6]_x$ (**6a** and **6b**), respectively. These new (iminophosphorane)silver(I) coordination polymers are efficient catalyst precursors for the Meyer−Schuster isomerization of both terminal and internal alkynols. Reactions proceeded in water, under aerobic conditions and using microwave irradiation as heating source, to afford the corresponding *α*,*β*-unsaturated carbonyl compounds in excellent yields, without the addition of any cocatalyst. Remarkably, it should be noted that this catalytic system can be recycled up to 10 consecutive runs (1st cycle 45 min, 99%; 10th cycle 6 h, 97%). ESI-MS analysis of **5a** in water has been carried out providing valuable insight into the monomeric active species responsible for catalytic activity in water.



## ■ INTRODUCTION

During the past decade, construction of new coordination polymers has emerged as one of the most important research topics due to their wide application in many fields such as crystal engineering and coordination and materials chemistry,[1] to name a few. In this sense, the water-soluble phosphine PTA [1,3,5-triaza-7-phosphaadamantane (**1**), Figure 1] and its derivatives [i.e., DAPTA, 3,7-diacetyl-1,3,7-triaza-5-bicyclo[3.3.1]nonane (**2**), Figure 1] have been previously used as versatile building blocks for design of both one- and two-dimensional coordination polymers.[2] However, to our knowledge, the ability of their iminophosphorane derivatives [general formula (PTA)=NR and (DAPTA)=NR, respectively] to act as the cornerstone piece for easy synthesis of new coordination polymers has been totally neglected. In this sense, we recently reported the synthesis of the first water-stable iminophosphorane ligands based on the water-soluble phosphines PTA and DAPTA [$(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2$ (R = Et (**3a**), Ph (**3b**); $(\mathrm{DAPTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2$ (R = Et (**4a**), Ph (**4b**), see Figure 1] as well as studying their coordination in a Cu(I) precursor, yielding the corresponding one-dimensional coordination polymers $[\mathrm{Cu}\{\mu^2\text{-}N,S\text{-}(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2\}_2]_x[\mathrm{PF}_6]_x$.[3] These compounds have proved to be efficient catalysts for copper-catalyzed cycloaddition of azides and alkynes (both terminal and internal) in water and under aerobic reaction conditions.[3]

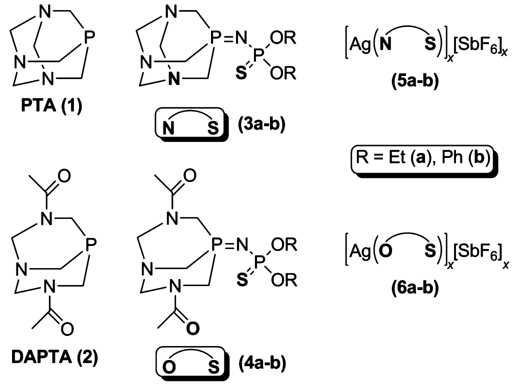


**Figure 1.** Structure of ligands **3**, **4a**, and **4b** and their Ag(I)-coordination polymers **5a**, **5b**, **6a**, and **6b**.

On the other hand, the search for novel efficient organic methodologies which proceed with high levels of selectivity and

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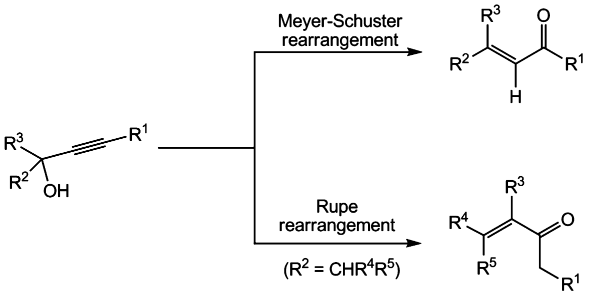
atom economy (i.e., all atoms of the reaction end up in the final product) constitutes one of the major challenges in modern synthesis.[4] In this sense, isomerization reactions are typical examples of atom economic processes as no byproducts are generated. In this regard, isomerization reactions of propargylic alcohols provide straightforward synthetic routes to *α,β*-unsaturated carbonyl compounds which are (i) useful building blocks in organic synthesis, (ii) advanced intermediates in the manufacture of aromes and fragrances, and (iii) key structural units in a large number of biologically active natural products.[5] The isomerization process of these propargylic alcohols proceeds through a formal 1,3-shift of the hydroxyl moiety, known as the Meyer−Schuster rearrangement (Scheme 1).[6]

**Scheme 1. Meyer−Schuster and Rupe Rearrangements of Propargylic Alcohols**



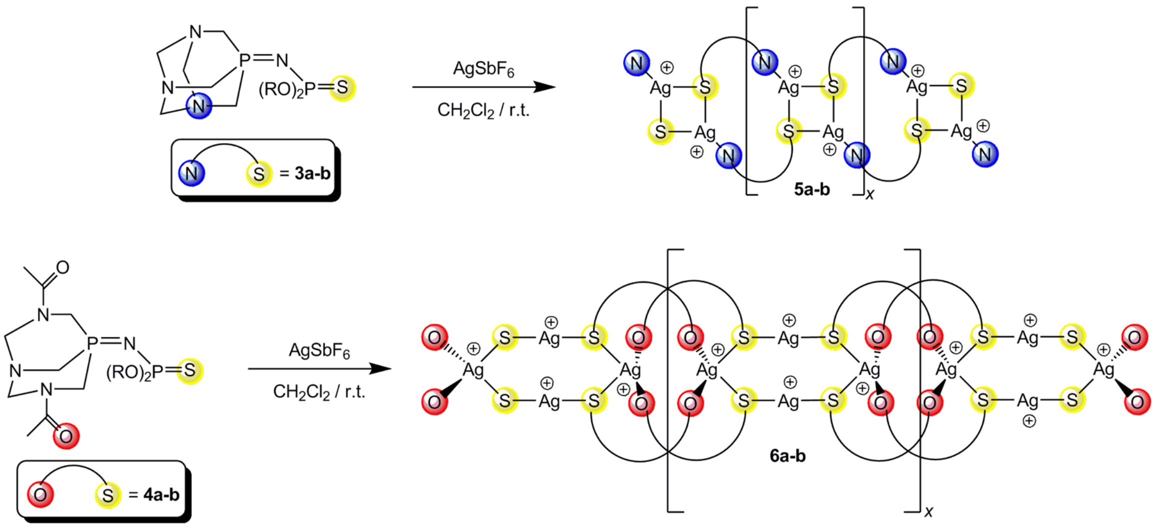
This method represents a significant upgrade to more traditional protocols for synthesis of *α,β*-unsaturated carbonyl compounds,[7] which required the use of Brønsted acids under harsh reaction conditions, leading usually to nonregioselective transformations and poor functional group tolerance. In particular, starting from substrates able to undergo a competitive Rupe-type rearrangement (Scheme 1),[8] non-regioselective transformations are usually observed.[9] In this sense and with the gradual emergence of new catalysts, both the Meyer−Schuster and the Rupe rearrangements have gained a prominent role in organic synthesis,[10] as clearly exemplified by their implication in (i) synthetic protocols for total synthesis of several natural organic products[11] and (ii) tandem processes involving combination of these isomerization processes with other well-established synthetic organic reactions.[12−15]

Despite the growing interest in this metal-catalyzed isomerization reaction, efforts devoted to develop catalytic systems able to operate in environmentally friendly solvents (i.e., water) have been scarce. In fact, only a very limited number of active catalysts in the Meyer−Schuster[16] or Rupe[17] rearrangement of propargylic alcohols in water have been described to date in the literature.[18] This is particularly surprising considering (i) water is a safe, a nontoxic, an eco-friendly, and a cheap solvent,[19] (ii) it may give rise to a completely new reactivity, and (iii) the strong acceleration effect and regioselectivity of many organic reactions in aqueous media have been previously reported.[20] With these precedents in mind and continuing with our studies aimed at exploiting the utility of new organometallic complexes containing the iminophosphorane ligands **3a**, **3b**, **4a**, and **4b** in metal-catalyzed organic reactions in water,[3,21] herein we describe (i) the synthesis and characterization of the new one-dimensional Ag(I) coordination polymers $[Ag\{\mu^2\text{-}N,S\text{-}(PTA){=}NP({=}S)(OR)_2\}]_x[SbF_6]_x$ (**5a** and **5b**) and $[Ag\{\mu^2\text{-}O,S\text{-}(DAPTA){=}NP({=}S)(OR)_2\}]_x[SbF_6]_x$ (**6a** and **6b**), (ii) the high catalytic activity of complex **5a** for the regioselective isomerization of propargylic alcohols into *α,β*-unsaturated compounds with both terminal and internal alkynols, without addition of any cocatalyst, in water, under microwave irradiation and under air, and (iii) the recyclability of the catalytic system in water (up to 10 consecutive runs).

## RESULTS AND DISCUSSION

**Synthesis and Characterization of the New Silver(I) Coordination Polymers $[Ag\{\mu^2\text{-}N,S\text{-}(PTA){=}NP({=}S)(OR)_2\}]_x[SbF_6]_x$ (R = Et (5a), Ph (5b)) and $[Ag\{\mu^2\text{-}O,S\text{-}(DAPTA){=}NP({=}S)(OR)_2\}]_x[SbF_6]_x$ (R = Et (6a), Ph (6b)).** Following our previous interest on the design of Ag(I) coordination polymers containing iminophosphorane ligands $[Ag\{\mu^2\text{-}S,S\text{-}(CH_2)_n[P\{{=}NP({=}S)(OR)_2\}Ph_2]_2\}]_x[SbF_6]_x$ ($n$ = 4, 6)][22] and our recent studies on coordination of the PTA−iminophosphorane ligands,[3,21] we decided to investigate reaction of the iminophosphorane ligands **3a**, **3b**, **4a**, and **4b** with a silver(I) precursor.[23,24] In this sense, we found that treatment of the silver(I) precursor $AgSbF_6$ with a stoichio-

**Scheme 2. Synthesis of the Silver(I) Complexes 5a, 5b, 6a, and 6b**



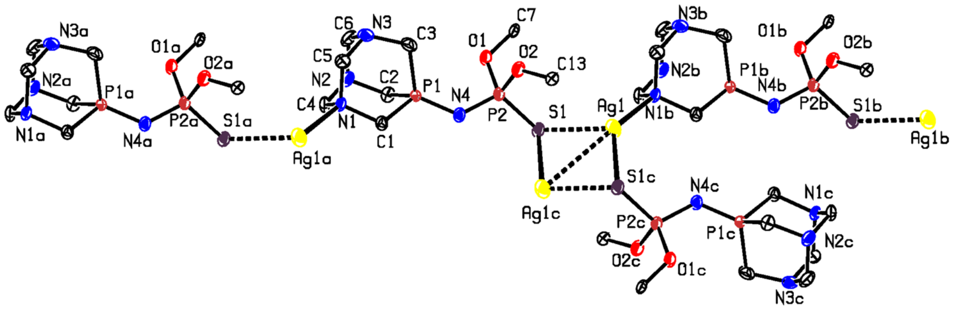


**Figure 2.** ORTEP-type view of the unit cell of compound **5b** showing the crystallographic labeling scheme. Hydrogen atoms, aryl groups (except the ipso carbons), and $SbF_6^-$ anions have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Angstroms): Ag(1)−S(1) = 2.517(1); Ag(1)−S(1c) = 2.680(1); Ag(1)−Ag(1c) = 3.1548(8); Ag(1)−N(1b) = 2.301(4); P(1)−N(4) = 1.587(4); N(4)−P(2) = 1.564(4); P(2)−S(1) = 1.990(2). Selected bond angles (degrees): S(1)−Ag(1)−S(1c) = 105.32(4); S(1)−Ag(1)−Ag(1c) = 50.31(3); S(1)−Ag(1c)−Ag(1) = 55.01(3); Ag(1)−S(1)−Ag(1c) = 74.68(4); P(1)−N(4)−P(2) = 127.0(3); N(4)−P(2)−S(1) = 115.1(2); P(2)−S(1)−Ag(1) = 102.33(6); P(2)−S(1)−Ag(1c) = 115.56(7).

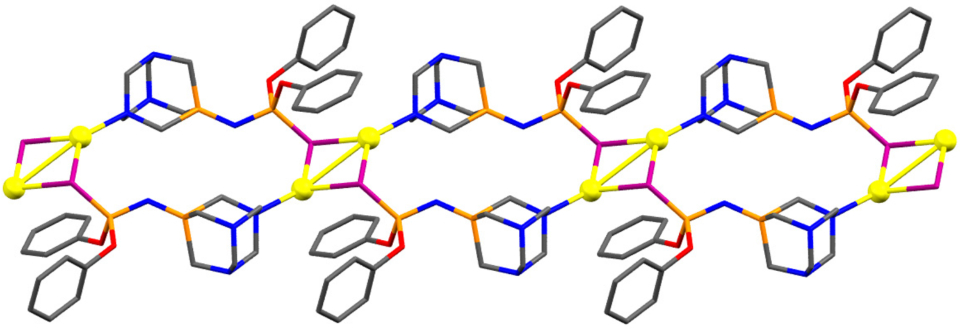


**Figure 3.** Part of the polymeric chain of complex **5b** showing formation of alternated fused 4- and 14-membered rings (yellow = silver; pink = sulfur; blue = nitrogen; orange = phosphorus; red = oxygen; gray = carbon).

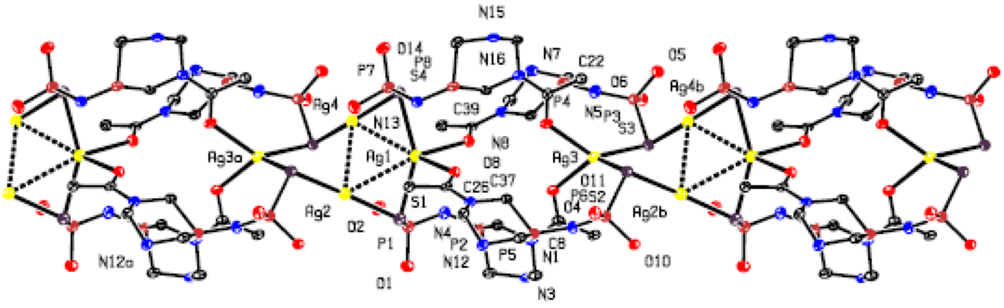


**Figure 4.** ORTEP-type view of the unit cell of compound **6a** showing the crystallographic labeling scheme. Hydrogen atoms, ethyl groups, the $-(CH_2)N(C(=O)CH_3)CH_2-$ arm of the ligand **4a** that does coordinate to the silver atoms, and the $SbF_6^-$ anions have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Angstroms): Ag(1)−S(1) = 2.515(3); Ag(1)−S(4) = 2.531(3); Ag(2)−S(1) = 2.371(3); Ag(2)−S(2) = 2.391(3); Ag(3)−S(2) = 2.607(3); Ag(3)−S(3) = 2.606(3); Ag(4)−S(3) = 2.405(3); Ag(4)−S(4) = 2.389(3); Ag(1)−O(8) = 2.384(7); Ag(1)−O(9) = 2.394(8); Ag(3)−O(4) = 2.346(8); Ag(3)−O(16) = 2.339(8); Ag(1)−Ag(2) = 3.124(1); Ag(1)−Ag(4) = 3.015(1); Ag(2)−Ag(4) = 3.074(2); P(1)−N(4) = 1.58(1); P(2)−N(4) = 1.57(1); P(3)−N(5) = 1.56(1); P(4)−N(5) = 1.576(9); P(5)−N(10) = 1.589(9); P(6)−N(10) = 1.555(9); P(7)−N(13) = 1.575(9); P(8)−N(13) = 1.58(1); C(8)−O(4) = 1.25(1); C(25)−O(8) = 1.24(1); C(26)−O(9) = 1.24(1); C(51)−O(16) = 1.23(1). Selected bond angles (degrees): S(1)−Ag(1)−S(4) = 150.5(1); Ag(1)−S(4)−Ag(4) = 75.54(9); S(4)−Ag(4)−S(3) = 164.9(1); Ag(4)−S(3)−Ag(3) = 102.3(1); S(3)−Ag(3)−S(2) = 96.71(9); Ag(3)−S(2)−Ag(2) = 102.8(2); S(2)−Ag(2)−S(1) = 167.6(1); S(1)−Ag(1)−O(8) = 114.3(2); S(1)−Ag(1)−O(9) = 87.0(2); S(4)−Ag(1)−O(8) = 89.0(2); S(4)−Ag(1)−O(9) = 115.5(2); O(8)−Ag(1)−O(9) = 81.2(3); S(2)−Ag(3)−O(4) = 129.0(2); S(2)−Ag(3)−O(16) = 108.0(2); S(3)−Ag(3)−O(4) = 112.3(2); S(3)−Ag(3)−O(16) = 132.6(2); O(4)−Ag(3)−O(16) = 82.6(3).

metric amount of the PTA-based iminophosphorane ligands **3a** and **3b**, in dichloromethane at room temperature, leads to selective formation of polymeric complexes $[Ag\{\mu^2\text{-}N,S\text{-}(PTA){=}NP({=}S)(OR)_2\}]_x[SbF_6]_x$ (R = Et (**5a**), Ph (**5b**); 76−79%, Scheme 2). Both **5a** and **5b** are formed via selective bidentate (i) *S*-coordination of the *N*-thiophosphoryl fragment and (ii) *N*-coordination of one nitrogen atom from the adamantane ring. In contrast, the DAPTA-base iminophosphorane ligands **4a** and **4b** containing carbonyl groups ($C({=}O)CH_3$) generate, under the same reaction conditions, new polymeric derivatives $[Ag\{\mu^2\text{-}O,S\text{-}(DAPTA){=}NP({=}S)(OR)_2\}]_x[SbF_6]_x$ (R = Et (**6a**), Ph (**6b**); 87−91%, Scheme 2) via selective bidentate (i) *S*-coordination of the *N*-

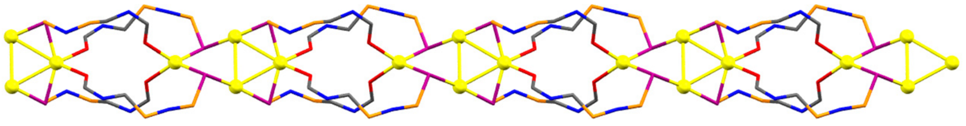


**Figure 5.** Core of the polymeric double chain of complex **6a** showing only the atoms involved in the chain (yellow = silver; pink = sulfur; blue = nitrogen; orange = phosphorus; red = oxygen; gray = carbon).

thiophosphoryl fragment and in this case (ii) *O*-coordination of the oxygen atom of the $C(=O)CH_3$ unit.

Compounds **5a**, **5b**, **6a**, and **6b** have been isolated in high yields as air- and light-stable white solids that behave as 1:1 electrolytes in acetone solutions ($\Lambda_M$ = 105−115 $\Omega^{-1}\cdot cm^{-2}\cdot mol^{-1}$). As we previously described for the iminophosphorane Cu(I) coordination polymers $[Cu\{\mu^2\text{-}N,S\text{-}(PTA)=NP(=S)(OR)_2\}_2]_x[PF_6]_x$,[3] we found that only complexes **5** and **6a**, which contain ethyl groups in the *N*-thiophosphorylated units $-P(=S)(OEt)_2$, were soluble in water ($S_{25\,°C}$ values of 5.0 and 7.0 mg $mL^{-1}$, respectively), while complexes **5** and **6b** were scarcely soluble in water. Complexes **5a**, **5b**, **6a**, and **6b** have been characterized by means of standard spectroscopic techniques [IR and $^{31}P\{^1H\}$, $^1H$, and $^{13}C\{^1H\}$ NMR] and elemental analysis, which support the proposed formulations. Complexation of ligands **3a**, **3b**, **4a**, and **4b** to silver is reflected in the $^{31}P\{^1H\}$ NMR spectra of **5a**, **5b**, **6a**, and **6b** (see Experimental Section) by slight variations in the P=N [$\Delta\delta$ = 3−9 ppm; $\delta_P$ = −31.94 to −10.92 ppm] and $(RO)_2P=S$ [$\Delta\delta$ = 2−5 ppm; $\delta_P$ = 49.90−55.46 ppm] resonances. As expected, $^1H$ and $^{13}C\{^1H\}$ NMR spectra display the corresponding phosphine backbone signals of PTA and DAPTA. The observed preference for *S*- vs *N*-coordination of the iminophosphoranyl units $P=N-P(=S)(OR)_2$ in complexes **5a**, **5b**, **6a**, and **6b** is in complete accord with the well-known coordination chemistry of *N*-thiophosphorylated iminophosphoranes $R_3P=N-P=S(OR)_2$, which is almost entirely dominated by coordination of the sulfur atom.[25] Although formation of formally 1:1 adducts of the starting reagents $[AgSbF_6\cdot ligand]$ is readily deduced from their elemental analysis (details are given in Experimental Section), the real nature of these complexes could only be determined by single-crystal X-ray diffraction methods. Drawings of the unit cell and polymeric chains of complexes **5b** and **6a** are shown in Figures 2−4; selected bonding parameters for **5b** and **6a** are listed in the captions of Figures 2 and 4, respectively.

Concerning the structure of complex **5b** (see Figure 2), the unit cell corresponds to the fragment $[Ag\{\mu^2\text{-}N,S\text{-}(PTA)=NP(=S)(OR)_2\}]_4[SbF_6]_4$ containing four silver atoms and four ligands $(PTA)=NP(=S)(OPh)_2$ (**3b**), which gives rise to a polymeric double chain along the *z* axis. Thus, this X-ray analysis unambiguously confirms formation of a 14-membered dimetalla ring formed by two silver atoms bridged by two iminophosphorane ligands in a head-to-tail conformation. The coordination sphere around silver consists of (i) one *S*-coordinated $(PhO)_2P=S$ unit, as suggested by the $^{31}P\{^1H\}$ NMR data, and (ii) one *N*-coordinated amino group from the aminophosphine ring. The Ag(1)−S(1) (2.517(1) Å) bond length inside the 14-membered dimetalla ring is longer than those previously described for Ag(I) complexes containing *S*-coordinated *N*-thiophosphorylated bis(iminophosphorane) ligands[22] (Ag−S = 2.324(3)−2.449(2) Å) but compare well with those shown by Ag(I) complexes containing *S*-coordinated phosphine−sulfides.[26] In contrast, the Ag(1)−N(1b) (2.301(4) Å) bond length is smaller than those previously described for (i) the silver(I) complex $[Ag(PTA)(H_2O)][NO_3]$ (Ag−N = 2.441(4) and 2.468(4) Å) with tridentate *P,N,N′*-coordinated PTA in a polymeric net structure[2b] and (ii) the mixed-metal Ag(I)/Ru(II) water-soluble organometallic polymer $[CpRu(H_2O)(\mu^2\text{-}P,N\text{-}PTA)_2AgCl_2]_x$ (Ag−N = 2.423(6) Å).[2a]

Remarkably, intermolecular silver−sulfur interactions take place leading to a polymeric chain with alternating 14-membered (Ag−S−P−N−P−C−N−Ag-S−P−N−P−C−N) and 4-membered (Ag−S−Ag−S) dimetalla fused rings (see Figure 3). The Ag(1)−S(1c) (2.680(1) Å) bond length can be reasonably regarded as a real bonding interaction since it falls within the accepted range for single Ag−S bonds (ca. 2.2−3.0 Å).[22,26] A weak silver−silver contact is also present in the polymer (Ag(1)−Ag(1a) = 3.1548(8) Å).[27] The existence of all these intermolecular bonding interactions is clearly reflected in the S(1)−Ag(1)−S(1c) angle, which deviates considerably from the expected linearity (105.32(4)°). It is also interesting to note that bond distances within the P=N−P=S framework are almost identical (ca. ±0.02 Å) to those found in the structure of the free ligand **3b**,[3] indicating that electronic delocalization of the nitrogen lone pair is maintained upon coordination of the thiophosphoryl unit to the metal.

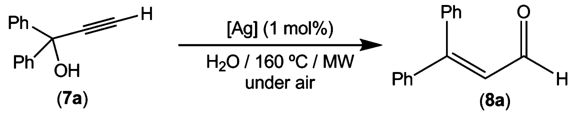
In contrast to **5b**, the unit cell of complex **6a** corresponds to the fragment $[Ag\{\mu^2\text{-}S,O\text{-}(DAPTA)=NP(=S)(OEt)_2\}]_{12}[SbF_6]_{12}$ (see Figure 4), which contains 12 silver atoms and 12 ligands $(DAPTA)=NP(=S)(OEt)_2$ (**4a**). Selective $\mu^2$-*S,O* coordination of the *N*-thiophosphoryl $((EtO)_2P=S)$ and carbonylic $(C(=O)CH_3)$ units of the iminophosphorane ligand **4a** is observed, which acts as a bridge between the silver atoms, while the nitrogen atoms of the aminophosphine remain uncoordinated. To our knowledge, **6a** represents the first example of an organometallic complex that shows *O*-coordination of DAPTA to a metal.[28] X-ray crystallographic analysis revealed formation of an eight-membered ring (Ag−S−Ag−S−Ag−S−Ag−S)[29] in which three of the silver atoms (Ag(1), Ag(2), and Ag(4)) are closer [with small Ag−S interactions; Ag(1)−S(1) = 2.514(3) Å, Ag(1)−S(4) = 2.531(3) Å, Ag(2)−S(1) = 2.371(3) Å, Ag(4)−S(4) = 2.389(3) Å], adopting a triangle-like disposition,[30] while the fourth silver atom (Ag(3)) is located further away, bridged to the Ag(2) and Ag(4) atoms by a longer Ag−S interaction (Ag(3)−S(2) = 2.607(3) Å, Ag(3)−S(3) = 2.606(3) Å). All these Ag−S contacts compare well with those previously described for the polymeric structure of the Ag(I) complex **5b** (see caption of Figure 2). The three Ag−Ag bond lengths [Ag(1)−Ag(2) = 3.124(1) Å, Ag(2)−Ag(4) = 3.074(1) Å, Ag(4)−Ag(1) = 3.015(1) Å] are consistent with the presence of weak silver−silver contacts as in polymer **5b**.[27] It should be noticed that the central silver atoms (Ag(2) and Ag(4)) of the eight-membered ring adopt a pseudolinear arrangement [S(1)−Ag(2)−S(2) = 167.6(1)° and S(3)−Ag(4)−S(4) = 164.9(1)°], while the terminal silver atoms display a distorted tetrahedral geometry [subtending bond angles from 82.6(3)° (O(4)−Ag(3)−O(16)) to 132.6(2)° (O(16)−Ag(3)−S(3)) (mean 110.2°) for Ag(3) and from 81.2(3)° (O(8)−Ag(1)−O(9)) to

150.5(1)° (S(1)−Ag(1)−S(4)) (mean 106.3°) for Ag(1))]. These tetracoordinated silver(I) atoms (Ag(3) and Ag(1)) allow the connection of two eight-membered rings ($Ag_4S_4$) through the *O*-coordination of the carbonylic unit ($C(=O)CH_3$) of the iminophosphorane ligand **4a**, giving rise to a polymeric double chain (see Figure 5) along the *y* axis. The Ag−O bond lengths [from 2.339(8) Å for Ag(3)−O(16) to 2.394(8) Å for Ag(1)−O(9)] fall within the previously reported values for silver(I) complexes containing *O*-coordinated carbonylic (NC(=O)R) fragments.[31] As we have previously seen in the case of the free iminophosphorane ligands[3] and in the aforementioned polymeric Ag(I) complex **5b** (see Figure 2), the bond distances within the P=N−P=S framework are again almost identical (ca. ±0.02 Å, see caption to Figure 4), indicating that electronic delocalization of the nitrogen lone pair is maintained upon coordination of the thiophosphoryl unit to the metal. As expected, the C=O bond distances in **6b** [from 1.23(1) (C(51)−O(16) to 1.24(1) Å (C(8)−O(4)] are slightly longer than those previously observed in the free ligand **4b** (ca. 1.222 Å).[3]

In order to gain more information about the integrity and nature of the species present in aqueous solution, electrospray ionization (ESI) mass spectrometric measurements of a solution of **5a** in water were performed.[32] Positive ESI mass spectra recorded upon gentle ionization conditions (cone voltage $U_c$ = 10 V) revealed the presence of a variety of Ag-containing species readily identified on the basis of their characteristic isotopic pattern. The base peak corresponds to the $[Ag\{(PTA)=NP(=S)(OEt)_2\}_2]^+$ cation at *m*/*z* 755.0, and additional (i) monomeric species formulated as $[Ag\{(PTA)=NP(=S)(OEt)_2\}]^+$ (*m*/*z* 431.0) and $[Ag\{(PTA)=NP(=S)(OEt)_2\}(H_2O)]^+$ (*m*/*z* = 449.0) (ii) and dimeric $[Ag_2\{(PTA)=NP(=S)(OEt)_2\}_3]^{2+}$ (*m*/*z* 593.0) were also observed. Assignments were based on accurate *m*/*z* determinations as well as comparison of simulated an experimental isotopic pattern (see Figures ESI-1 and ESI-2 in the Supporting Information). Interestingly, mononuclear complexes were observed as dominant species in solution, suggesting that unlike in the solid state complex **5a** is dismantled in aqueous solution to give predominantly monomeric species. It is apparent that these monomeric species are readily formed and therefore can be proposed as the active catalytic species in aqueous medium (see below).

**Isomerization of Propargylic Alcohols into *α*,*β*-Unsaturated Carbonyl Compounds Catalyzed by the Cationic Ag(I) Compound $[Ag\{\mu^2\text{-}N,S\text{-}(PTA)=NP(=S)(OEt)_2\}]_x[SbF_6]_x$ (5a).** Although in recent years Ag(I) complexes containing water-soluble PTA ligands have been screened for their potential antimicrobial activity[2j,24] and luminescent properties,[2i] their applications as catalysts for organic transformations in water are virtually unknown.[33] With this precedent in mind, we decided to test the silver(I) coordination polymers **5a**, **5b**, **6a**, and **6b** as potential catalyst precursors in the Meyer−Schuster rearrangement of propargylic alcohols in aqueous media[34,35] using the isomerization of the commercially available 1,1-diphenyl-2-propyn-1-ol (**7a**) into 3,3-diphenylpropenal (**8a**) as a model reaction (see Scheme 3). Thus, in a typical experiment, the corresponding Ag(I) precursor (1 mol % of Ag) and the propargylic alcohol **7a** were added to 1 mL of water under air using as the heating source microwave irradiation at 160 °C,[36] the course of the reaction being monitored by gas chromatography. Pleasingly, all Ag(I) complexes tested were found to be active and selective catalysts in water, affording 3,3-diphenylpropenal (**8a**) as the unique reaction product. Interestingly, the catalytic activity of complex **5a** (containing the ligand PTA−iminophosphorane) is higher than that of complex **6a** (containing the ligand DAPTA−iminophosphorane) [45 min (99%) vs 1.5 h (97%)]. A similar catalytic trend has also been found in their water-insoluble counterpart catalysts **5b** and **6b** [1 h (98%) vs 3 h (96%)], demonstrating the influence of the iminophosphorane ligand on the reaction rate. The presence of catalytic amounts of silver(I) complexes **5a**, **5b**, **6a**, and **6b** was found to be essential as no isomerization reaction was observed in their absence. Use of other reaction conditions (like, for example, conventional heating, lower temperatures, and/or lower catalyst loadings) slowed down the reaction considerably; as an example, using 1 mol % of complex **5a** in refluxing water, 20% conversion of 1,1-diphenyl-2-propyn-1-ol into 3,3-diphenylpropenal was only achieved after 24 h. At this point it should be noticed that under similar reactions conditions (1 mol % of catalyst loading, in water, at 160 °C, and under microwave irradiation) $InCl_3$ is able to catalyze the isomerization reaction of the alkynol **7a** into the corresponding enal **8a** in a shorter reaction time (5 min).[16h]

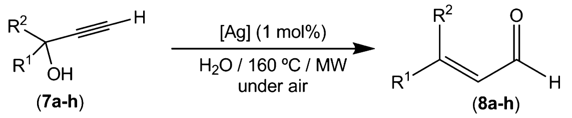
**Scheme 3. Ag(I)-Catalyzed Isomerization of 1,1-Diphenyl-2-propyn-1-ol (7a) to 3,3-Diphenylpropenal (8a) Catalyzed by Complexes 5a, 5b, 6a, and 6b**[a]



[a]Reactions were performed under air with microwave irradiation at 160 °C in water and using 1 mmol of the alkynol **7a**. [Substrate]/[Ag] ratio = 100:1.

Under these optimized reaction conditions, the most active Ag(I) complex $[Ag\{\mu^2\text{-}N,S\text{-}(PTA)=NP(=S)(OEt)_2\}]_x[SbF_6]_x$ (**5a**) was found to be an efficient catalyst precursor for selective isomerization of a large number of other terminal propargylic alcohols, highlighting the wide substrate scope and synthetic utility of this catalytic transformation. Thus, as observed for 1,1-diphenyl-2-propyn-1-ol (entry 1 in Table 1), other tertiary alkynols **7b−f** underwent selective isomerization into the corresponding enals **8b−f**, which could be isolated after appropriate chromatographic workup in excellent yields (91−95%; entries 1−5 in Table 1). An influence of the electronic properties of the aryl rings on the reaction rates was observed. Thus, alkynols with electron-withdrawing groups showed less reactivity (entry 4) as compared to substrates with electron-donating substituents (entry 5). It is important to note that for the propargylic alcohol 2-phenyl-3-butyn-2-ol (**7f**, entry 6), in which the isomerization process can proceed through the competitive Rupe-type rearrangement to generate the corresponding *α*,*β*-unsaturated enone (see Scheme 1), exclusive formation of the *α*,*β*-unsaturated enal **8f** as a mixture of the corresponding *E* and *Z* stereoisomers in a ca. 3:2 ratio was observed.[37] Secondary terminal alkynols (entries 7 and 8, Table 1) can also be efficiently and selectively isomerized into the corresponding enals using complex $[Ag\{\mu^2\text{-}N,S\text{-}(PTA)=NP(=S)(OEt)_2\}]_x[SbF_6]_x$ (**5a**) as catalyst in water. Again, reactions proceeded to completion in the absence of any cocatalyst. Interestingly, resulting enals **7g−h** were exclusively obtained as the thermodynamically more stable *E* isomers.[38]

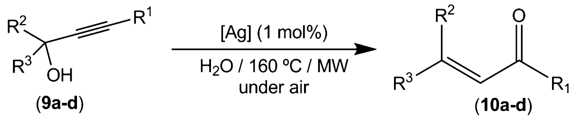
**Table 1. Isomerization of Terminal Propargylic Alcohols 7a–h into Enals 8a–h Catalyzed by Complex $[Ag\{\mu^2\text{-}N,S\text{-}(PTA){=}NP({=}S)(OEt)_2\}]_x[SbF_6]_x$ (5a) in Water**[a]



| entry | substrate 7 | $T$ [min] | yield of 8$^b$ |
|---|---|---|---|
| 1 | $R^1 = R^2 = Ph$ (**7a**) | 45 | **8a**; 99 (95) |
| 2 | $R^1R^2 = 2,2'\text{-}C_6H_4{-}C_6H_4$ (**7b**) | 30 | **8b**; 95 (91) |
| 3 | $R^1R^2 = 2,2'\text{-}C_6H_4{-}CH{=}CH{-}C_6H_4$ (**7c**) | 30 | **8c**; 97 (92) |
| 4 | $R^1 = R^2 = 4\text{-}C_6H_4F$ (**7d**) | 300 | **8d**; 99 (95) |
| 5 | $R^1 = R^2 = 4\text{-}C_6H_4Me$ (**7e**) | 15 | **8e**; 98 (93) |
| 6 | $R^1 = Ph$, $R^2 = Me$ (**7f**) | 90 | **8f**; 97 (91)[c] |
| 7 | $R^1 = Ph$, $R^2 = H$ (**7g**) | 300 | **8g**; 99 (91) |
| 8 | $R^1 =$ 2-naphthyl, $R^2 = H$ (**7h**) | 240 | **8h**; 97 (93) |

[a] Reactions were performed under air in a CEM Discover S-Class microwave synthesizer at 160 °C through moderation of the initial power (300 W). A 1 mmol amount of the corresponding alkynol was used (1 mL of water). [Substrate]/[Ag] ratio = 100:1. [b] Determined by GC. Isolated yields after chromatographic workup are given in brackets. [c] A mixture of *E* and *Z* isomers in ca. 3:2 ratio is formed.

**Table 2. Isomerization of Internal Propargylic Alcohols 9a–d into Enones 10a–d Catalyzed by Complex $[Ag\{\mu^2\text{-}N,S\text{-}(PTA){=}NP({=}S)(OEt)_2\}]_x[SbF_6]_x$ (5a) in Water**[a]



| entry | substrate 9 | $T$ [min] | yield of 10$^b$ |
|---|---|---|---|
| 1 | $R^1 = R^2 = R^3 = Ph$ (**9a**) | 15 | **10a**; 99 (92) |
| 2 | $R^1 = Me$; $R^2 = Ph$; $R^3 = H$ (**9b**) | 60 | **10b**; 96 (90) |
| 3 | $R^1 = Me$; $R^2 = 4\text{-}C_6H_4OMe$; $R^3 = H$ (**9c**) | 90 | **10c**; 96 (91) |
| 4 | $R^1 = Ph$; $R^2 = Ph$; $R^3 = H$ (**9d**) | 30 | **10d**; 99 (94) |

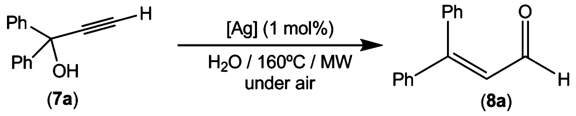
[a] Reactions were performed under air in a CEM Discover S-Class microwave synthesizer at 160 °C through moderation of the initial power (300 W). A 1 mmol amount of the corresponding alkynol was used (1 mL of water). [Substrate]/[Ag] ratio = 100:1. [b] Determined by GC. Isolated yields after chromatographic workup are given in brackets.

Use of MW heating has received considerable attention as a new method for one-pot synthesis of silver nanostructures in solution.[39] In all the catalytic reactions listed in Table 1, formation of silver nanoparticles was studied by means of TEM (transmission electron microscopy) or SEM/EDX (scanning electron microscopy/energy-dispersive X-ray spectroscopy) techniques (see Supporting Information), and silver nanoparticles were detected in the reaction (see Supplementary Infomation). Thus and in order to determine whether the process is really homogeneous, isomerization of the propargylic alcohol **7a** into the enal **8a** promoted by the silver(I) complex **5a**, in the presence of Hg, was studied. The Hg-poisoned catalytic reactions proceed with the same conversion (99%, 45 min), thus suggesting that the formed silver nanoparticles do not play a role in this catalytic transformation. This Hg(0)-poisoning test is the most direct method to distinguishing homogeneous from heterogeneous catalysis when transition metals able to form an amalgam are employed.[40] In line with this, the isolated silver nanoparticles generated from complex **5a** showed no catalytic activity toward formation of the desired enal **8a**. These experimental facts seem to indicate that possible catalysis by silver nanoparticles is not involved in this isomerization process.

Finally, and as shown in Table 2, it is also worth noting that the activity of complex **5a** is not restricted to terminal alkynols, as the internal propargylic alcohols **9a–d** can be also efficiently transformed into the corresponding enones **10a–d**. As previously observed, complete *E* stereoselectivity was once again reached starting from secondary alcohols. The limitation of this methodology concerns the use of primary propargylic alcohols $RC{\equiv}CCH_2OH$, which under standard reaction conditions give rise to intractable polymeric materials.[41] The observed catalytic activity of complex **5a** with internal alkynols seems to indicate that silver(I) hydroxyvinylidene derivatives are not involved as key intermediate complexes in this isomerization reaction.[42] In this sense, a possible dehydration/hydration sequence through a carbocation intermediate is in accord with the experimental fact that electron-rich aryl groups on the propargylic alcohol were more reactive than propargylic alcohols with electron-poor aryl groups (see Table 1).[10]

It is well known that one of the major advantages associated with the use of water as reaction media in metal-catalyzed organic reactions is the possibility of recycling the catalyst previous separation of the organic product formed by simple extraction with organic solvents (without the need of recovering the catalyst; see the general procedure for catalyst recycling in the Supporting Information).[20] In addition, the lifetime of a catalytic system and its level of reusability are very important factors.[43] Thus, under the aforementioned reaction conditions (Tables 1 and 2) and using as a model reaction isomerization of the propargylic alcohol **7a**, we found that the catalytic system remains active (97–99% yield) after recycling up to 10 consecutive times (see Table 3) with a gradual decrease of the activity after each recycling. Thus, for the first five cycles less than 2 h was needed to achieve quantitative conversion, while more than 3 h was required after the fifth cycle, probably due to both leaching during workup and decomposition of the catalyst.

**Table 3. Ag(I)-Catalyzed Isomerization of the Propargylic Alcohol 7a into Enal 8a in Water: Catalyst Recycling**[a]



| cycle | $T$ [min] | yield$^b$ | TON$^c$ | cycle | $T$ [min] | yield | TON$^c$ |
|---|---|---|---|---|---|---|---|
| 1 | 45 | 99 | 99 | 6 | 180 | 99 | 592 |
| 2 | 60 | 99 | 198 | 7 | 180 | 98 | 690 |
| 3 | 60 | 99 | 297 | 8 | 240 | 99 | 789 |
| 4 | 90 | 99 | 396 | 9 | 300 | 99 | 1089 |
| 5 | 90 | 97 | 493 | 10 | 360 | 97 | 1189 |

[a] Reactions were performed under air in a CEM Discover S-Class microwave synthesizer at 160 °C through moderation of the initial power (300 W). A 1 mmol amount of the corresponding alkynol was used (1 mL of water). [Substrate]/[Ag] ratio = 100:1. [b] Determined by GC. [c] Cumulative TON values (turnover number = (mol of product/mol of Ag)).

## ■ CONCLUSION

In summary, in the present work we described the use, for the first time, of PTA- or DAPTA-base iminophosphorane ligands as versatile building blocks for high-yield synthesis of a series of new Ag(I) coordination polymers $[\mathrm{Ag}\{\mu^2\text{-}N,S\text{-}(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2\}]_x[\mathrm{SbF}_6]_x$ (R = Et (**5a**), Ph (**5b**)) and $[\mathrm{Ag}\{\mu^2\text{-}O,S\text{-}(\mathrm{DAPTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2\}]_x[\mathrm{SbF}_6]_x$ (R = Et (**6a**), Ph (**6b**)). To our knowledge, complexes **6a** and **6b** represent the first examples in which coordination of the acetyl group of DAPTA is achieved. In addition, we have also shown that the complex $[\mathrm{Ag}\{\mu^2\text{-}N,S\text{-}(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OEt})_2\}]_x[\mathrm{SbF}_6]_x$ (**5a**), always in neutral conditions, is a highly efficient catalyst precursor for isomerization of both terminal and internal propargylic alcohols into *α,β*-unsaturated carbonyl compounds, which can be obtained in excellent yields in water. This catalytic system has also proven to promote chemoselective transformations producing enals (terminal alkynols) or enones (internal alkynols) depending on the nature of the propargylic alcohol. Finally, we must also note that (i) the highly effective catalyst recycling observed using water as solvent and (ii) the total atom economy of this process are in good agreement with the principles of so-called "Green Chemistry".[19]

## ■ EXPERIMENTAL SECTION

**General Comments.** All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds $(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2$ (R = Et (**3a**), Ph (**3b**)) and $(\mathrm{DAPTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2$ (R = Et (**4a**), Ph (**4b**)), which were prepared by the following methods reported in the literature.[3] Propargylic alcohols **7a**–**h** and **9a**–**d** were obtained from commercial suppliers or synthesized following the classical Midlands procedure.[44] Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. For electrospray ionization mass spectrometry (ESI-MS) studies, a QTOF Premier instrument with an orthogonal Z-spray-electrospray interface (Waters, Manchester, U.K.) was used operating in the W mode at a resolution of ca. 15 000 (fwhm). The drying and cone gas was nitrogen set to flow rates of 300 and 30 L/h, respectively. A capillary voltage of 3.5 kV was used in the positive scan mode, and the cone voltage was set to $U_c$ = 10 V. For accurate mass measurements, a 2 mg/L standard solution of leucine enkephalin was introduced via the lock spray needle at a cone voltage set to 45 V and a flow rate of 30 μL/min. C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX300 instrument at 300 ($^1$H), 121.5 ($^{31}$P), and 75.4 MHz ($^{13}$C) using $\mathrm{SiMe_4}$ or 85% $\mathrm{H_3PO_4}$ as standards. DEPT experiments have been carried out for all compounds reported in this paper.

**Preparations.** *Synthesis of Ag(I) Coordination Polymers ($[\mathrm{Ag}\{\mu^2\text{-}N,S\text{-}(\mathrm{PTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2\}]_x[\mathrm{SbF}_6]_x$ (R = Et (**5a**), Ph (**5b**)) and $[\mathrm{Ag}\{\mu^2\text{-}O,S\text{-}(\mathrm{DAPTA}){=}\mathrm{NP}({=}\mathrm{S})(\mathrm{OR})_2\}]_x[\mathrm{SbF}_6]_x$ (R = Et (**6a**), Ph (**6b**)).* A solution of the corresponding iminophosphorane ligands **3a**, **3b**, **4a**, and **4b** (1 mmol) in 30 mL of $\mathrm{CH_2Cl_2}$ was treated with $\mathrm{AgSbF_6}$ (0.343 g, 1 mmol) and stirred for 1 h to yield a pale-yellow clear solution. The solvent was then concentrated (ca. 1 mL) in vacuo, and addition of diethyl ether (ca. 50 mL) precipitated a white solid, which was washed with diethyl ether (3 × 10 mL) and dried in vacuo. **5a**: Yield 76% (0.508 g). Anal. Calcd for $\mathrm{AgC_{10}H_{22}F_6N_4O_2P_2SbS}$: C, 17.98; H, 3.32; N, 8.39. Found: C, 18.04; H, 3.29; N 8.45. Conductivity (acetone, 20 °C): 105 $\Omega^{-1}\cdot\mathrm{cm}^2\cdot\mathrm{mol}^{-1}$. IR (KBr, $\mathrm{cm}^{-1}$): $\nu$ 542 (w), 594 (s), 660 (vs), 744 (m), 783 (m), 818 (m), 834 (m), 907 (m), 942 (s), 972 (s), 1010 (vs), 1096 (m), 1161 (m), 1238 (s), 1299 (s), 1369 (m), 1391 (m), 1412 (m), 1447 (m), 1473 (w), 1521 (w), 1635 (w), 1700 (w), 2090 (w), 2984 (m). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ −31.94 (d, $^2J_{\mathrm{PP}}$ = 2.4 Hz, $\mathrm{Ph_2P{=}N}$), 53.62 (d, $^2J_{\mathrm{PP}}$ = 2.4 Hz, $(\mathrm{RO})_2\mathrm{P{=}S}$) ppm. $^1$H NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 1.39 (t, 6H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{OCH_2C}H_3$), 4.18 (m, 4H, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.47 (d, 6H, $^2J_{\mathrm{HP}}$ = 9.4 Hz, $\mathrm{PCH_2N}$), 4.52 and 4.63 (AB spin system, 3H each, $J_{\mathrm{HA,HB}}$ = 15.5 Hz, $\mathrm{NCH_2N}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 15.63 (d, $^3J_{\mathrm{CP}}$ = 9.7 Hz, $\mathrm{OCH_2CH_3}$), 53.49 (dd, $^1J_{\mathrm{CP}}$ = 50.6 Hz, $^3J_{\mathrm{CP}}$ = 2.8 Hz, $\mathrm{PCH_2N}$), 64.60 (d, $^2J_{\mathrm{CP}}$ = 7.4 Hz, $\mathrm{OCH_2CH_3}$), 71.98 (d, $^3J_{\mathrm{CP}}$ = 9.9 Hz, $\mathrm{NCH_2N}$) ppm. **5b**: Yield 79% (0.603 g). Anal. Calcd for $\mathrm{AgC_{18}H_{22}F_6N_4O_2P_2SbS}$: C, 28.30; H, 2.90; N, 7.33. Found: C, 28.22; H, 2.96; N 7.40. Conductivity (acetone, 20 °C): 110 $\Omega^{-1}\cdot\mathrm{cm}^2\cdot\mathrm{mol}^{-1}$. IR (KBr, $\mathrm{cm}^{-1}$): $\nu$ 584 (w), 605 (s), 639 (s), 714 (m), 760 (m), 797 (m), 827 (m), 903 (m), 939 (m), 991 (s), 1073 (s), 1087 (w), 1127 (m), 1205 (s), 1297 (s), 1363 (m), 1412 (w), 1507 (w), 1538 (m), 1583 (w), 1669 (w), 1739 (m), 2096 (m), 2974 (m), 3041 (w). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ −28.90 (bs, $\mathrm{Ph_2P{=}N}$), 49.99 (bs, $(\mathrm{RO})_2\mathrm{P{=}S}$) ppm. $^1$H NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 4.35 (d, 6H, $^2J_{\mathrm{HP}}$ = 9.7 Hz, $\mathrm{PCH_2N}$), 4.52 and 4.61 (AB spin system, 3H each, $J_{\mathrm{HA,HB}}$ = 13.3 Hz, $\mathrm{NCH_2N}$), 7.30−7.51 (m, 10H, $\mathrm{CH_{arom}}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 53.58 (d, $^1J_{\mathrm{CP}}$ = 51.5 Hz, $\mathrm{PCH_2N}$), 72.59 (d, $^3J_{\mathrm{CP}}$ = 9.5 Hz, $\mathrm{NCH_2N}$), 121.88−131.18 (m, $\mathrm{CH_{arom}}$), 151.74 (d, $^2J_{\mathrm{CP}}$ = 8.5 Hz, $\mathrm{C_{ipso}}$ of OPh) ppm. **6a**: Yield 87% (0.644 g). Anal. Calcd for $\mathrm{AgC_{13}H_{26}F_6N_4O_4P_2SbS}$: C, 21.10; H, 3.54; N, 7.57. Found: C, 21.17; H, 3.56; N 7.61. Conductivity (acetone, 20 °C): 110 $\Omega^{-1}\cdot\mathrm{cm}^2\cdot\mathrm{mol}^{-1}$. IR (KBr, $\mathrm{cm}^{-1}$): $\nu$ 483 (w), 591 (m), 623 (m), 659 (s), 702 (w), 753 (s), 781 (s), 839 (w), 894 (s), 956 (s), 989 (s), 1042 (vs), 1095 (w), 1123 (w), 1161 (m), 1223 (vs), 1261 (s), 1303 (s), 1333 (s), 1355 (m), 1428 (s), 1651 (vs), 2929 (w), 2981 (w). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ −10.92 (d, $^2J_{\mathrm{PP}}$ = 13.7 Hz, $\mathrm{Ph_2P{=}N}$), 53.30 (d, $^2J_{\mathrm{PP}}$ = 13.7 Hz, $(\mathrm{RO})_2\mathrm{P{=}S}$) ppm. $^1$H NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 1.33 (t, 6H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{OCH_2C}H_3$), 2.09 and 2.12 (s, 3H each, $\mathrm{COCH_3}$), 3.78 (m, 1H, $\mathrm{NCH_2N}$), 4.18 (m, 8H, 4H for $\mathrm{OC}H_2\mathrm{CH_3}$ and 4H for $\mathrm{PCH_2NCO}$), 4.71 and 5.10 (d, 1H each, $J_{\mathrm{HH}}$ = 14.0 Hz, $\mathrm{NCH_2N}$), 4.88 (m, 1H, $\mathrm{PCH_2N}$), 5.66 (m, 2H, 1H for $\mathrm{NCH_2N}$ and 1H for $\mathrm{PCH_2N}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 21.27 (d, $^3J_{\mathrm{CP}}$ = 8.5 Hz, $\mathrm{OCH_2CH_3}$), 26.33 and 26.74 (s, $\mathrm{COCH_3}$), 45.73 (dd, $^1J_{\mathrm{CP}}$ = 70.2 Hz, $^3J_{\mathrm{CP}}$ = 4.0 Hz, $\mathrm{PCH_2N}$), 50.94 (dd, $^1J_{\mathrm{CP}}$ = 69.4 Hz, $^3J_{\mathrm{CP}}$ = 4.8 Hz, $\mathrm{PCH_2N}$), 56.05 (dd, $^1J_{\mathrm{CP}}$ = 59.9 Hz, $^3J_{\mathrm{CP}}$ = 2.1 Hz, $\mathrm{PCH_2N}$), 66.79 and 72.02 (d, $^3J_{\mathrm{CP}}$ = 6.9 Hz, $\mathrm{NCH_2N}$), 68.48 (d, $^2J_{\mathrm{CP}}$ = 6.9 Hz, $\mathrm{OCH_2CH_3}$), 174.51 and 174.95 (s, $\mathrm{COCH_3}$) ppm. **6b**: Yield 91% (0.761 g). Anal. Calcd for $\mathrm{AgC_{21}H_{26}F_6N_4O_4P_2SbS}$: C, 30.17; H, 3.13; N, 6.70. Found: C, 30.10; H, 3.09; N, 6.65. Conductivity (acetone, 20 °C): 115 $\Omega^{-1}\cdot\mathrm{cm}^2\cdot\mathrm{mol}^{-1}$. IR (KBr, $\mathrm{cm}^{-1}$): $\nu$ 474 (w), 537 (m), 585 (m), 599 (m), 658 (m), 690 (m), 743 (s), 782 (s), 839 (m), 898 (s), 931 (s), 945 (s), 1022 (s), 1081 (m), 1170 (w), 1153 (w), 1162 (m), 1195 (w), 1212 (s), 1267 (s), 1306 (s), 1320 (s), 1359 (w), 1425 (s), 1460 (w), 1657 (vs), 1891 (w), 1965 (w), 2933 (w), 2988 (w). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ −14.64 (d, $^2J_{\mathrm{PP}}$ = 21.4 Hz, $\mathrm{Ph_2P{=}N}$), 55.46 (d, $^2J_{\mathrm{PP}}$ = 21.4 Hz, $(\mathrm{RO})_2\mathrm{P{=}S}$) ppm. $^1$H NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 1.99 and 2.01 (s, 3H each, $\mathrm{COCH_3}$), 3.50 (m, 1H, $\mathrm{NCH_2N}$), 4.04 (m, 4H, $\mathrm{PCH_2NCO}$), 4.58 and 5.51 (m, 2H each, 1H for $\mathrm{NCH_2N}$ and 1H for $\mathrm{PCH_2N}$), 5.00 (d, 1H, $J_{\mathrm{HH}}$ = 14.3 Hz, $\mathrm{NCH_2N}$), 7.17−7.40 (m, 10H, $\mathrm{CH_{arom}}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($(\mathrm{CD_3})_2\mathrm{C{=}O}$): $\delta$ 21.01 and 21.40 (s, $\mathrm{COCH_3}$), 39.99 (dd, $^1J_{\mathrm{CP}}$ = 71.0 Hz, $^3J_{\mathrm{CP}}$ = 4.8 Hz, $\mathrm{PCH_2N}$), 45.20 (dd, $^1J_{\mathrm{CP}}$ = 69.4 Hz, $^3J_{\mathrm{CP}}$ = 4.2 Hz, $\mathrm{PCH_2N}$), 50.42 (dd, $^1J_{\mathrm{CP}}$ = 59.9 Hz, $^3J_{\mathrm{CP}}$ = 2.7 Hz, $\mathrm{PCH_2N}$), 61.52 and 66.75 (d, $^3J_{\mathrm{CP}}$ = 6.9 Hz, $\mathrm{NCH_2N}$), 122.05−129.73 (m, $\mathrm{CH_{arom}}$), 152.39 (d, $^2J_{\mathrm{CP}}$ = 7.4 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.44 (d, $^2J_{\mathrm{CP}}$ = 8.0 Hz, $\mathrm{C_{ipso}}$ of OPh), 169.13 (s, $\mathrm{COCH_3}$), 169.61 (d, $^3J_{\mathrm{CP}}$ = 2.1 Hz, $\mathrm{COCH_3}$) ppm.

*General Procedure for Catalytic Propargylic Isomerization in Water.* Under air, a pressure-resistant septum-sealed glass microwave reactor vial was charged with the corresponding alkynol (1 mmol), silver catalyst **5a** (0.0067 g, 1 mol % of Ag), a magnetic stirring bar, and distilled water (1 mL). The vial was then placed inside the cavity of a CEM Discover S-Class microwave synthesizer, and power was held at 300 W until the desired temperature (160 °C) was reached. Microwave power was automatically regulated for the remainder of the experiment to maintain the temperature monitored by a built-in infrared sensor (the course of the reaction was monitored by regular sampling and analysis by GC). The internal pressure during the reaction ranged between 5 and 95 psi. After completion of the reaction, the organic product was extracted with diethyl ether (3 × 5 mL). The organic crude reaction was purified by flash chromatography over silica gel using EtOAc/hexane (1:10) as eluent. The identity of the resulting *α,β*-unsaturated carbonyl compounds was assessed by comparison of their $^1$H and $^{13}$C{$^1$H} NMR spectroscopic data with those reported in the literature and by their fragmentation in GC/MS.

*General Procedure for Catalyst Recycling.* The recyclability of the Ag(I) complex **5a** was investigated using isomerization of the commercially available alkynol 1,1-diphenyl-2-propyn-1-ol (**7a**) to 3,3-diphenylpropenal (**8a**) as a model reaction. Under air, a pressure-resistant septum-sealed glass microwave reactor vial was charged with the alkynol **7a** (0.208 g, mmol), silver catalyst **5a** (0.0067 g, 1 mol % of Ag), a magnetic stirring bar, and distilled water (1 mL). The vial was then placed inside the cavity of a CEM Discover S-Class microwave synthesizer, and power was held at 300 W until the desired temperature (160 °C) was reached. Microwave power was automatically regulated for the remainder of the experiment to maintain the temperature monitored by a built-in infrared sensor (the course of the reaction was monitored by regular sampling and analysis by GC). The internal pressure during the reaction ranged between 5 and 95 psi. Complete consumption of **7a** was observed after 45 min. Aqueous phase was extracted with diethyl ether (3 × 5 mL). To the aqueous layer, 0.208 g (1 mmol) of alkynol **7a** was again added, and the mixture was stirred again under the same conditions for the required time. This procedure was repeated up to 10 consecutive times.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data for **5b** and **6a**, ESI-MS spectrum of an aqueous solution of complex **5a**, and micrographs of the silver nanoparticles (TEM and SEM images). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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