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Additional Information

Catalytic Activity of Cationic and Neutral Silver(I) XPhos Complexes with N ligands or Tolylsulfonate for Mannich and Aza-Diels-Alder Couplings

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Abstract: Cationic and neutral silver(I)-L complexes (L = Buchwald-type biaryl phosphanes) with N co-ligands and organosulfonate counterion have been synthesized and characterized by structural and spectroscopic properties. At room temperature, both cationic and neutral silver(I)-L complexes are extremely active catalysts to promote the single and double A³-coupling of terminal (di) alkynes, pyrrolidine and formaldehyde. Also the aza-Diels-Alder two and three -coupling of Danishefsky's diene with imine or with amine and aldehyde can be efficiently catalysed by these cationic or neutral silver(I)-L complexes. The solvent can influence the catalytic activity performance due to limited complex solubility or to solvent decomposition and reactivity. Isolation of new silver(I)-L complexes with reagents as ligands lend support to mechanistic proposals for such catalytic processes. The activity, stability and metal-distal arene interaction of these silver(I)-L catalysts have been compared with that of analogous cationic gold(I) and copper(I) complexes.

Introduction

Compared to silver, gold and copper are considered among the best transition metals to activate and promote a variety of organic reactions. However, silver (I) has recently also emerged as an efficient metal catalyst.^[1] The interest in silver (I) catalysts stems from its possible coordination modes^[2] and its affinity for hard donor atoms such as nitrogen or oxygen.^[3] The instable, low-activity and easily decomposed AgI,^[4] Ag₂CO₃,^[5] AgSbF₆^[6] and AgOTf salts^[7] are used as Lewis acids and as sacrificial agents in some procedures for the preparations of gold (I) complexes.^[8] In this context, it is important to establish whether or not stable Ag^I complexes can exhibit good catalytic activity with respect to their silver salt precursors for certain reactions.^[9] Herein, cationic bulky 2-di-tert-butylphosphanylbiaryl (L1) and

2-di-tert-butylphosphanyl(2',4',6'-triisopropyl)biphenyl (L2) (Buchwald phosphanes)^[10] Ag^I complexes have been synthesized, characterized and their catalytic activity compared with that of their Au^I and Cu^I analogs. These cationic silver (I)-L complexes have herein been tested as catalysts for the single and double three-component (A³) Mannich type coupling, providing at room temperature high-value propargylamines^[11] in high yield and selectivity, often in minutes. The catalytic activity of these Ag(I)-L complexes has also been extended to aza-Diels-Alder two and three -component couplings of Danishefsky's diene with imine or with amine and aldehyde exhibiting good performance and efficiency, providing a powerful methodology for the construction of nitrogen-containing six-membered ring dihydropyridin-4-one.^[6, 12] Also neutral silver(I) complexes [(L1)AgX] and [(L2)AgX] with mixed ligand combinations L1 or L2 and p-tolylsulfonate (X = p-MeC₆H₄SO₃), with L being very soft and X being hard, have been seen to be catalytically active. The Ag-distal C_{arene} interaction in Ag (I) complexes has been analysed by single crystal X-ray crystallography and compared with the interaction present of analogous Cu- and Au-C_{arene} complexes. Activity data show, on the other hand, possible ways in which the solvent can influence the catalytic performance due to limited complex solubility, solvent coordination and reaction or solvent decomposition. For instance, In a recent contribution in this area, it has been shown that Au^I and Cu^I catalysts in the presence of pyrrolidine react with CH₂Cl₂ used as reaction solvent, to give less-active chloride forms of the catalyst.^[13] To expand the scope of these studies, herein, several Ag^I complexes considered as reaction intermediates have been isolated and characterized, providing insight into the reaction mechanisms of propargylamine formation and aza-Diels-Alder cycloaddition of Danishefsky's dienes. Also with the aid of single crystal crystallography the lengths for selected Ag-N, Ag-P, Ag-C_{ipso} bonds and the shortest distance between Ag and a carbon (Cx) of the distal phenyl ring for synthesized cationic and neutral silver(I)-L complexes have been measured and compared with those for analogous copper(I) and gold(I) complexes. These data have made possible to draw some important conclusions respect the stability of these complexes and the lability of the aquo-, N- and organosulfonate ligands.

Results and Discussion

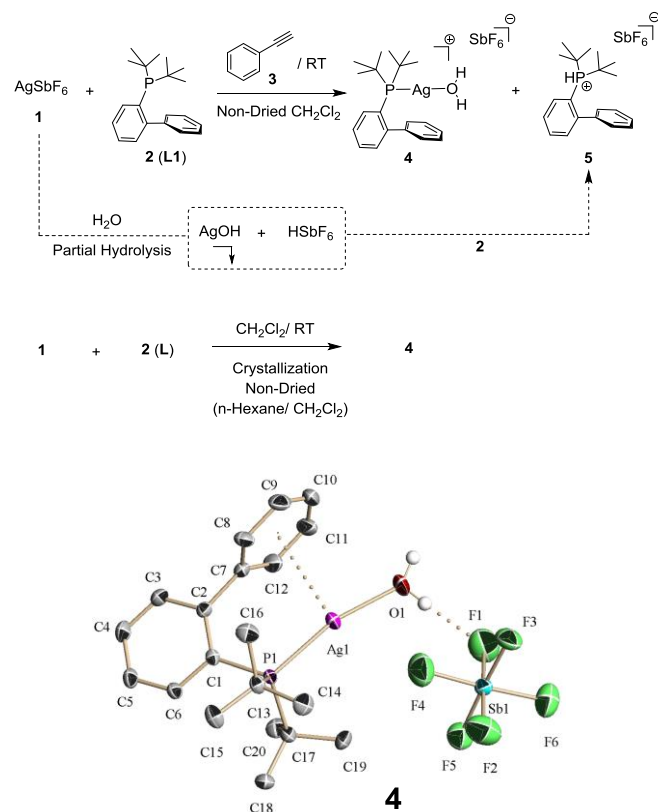
In the initial stage of our study and with the aim to isolate the presumed silver (I) acetylide complexes, [Ag]⁺[SbF₆]⁻ salt (1),

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bulky 2-di-tert-butylphosphanylbiaryl (L = **2**) and phenylacetylene (**3**) as ligand and reagent were dissolved in non-dried CH₂Cl₂ at RT for 24 h with the following stoichiometric proportion (1:1:2) (Scheme 1, Top). Filtration of the resulting transparent, colourless solutions followed by addition of n-hexane at -8 °C leads to the formation of a mixture of white precipitate and colourless needles crystals (see the Experimental Section) that could be isolated by filtration.



Scheme 1. Top: Synthesis of cationic-aquo silver(I) complex **4** by simultaneous addition of reagents **1**, **2** and **3** in 1:1:2 stoichiometry in non-dried CH₂Cl₂ at RT. Phosphonium salt **5** was detected also as product derived from the formal neutralization of HSBF₆ by **2**. Middle: Synthesis of pure cationic-aquo silver(I) complex **4**. Bottom: ORTEP view of the structure of **4**; ellipsoids are given at the 30 % probability level (C-H hydrogen atoms are omitted for clarity). (single-crystal X-ray data, ortep and crystal packing details are given in Table S1 and Fig. S6 in the supporting information).

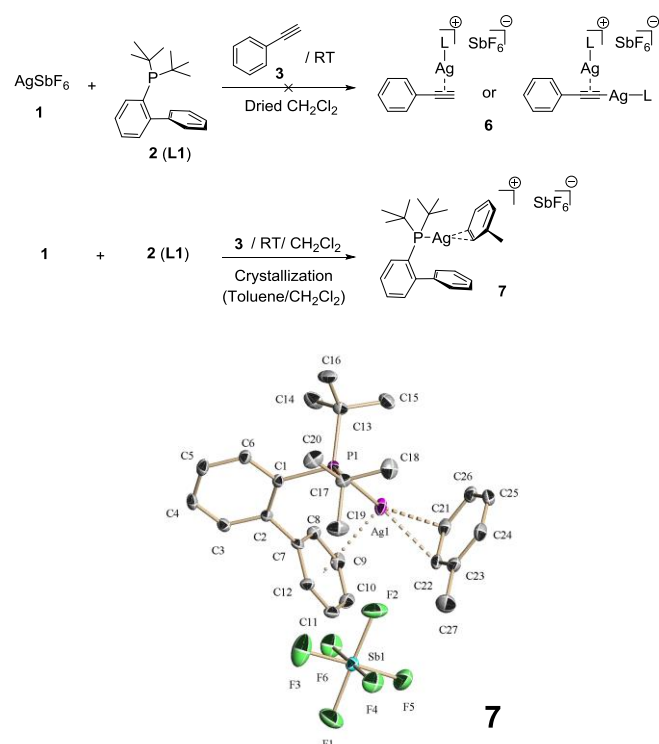
¹H and ³¹P NMR spectroscopy of this solid mixture in CD₂Cl₂ provides evidence of the presence of two kinds of coordinated phosphine ligand (See the Experimental Section and Fig. S1 and Fig. S2 in the supporting information). Under the conditions indicated in Scheme 1, the initial phosphine ligand **2** is completely converted to a mixture of **4** (78 %) and **5** (22 %). Thus, ¹H NMR spectroscopy shows new signals at δ = 1.28 and 1.23 ppm for the methyl groups of cationic-aquo silver(I) complex **4** and at δ = 1.44 and 1.38 ppm for phosphonium salt **5** (Fig. S1 in the Supporting Information) instead of those corresponding to the initial phosphine ligand **2** at δ = 1.11 and

1.07 ppm. Similarly to the ¹H NMR spectroscopy, ³¹P NMR spectroscopy also shows the disappearance of the signal corresponding to the initial phosphine ligand **2** at δ = 18.11 ppm (singlet) and the appearance of new signals at 45.21 ppm (two doublets) for **4** and at 33.16 ppm for phosphonium salt **5** (singlet) (Fig. S2 in the supporting information). Complex **4** can be obtained pure by reaction of [Ag]⁺[SbF₆]⁻ (**1**) and phosphine ligand (L = **2**) in non dried CH₂Cl₂ at RT for 8 h with the stoichiometric reaction mixture (1:1) (Scheme 1, Middle) followed by crystallization in a mixture of non-dried dichloromethane/n-hexane (1/2) at -30 °C for 24 h. After filtration, complex **4** could be isolated in 84 % yield (see the experimental section). Cationic aquo-silver(I) complex **4** was isolated and characterized by analytical and spectroscopic data (see the Experimental Section, Table S1 and Figs. S3-S6). ESI-MS of a solution obtained after dissolving complex **4** in CH₂Cl₂/MeOH (1:1) showed weak positive MS peak at 463.1 Da and intense positive MS peak at 405.1 Da (see Fig. S5 in the Supporting Information) that are attributable, respectively, to the cationic [C₂₀H₂₈AgF₆OPSb (**4**) - SbF₆⁻ + K]⁺ and [C₂₀H₂₈AgF₆OPSb (**4**) - SbF₆⁻ - H₂O]⁺ species, and intense negative MS peaks at 234.6 Da and 236.6 Da corresponding to the [SbF₆]⁻ counter anion (see Fig. S5 in the supporting information). The formation of a silver-phosphorous bond in complex **4** is firmly confirmed by the appearance in ³¹P NMR spectroscopy two doublets due to coupling of ³¹P with the two silver isotopes (¹⁰⁷Ag and ¹⁰⁹Ag) of spin ½ at 46.08 ppm with ¹J(¹⁰⁷Ag-³¹P) = 714.28 Hz and ¹J(¹⁰⁹Ag-³¹P) = 824.42 Hz (see Fig. S4 in the supporting information). On the other hand, in our previous report with copper complexes,^[14] phosphonium salt with hexafluorophosphate as counter anion instead of hexafluoroantimonate as in the case of **5**, already presented similar ³¹P chemical shift at 33.11 ppm (see Fig. S2 in the Supporting Information for **5** and our previous work^[14] for similar compound observed in the case of copper). Combustion elemental analysis for complex **4** is in accordance with the percentages expected for its formula (see experimental section). Solid state structure of cationic aquo-Ag^I-L complex **4** was solved by single-crystal X-ray diffraction studies. The corresponding ORTEP of complex **4** is shown in Scheme 1 bottom (for more details, see Table S1 and Fig. S6 in the supporting information). Selected bond lengths for Ag-O, Ag-P, Ag-C₇_{ipso} and shortest distance between Ag and carbon (C12) of distal phenyl ring were 2.148(5), 2.3651(15), 2.976 and 2.885 Å, respectively. The structure obtained was a polymorph of a previously reported one for complex **4**.^[3]

Another additional unsuccessful experiment aimed to isolate the silver (I) acetylide complex (**6**) (Scheme 2, top) was performed by starting from the same conditions of the first experiment (Scheme 1), but using in this case dried CH₂Cl₂. The addition of n-hexane over the resulting transparent colourless solution followed by standing over night at -30 °C did not lead to the isolation of any solid product. When toluene was added to this resulting mixture and after slow crystallization at RT, the arene silver(I) complex **7** (Scheme 2, middle) was isolated in 88 % yield (see the experimental section). The structure of **7** (Scheme 2, bottom) was confirmed by single-crystal X-ray diffraction

(Table S2 and Fig. S7 in the supporting information). Selected distances for Ag- η^2 -toluene C(21) and C(22), Ag-P, Ag-C(7)_{ipso} and shortest distance between Ag and the closest carbon atom (C8) of distal phenyl ring are 2.367(6) and 2.480(6), 2.3873(14), 2.906 and 2.838 Å, respectively. The structure of **7** was coincident with the previous reported structure for this complex **7**^[3] with η^2 -arene coordination of toluene to Ag^I. Complex **7** was also characterized by NMR spectroscopy and combustion elemental analysis (see experimental section and Figs. S8-S9 in the supporting information).

From the previous experiments, it can be concluded that silver (I) does not form σ , π -disilver- or any other type of isolable phenylacetylene adduct. Therefore, Ag(I) behaves similarly to Cu(I) for which it has also not been possible to isolate adducts with phenylacetylene^[13-14] and exhibits different chemistry than Au(I) that form fluxional di-cationic $[(\sigma, \pi)](LAu)_2(\mu\text{-phenylacetylene})[SbF_6]_2$ complexes.^[15]

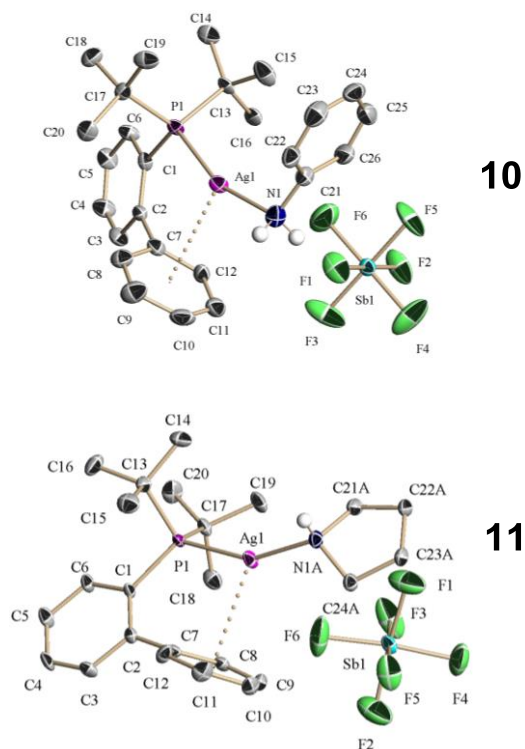
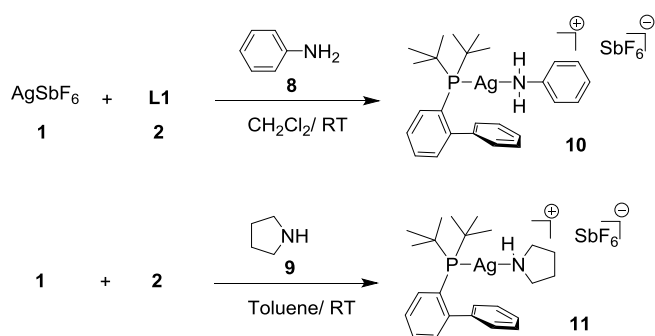


Scheme 2. Top: Failure to isolate any silver acetylide complex. Middle: Synthesis of cationic complex **7**. Bottom: ORTEP view of the structure of **7**; ellipsoids are given at the 30 % probability level (C-H hydrogen atoms are omitted for clarity. (single-crystal X-ray data and crystal packing detail are given in Table S2 and Fig. S7 in the supporting information).

At this stage of the work, and aimed at determining the activity of Ag(I)-L complexes as catalysts, the synthesis of a new cationic Ag^I dialkylbiarylphosphane complex that can be used as precatalyst, was carried out. A stoichiometric (1:1:1) mixture of **1**, **2** and aniline **8** or pyrrolidine **9** was stirred for 18 h at room temperature in CH₂Cl₂ or toluene (Scheme 3, top). Then, the

resulting mixture was diluted with additional 2 ml of CH₂Cl₂, filtered and the supernatant was layered carefully by 2 ml of n-pentane. After standing 48 h at -30 °C, isolation of colourless crystals of complex **10** in 89 % yield (see experimental section) was achieved. For similar mixtures in toluene using pyrrolidine **9** as nucleophile, the precipitate initially formed was subsequently dissolved adding 2 ml of 1,2-dichloroethane (ClCH₂CH₂Cl), filtered and then a layer of n-pentane was carefully added, resulting in the isolation of colourless crystals of complex **11** in 91 % yield (see experimental section). These new cationic Ag^I-aniline (**10**) and Ag^I-pyrrolidine (**11**) complexes were fully characterized on the basis of combustion elemental analysis and spectroscopic data (see the experimental details as well as Figs. S10-S15 and Table S3 for **10** and Figs. S16-S20 and Table S4 for **11** in the Supporting Information). Single crystals of both complexes **10** and **11** were air-stable and of suitable quality for an X-ray crystallographic diffraction study.

The solid structure of these new cationic silver (I) complexes **10** (L1-aniline-Ag^I) and **11** (L1-pyrrolidine-Ag^I) were, respectively, closely related to the previously reported hexafluorophosphate salt of Cu^I analogues (L1-aniline-Cu^I)^[13] and (L1-pyrrolidine-Cu^I)^[13-14] but with different counterion. Selected bond lengths for Ag-N, Ag-P, Ag-C(7)_{ipso} and the distance between Ag and the closest carbon atom (C12) of the distal phenyl ring for complex **10** (Table S3 and Fig. S10 in the supporting information) are 2.189(11), 2.374(3), 2.902 and 2.954 Å, respectively. Also the bond lengths of Ag-N(1A), Ag-P, Ag-C(7)_{ipso} and the distance between Ag and the closest carbon atom (C8) of the distal phenyl ring for complex **11** (Table S4 and Fig. S16 in the supporting information) are 2.182(10), 2.3697(13), 3.090 and 2.812 Å, respectively, which are longer than the corresponding values for Cu-N, Cu-P, Cu-C_{ipso} and the shortest distance between Cu1 and the closest carbon atom (C13) of the distal phenyl ring of the complexed biphenyl in our recently published cationic Cu^I analogues (L1-aniline-Cu^I) 1.964(2), 2.182(7), 2.786 and 2.577 Å^[13] and (L1-pyrrolidine-Cu^I) 1.956(6), 2.189(19), 2.861 and 2.540 Å, respectively.^[13] It is worth commenting that our previous published cationic gold (I) L1-aniline-Au(I) complex^[15b] present intermediate bond lengths compared to the silver and copper analogs in the case of Au-N(1) and Au-P(1) with 2.118(8), 2.250(2) Å and larger distance in the case of Au-C(13)_{ipso} and the distance between Au1 and the closest carbon atom (C14) of the distal phenyl ring around 2.985 and 3.211 Å, thus, showing the influence of the metal (Cu, Ag and Au) on the metal-arene interaction.



Scheme 3. Top: Synthesis of cationic silver (I) complexes **10** and **11**. Bottom: ORTEP views of **10** and **11**; ellipsoids are given at the 30 % probability level (C-H hydrogen atoms are omitted for clarity). (single-crystal X-ray data and crystal packing details are provided in Table S3 and S4 and Fig. S10 and S16 in the supporting information, respectively).

The silver (I) complexes **10** and **11** were also characterized by NMR spectroscopy and ESI-MS (see the experimental section and the Supporting Information). ^1H , ^{13}C , Dept and ^{31}P NMR spectra in CD_2Cl_2 provided evidence that the starting AgSbF_6 (**1**) salt was completely converted into **10** or **11** depending on the amine (see Figs. S11-S14 for **10** and Figs. S17-S20 for **11** in the supporting information). Thus, the formation of a Ag-P bonds in these complexes **10** and **11** was confirmed by the appearance of ^{31}P NMR spectroscopy of two doublets due to coupling of ^{31}P with the two silver isotopes of spin $\frac{1}{2}$ (^{107}Ag and ^{109}Ag), respectively, at 47.35 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) = 639.17$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 738.97$ Hz for **10** (Fig. S12 in the supporting information) and at 45.50 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) = 608.48$ Hz,

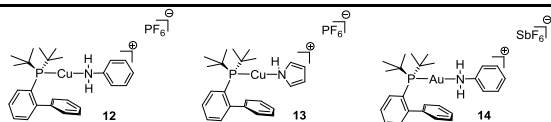
$^1J(^{109}\text{Ag}-^{31}\text{P}) = 701.65$ Hz for **11** (Fig. S18 in the supporting information). Similarly, ^1H NMR spectroscopy showed new signals for the methyl groups of complexes **10** and **11**, respectively, at 1.20 and 1.15 ppm (Fig. S11 for **10** in the supporting information) and at 1.29 and 1.24 ppm (Fig. S17 for **11** in the supporting information) instead of those corresponding to the initial phosphine ligand **2** at 1.11 and 1.07 ppm. ESI-MS of a solution obtained after dissolving complex **10** in MeOH shows mainly a cluster of peaks with major positive MS peaks at 405.1 and 407.1 Da attributable to cationic Ag(I) complex with the ^{107}Ag and ^{109}Ag isomers of $[\text{C}_{26}\text{H}_{33}\text{AgF}_6\text{NPSb}(\text{10}) - \text{SbF}_6^- - \text{aniline}]^+$ and other cluster of peaks with major positive MS peaks at 437.2 Da attributable to cationic Ag(I) complex with the ^{107}Ag and ^{109}Ag isomers of $[\text{C}_{26}\text{H}_{33}\text{AgF}_6\text{NPSb}(\text{10}) - \text{SbF}_6^- - \text{aniline} + \text{MeOH}]^+$ (see Fig. S15 for details in the supporting information). In negative MS mode the presence of peaks at 234.8 and 236.9 Da attributable to SbF_6^- counter-anion of complex **10** with the ^{121}Sb and ^{123}Sb isomers was also observed (see details in Fig. S15 in the supporting information).

With the aim of gaining understanding on the stability and activity of Ag(I) coordinated to bulky ligand **2** in complexes **7**, **10** and **11**, the Mannich A³ coupling of phenylacetylene (**3**), pyrrolidine (**9**) and aqueous formaldehyde (**15**) was performed in toluene using as catalysts cationic silver (I) complexes **7**, **10** and **11** (see Table 1). For the sake of comparison, the catalytic activity of related copper and gold complexes $[\text{LCu}(\text{aniline})][\text{SbF}_6]$ (**12**), $[\text{LCu}(\text{pyrrolidine})][\text{SbF}_6]$ (**13**)^[13-14] and $[\text{LAu}(\text{aniline})][\text{SbF}_6]$ (**14**)^[15b] were also screened (see Table 1) with the goal of shedding light on the real active species involved in the catalytic process for silver (I) compared to the previous studies on copper (I)^[13-14] and gold (I)^[15]. In these catalytic reactions, the expected product 1-(3-phenylprop-2-ynyl)pyrrolidine **16** was obtained in good yields (Table 1, entries 1-6) was isolated as light-yellow oil and characterized by ^1H , ^{13}C and GC-MS (see Figs. S21-S23 in the supporting information). It should be noted, however, that the reaction took place in only few minutes (6 min) at room temperature (26 °C) for Ag (I) complexes **7**, **10** and **11** (Table 1, entries 1, 2 and 3), compared to the slightly higher reaction temperature (50 °C) and time (12 min) required in the case of Cu (I) complexes **12** and **13** (Table 1, entries 4 and 5). Considerably longer time (24 h) at 50 °C was required for cationic Au (I) complex **14** (Table 1, entry 6).

Table 1. A³-coupling of phenylacetylene, pyrrolidine, and aqueous formaldehyde with complexes of Ag (I) **7**, **10**, **17**, **18**, **29** and **27**, complexes of Cu (I) **12**, **13** and complexes of Au (I) **14** as catalysts (6 mol %).^[a]

entry	Catalyst	Temperature (°C)	Time (h)	Conv. (%) ^[b]	Yield (%) ^[b]
1	7	RT	0.1	100	99
2	10	RT	0.1	100	98
3	11	RT	0.1	100	99
4	12	50	0.2	100	98
5	13	50	0.2	100	99

6	14	50	0.2	4	Trace
			24	90	81
7	17	RT	0.1	100	99
8	18	RT	0.1	1	Trace
9	11 ^[c]	RT	0.05	100	99
10	17 ^[c]	RT	0.05	100	99
11	29	RT	0.05	13	10
			2	48	46
12	29 ^[d]	RT	0.05	52	50
			0.3	99	97
13	29 ^[c]	RT	0.05	98	97
			0.1	100	99
14	27 ^[c]	RT	0.1	100	100

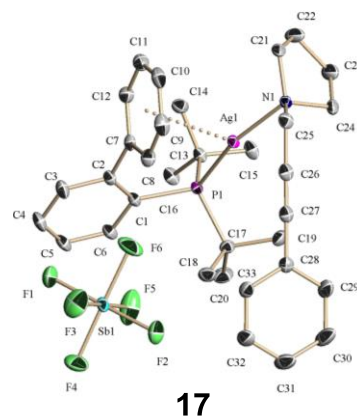
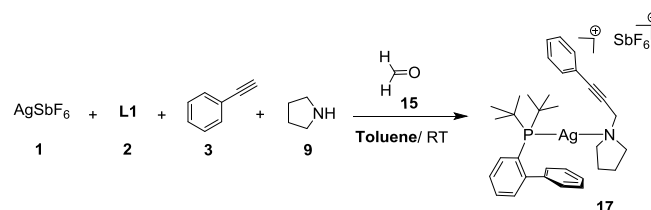


[a] All reactions were carried out using 0.25 mmol of phenylacetylene, 0.35 mmol of pyrrolidine and 0.7 mmol of aqueous formaldehyde and 1 ml of toluene. [b] conv. and yields (%) were determined by ¹H NMR spectroscopy and GC of the crude reaction mixture. [c] CH₂Cl₂ was used instead of toluene as solvent. [d] Dioxane was used instead of toluene as solvent.

One important conclusion from Table 1 (entries 1-6) is that the cationic Ag^I complexes were more active than the Cu^I complexes and considerably more active than the Au^I complex. This higher activity of Ag^I and Cu^I vs Au^I can be explained by the lack of formation of di-cationic σ , π -disilver- (scheme 2: Top) or dicopper-^[14] phenylacetylene adduct analogous to the fluxional di-cationic $[(\sigma, \pi)(L\text{Au})_2(\mu\text{-phenylacetylene})][\text{SbF}_6]_2$.^[15a] On the other hand, the higher catalytic activity of cationic Ag^I vs Cu^I complex can be explained by the more labile coordination between Ag^I and the hard donor nitrogen atom present in the neutral ligands **8**, **9** and **16** compared with the analogous Cu^I complexes. This rationalization is supported by crystallographic data of single crystals of cationic Ag^I **10** and **11** complexes compared with those of cationic L-Cu^I-aniline and L-Cu^I-pyrrolidine analogs where the bond lengths for Ag-N in the complexes **10** and **11** (Table S3 and Fig. S7 in the supporting information) are around 2.189(11) and 2.182(10) Å, respectively, compared to the shorter Cu-N bond lengths of 1.964 (2) and 1.956(6) Å in the cationic L-Cu^I-aniline and L-Cu^I-pyrrolidine complexes, respectively.^[13]

To isolate possible reaction intermediates the A³ coupling was performed in the presence of a stoichiometric amount of [Ag]⁺[SbF₆]⁻ (**1**), bulky 2-di-tert-butylphosphanylbiaryl (L1 = **2**), phenylacetylene (**3**), pyrrolidine (**9**) and aqueous formaldehyde (**15**) (37 %) at room temperature in toluene (Scheme 4, top). After 20 h, the resulting precipitate formed was dissolved by adding 2 ml of dichloroethane/dichloromethane (1/1), then the transparent resulting solution was filtered, followed by a slow evaporation at RT to afford colourless crystals of complex **17** in 90 % yield (see experimental section). The [L1Ag(propargylamine)][SbF₆] complex **17**, corresponding to the Ag (I) catalyst with the final propargylamine **16** compound, was isolated and characterized on the basis of analytical and spectroscopic data (see experimental details, Figs. S24-S28, and Table S5 in the supporting information). Combustion

elemental analysis of complex **17** was in accordance with the percentages expected for its formula. Crystals of complex **17** of sufficient quality for X-ray crystallography were obtained by slow evaporation of filtered mixture solutions (toluene/CH₂Cl₂/ClCH₂CH₂Cl) (2/1/1) of **17** (see experimental section and Table S5 and Fig. S28). Ortep structure and crystal packing details of the Ag^I complex **17** are given, respectively in Scheme 4 (bottom) and in Fig. S28 in the supporting information.



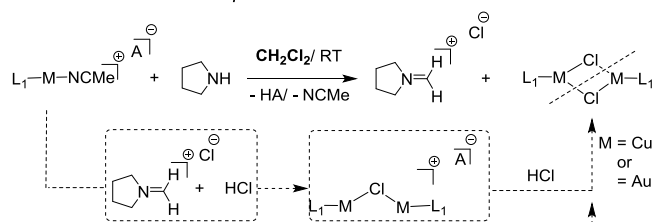
Scheme 4. Top: Synthesis of cationic silver (I) [L1Ag(propargylamine)][SbF₆] complex **17**. Bottom: ORTEP view of **17**; ellipsoids are given at the 30 % probability level (C-H hydrogen atoms are omitted for clarity). (single-crystal X-ray data and crystal packing details are given in Table S5 and Fig. S28 in the supporting information).

The bond lengths for Ag-N in complex **17** (Table S5 and Fig. S28 in the supporting Information) is 2.209(2) Å significantly longer than Cu-N bond length of 1.979(2) Å in the analog [L1Cu(propargylamine)][PF₆]^[13] complex. This difference in bond length shows the stronger coordination of propargylamine ligand with Cu^I vs Ag^I. Interestingly, the catalytic activity of the cationic silver (I) complex **17** for the Mannich A³ coupling (Table 1, entry 7) was as high as those of the initial cationic Ag^I complexes **7**, **10** and **11**.

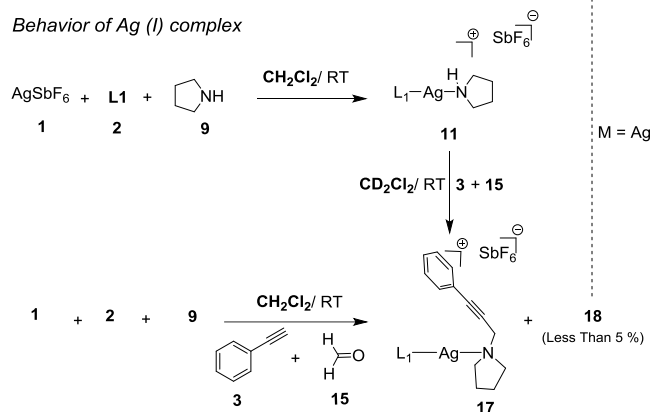
Previously, we found that the nature of the solvent for this A³-coupling plays a key role solubilizing the cationic precatalyst and the subsequent intermediates formed during the course of the catalytic cycle, making possible regeneration of the active form.^[13-14] To check the behaviour of cationic silver (I) complexes in CH₂Cl₂ in which previously cationic copper (I) and gold (I) complexes became inactive due to the formation of neutral bridged dichloride dicopper (I) [(L1-Cu(μ-Cl))₂]^[13] and chloride gold (I) [L1-AuCl]^[13] complexes (Scheme 5: Top), respectively,

new experiments for preparation of complexes **11** and **17** in CH_2Cl_2 instead of toluene were performed (Scheme 5: bottom).

Behavior of Cu or Au complexes



Behavior of Ag (I) complex



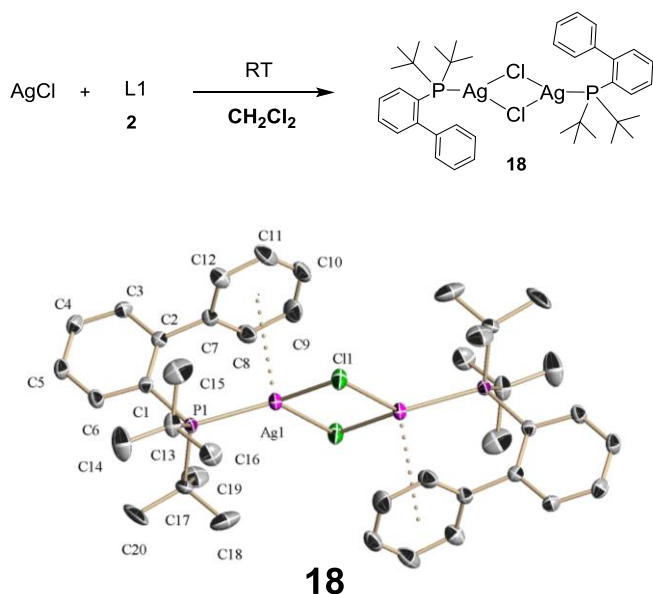
Scheme 5. Top: deactivation of cationic copper (I) and gold (I) complexes by formation of a less active neutral bridged dichloride dicopper (I) $[\{\text{L1-Cu}(\mu\text{-Cl})_2\}]$ and chloride gold(I) $[\text{L1-AuCl}]$, respectively.^[13] Bottom: preparation of complexes **11** and **17** in CH_2Cl_2 as solvent with formation of a small amount of a less active neutral bridged dichloride disilver (I) $[\{\text{L1-Ag}(\mu\text{-Cl})_2\}]$ complex **18**. Preparation of **17** starting from **11** in CD_2Cl_2 as solvent.

Transparent colourless solutions were observed from the beginning to the final reaction time (20 h) required for the preparation of complexes **11** and **17** (Scheme 5: bottom) due to the higher solubility of these complexes, reagents and products in CH_2Cl_2 compared to toluene. Importantly, in the case of Ag (I) complexes the presence of chlorine atoms in the medium that could be formed by the reaction of CH_2Cl_2 with pyrrolidine (**9**) do not deactivate apparently cationic Ag^{I} complexes **11** and **17** by direct coordination of chloride to the metal ion. In another independent experiment followed by ^{31}P NMR spectroscopy for preparation of **17** using CD_2Cl_2 (Scheme 5: bottom) a complete transformation of complex **11** into **17** (yield, 90 %) accompanied by two small peaks, one of them corresponding to a new species **18** and remaining at final reaction time (less than 5 %) (Scheme 5: bottom). Complex **18** showed two doublets due to coupling of ^{31}P with the two silver isotopes of spin $\frac{1}{2}$ (^{107}Ag and ^{109}Ag) at 43.67 ppm with $^1J(^{107}\text{Ag-}^{31}\text{P}) = 605.60$ Hz, $^1J(^{109}\text{Ag-}^{31}\text{P}) = 698.30$ Hz. The second small peak (also less than 5 %) disappeared at final reaction time can be attributable to the plausible cationic intermediate complex **19** (Scheme 7). This intermediate showed two doublets due to coupling of ^{31}P with the two silver isotopes of spin $\frac{1}{2}$ (^{107}Ag and ^{109}Ag) at 45.40 ppm with $^1J(^{107}\text{Ag-}^{31}\text{P}) =$

490.55 Hz, $^1J(^{109}\text{Ag-}^{31}\text{P}) = 567.26$ Hz (See Figs. S29-32 for the ^{31}P NMR mixtures complexes of **17**, **18** and **19** in the supporting information).

To confirm the identity of the neutral chloride-Ag complex **18** that would be the analog of the dichloride dicopper (I) $[\{\text{L1-Cu}(\mu\text{-Cl})_2\}]$ or chloride gold (I) $[\text{L1-AuCl}]$ complexes (Scheme 5: Top), we proceeded to its alternative synthesis by reaction of AgCl as precursor and bulky 2-di-tert-butylphosphanylbiaryl ($\text{L1} = \mathbf{2}$) in dried CH_2Cl_2 at RT for 48 h with the (1:1.2) stoichiometry (Scheme 6, Top). Filtration of the resulting transparent colourless solutions to remove the excess of insoluble AgCl , followed by slow evaporation of the resulting mixture in dichloromethane after standing for 4 h at RT lead to the formation of colourless crystals of **18** in 88 % yield (see experimental section). This new neutral dichloride-bridged disilver(I) complex $[\{\text{L1-Ag}(\mu\text{-Cl})_2\}]$ **18** was fully characterized on the basis of combustion elemental analysis and spectroscopic data (see the experimental details as well as Figs. S33-S37 and Table S6 in the supporting information). Single crystals of **18** are air-stable and have suitable quality for single crystal X-ray crystallographic diffraction (Scheme 6, bottom). Thus, according to Scheme 6, insoluble AgCl can become solubilized in CH_2Cl_2 when phosphines L are present in the medium. This finding has to be put in the context of the general practice of using Ag (I) salts to presumably remove Cl^- from Au^{I} that has led to erratic results^[16] with regard to their catalytic activity.

The solid structure of cationic complex **18** is closely related to that of the previously reported $[\{\text{L1-Cu}(\mu\text{-Cl})_2\}]^{\text{I}}$ dimer-Cu^I analog. Selected bond lengths for Ag-Cl(1), Ag-Cl(1)#1, Ag-P(1), Ag-C(7)_{ipso}, Ag-Ag, Cl-Cl and shortest distance between Ag and the closest carbon atom (C8) of distal phenyl ring of L1 (**2**) (Table S7 and Fig. S37 in the supporting information) are 2.4909(7), 2.6296(7), 2.3941(6), 3.109, 3.393, 3.837 and 2.823 Å, respectively. Interestingly the dichloride dicopper(I) $[\{\text{L1-Cu}(\mu\text{-Cl})_2\}]^{\text{I}}$ analog exhibits shorter distances with the Cu-Cl(1), Cu-Cl(1)#1, Cu-P(1), Cu-C(7)_{ipso}, Cu-Cu, Cl-Cl and shortest distance between Cu and the closest carbon atom (C8) of distal phenyl ring of 2.2954(4), 2.3572(4), 2.2005(4), 2.906, 3.0408, 3.522 and 2.559 Å, respectively.

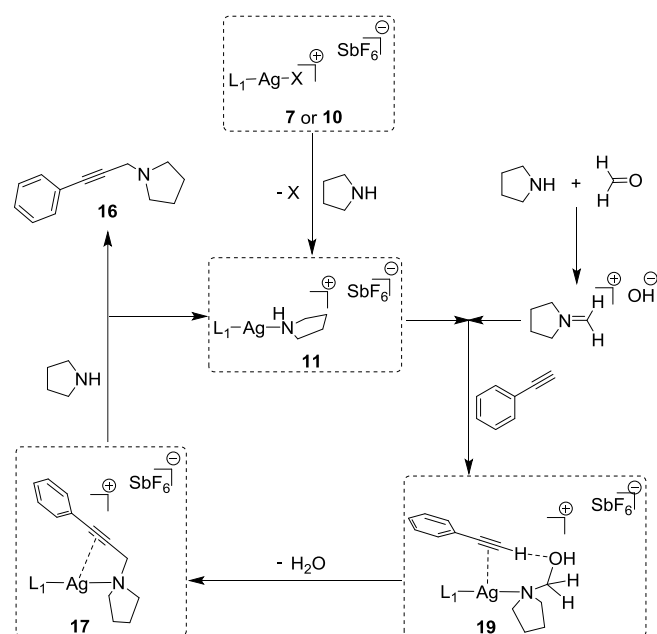


Scheme 6. Top: Synthesis of neutral dichloride di-silver (I) complex **18**. Bottom: ORTEP view of **18**; ellipsoids are given at the 30 % probability level (C-H hydrogen atoms are omitted for clarity). (single-crystal X-ray data and crystal packing details are given in Table S6 and Fig. S37 in the supporting information).

^1H and ^{31}P NMR spectroscopy of this neutral dimeric Ag^{I} complex provide evidence of the coordination of the initial free phosphine ligand **2** (see the Experimental Section and Figs. S33-S34 in the supporting information). Thus, ^1H NMR spectroscopy shows new signals at $\delta = 1.30$ and 1.25 ppm for the methyl groups of disilver(I) complex **18** (Fig. S33 in the supporting information) instead of the values corresponding to the initial phosphine ligand **2** at $\delta = 1.11$ and 1.07 ppm. Similarly to the ^1H NMR spectra, ^{31}P NMR spectra also show the disappearance of the signal corresponding to the initial phosphine ligand **2** at $\delta = 18.11$ ppm (singlet) and the appearance of new signal at 43.67 ppm (two doublets) due to coupling of ^{31}P with the two silver isotopes of spin $\frac{1}{2}$ (^{107}Ag and ^{109}Ag) at 43.67 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) = 605.60$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 698.30$ Hz for **18** (Fig. S34 in the supporting information). Also ^{13}C and Dept NMR spectroscopy (Figs. S35-S36 in the supporting information) shows the presence of signals exclusively attributable to **18**.

The catalytic activity of this neutral dichloride-bridged disilver (I) complex $[\{\text{L}^1\text{-Ag}(\mu\text{-Cl})_2\}]_2$ **18** was also tested for the Mannich A^3 coupling (Table 1, entry 8) resulting considerably lower activity than cationic Ag^{I} precatalysts **7**, **10**, **11** and **17**. The use of dichloromethane as solvent instead of toluene when cationic Ag^{I} complexes **11** and **17** were used as catalysts (Table 1, entries 9 and 10 compared with entries 3 and 7) resulting in higher reaction rate in this A^3 coupling catalytic reaction due to the higher solubility of this cationic silver (I) complexes and their negligible deactivation caused in the case of Ag^{I} by the presence of chlorine in the medium compared with its Cu^{I} and Au^{I} analogs.

According to these experimental results, a plausible reaction mechanism for the A^3 coupling with $[\text{Ag}(\text{L}^1)(\text{toluene})][\text{SbF}_6]$ (**7**) or $[\text{Ag}(\text{L}^1)(\text{NH}_2\text{Ph})][\text{SbF}_6]$ (**10**) as precatalyst in toluene or CH_2Cl_2 can be proposed (Scheme 7). The main point of this mechanism is the coordination of Ag^{I} precatalysts **7** or **10** with pyrrolidine leading to the isolated intermediate $[\text{Ag}(\text{L}^1)(\text{pyrrolidine})][\text{SbF}_6]$ (**11**) and the presumed formation of π -complex intermediate (**19**) (see Fig. S 32 in the supporting information) between silver and phenylacetylene. The condensation between formaldehyde and pyrrolidine would take place spontaneously or promoted by acids. Silver (I) propargylamine complex **17** will be formed from the plausible key Ag^{I} intermediate **19** followed by release of propargylamine **16** from the coordination sphere of Ag^{I} by replacement with free pyrrolidine present in reaction medium. According to this mechanistic proposal the first major difference between cationic $\text{L}^1\text{-Ag}(\text{I})$ and $\text{L}^1\text{-Cu}(\text{I})$ ^[13-14] with $\text{L}^1\text{-Au}(\text{I})$ ^[13] complexes used as catalyst in this Mannich A^3 Coupling reaction derives from the lack of formation of σ , π -disilver and dicopper-phenylacetylene adduct that, in contrast, is formed in the case of $\text{L}^1\text{-Au}(\text{I})$.^[15] The second major difference between $\text{L}^1\text{-Ag}(\text{I})$ on one hand and $\text{L}^1\text{-Cu}(\text{I})$ and $\text{L}^1\text{-Au}(\text{I})$ complexes on the other one derives from the higher stability of the cationic Ag^{I} intermediates against its inactivation by forming a neutral dichloride dicopper (I) $[\{\text{L}^1\text{-Cu}(\mu\text{-Cl})_2\}]_2$ or chloride gold (I) $[\text{L}^1\text{-AuCl}]$ complexes when CH_2Cl_2 is used as solvent.



Scheme 7. Proposed mechanism for the A^3 -coupling leading to propargylamine **16** using as precatalyst cationic Ag^{I} complexes **7** or **10** in the presence of toluene or CH_2Cl_2 as solvent. Intermediates **11** and **17** have been isolated. Intermediate **19** is proposed (see Fig. S 32 in the supporting information).

To expand the scope of this catalytic A^3 coupling, the double reaction of 1,4-diethynylbenzene (**20**), pyrrolidine and aqueous

formaldehyde with cationic Ag (I) complex **11** was performed in toluene, CH₂Cl₂ or dioxane as solvent (see Table 2). Controls in the absence of any catalyst do not allow the detection of any product. The expected reaction products of the mono- and di A³-coupling 1-[3-(4-ethynylphenyl)prop-2-yn-1-yl]pyrrolidine (**21**) and 1,4-bis(3-(pyrrolidin-1-yl)prop-1-yn-1-yl)benzene (**22**) (see Scheme in Table 2), respectively, were characterized and obtained in good yield. Moreover this double A³ coupling took place in short time when using cationic Ag (I) complex **11** as catalyst (Table 2), the solvent playing a significant influence on the catalytic process. Toluene as solvent (see Table 2, entry 1) was less convenient compared to dioxane or CH₂Cl₂ (see Table 2, entries 2 and 3). This lower reactivity in toluene is due to the limited solubility of cationic silver (I) complex (**11**) used as precatalyst as well as the reaction intermediates.

Table 2. Double A³-coupling of 1,4-diethynylbenzene (**20**) or 1,6-heptadiene (**23**), pyrrolidine and aqueous formaldehyde with Ag (I) **11** as catalyst (6 mol %).^[a]

entry	Solvent	Time (h)	Conversion (%) ^[b]	Yield (%) ^[b]
1	Toluene	0.2	90	87
2	Dioxane	0.2	100	98
3	CH₂Cl₂	0.1	100	98

entry	Solvent	Time (h)	Conversion (%) ^[b]	Yield (%) ^[b]
4	Dioxane	0.2	100	97
5	CH₂Cl₂	0.1	100	98

[a] All reactions were carried out using 0.25 mmol of bis-alkyne, 0.7 mmol of pyrrolidine and 1.4 mmol of aqueous formaldehyde and 1 ml of solvent. [b] Conversions and yields, respectively of **20** or **23** and **22** or **25** (%) were determined by ¹H NMR spectroscopy and GC of the crude reaction mixture.

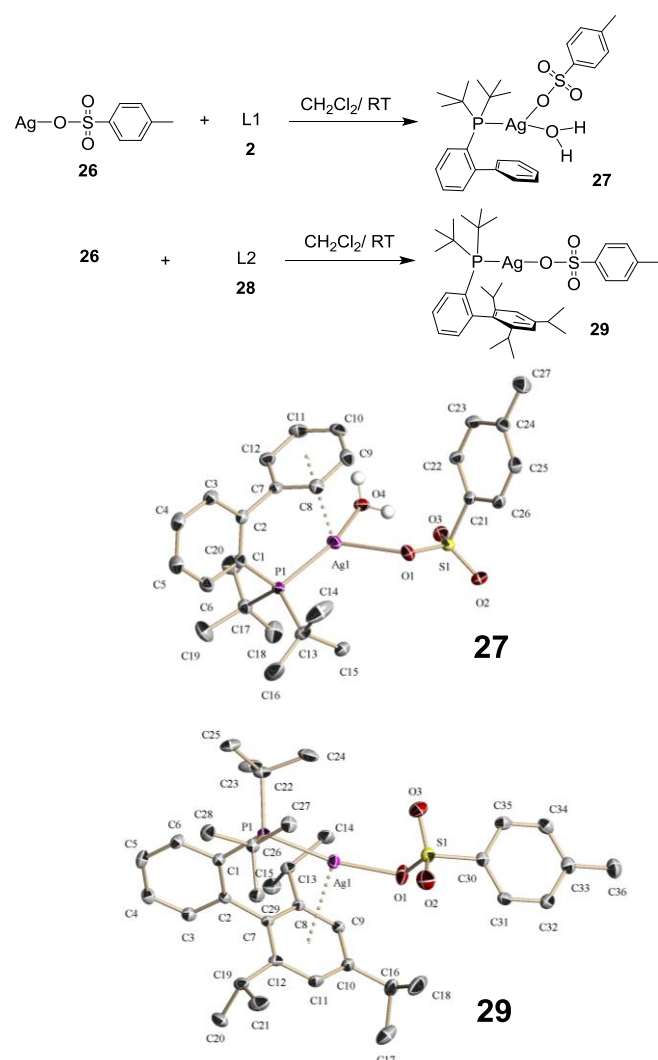
Bis-propargylamine compound **22** was isolated and characterized by ¹H, ¹³C and DEPT NMR spectroscopy (see Figs. S38-S40 in the Supporting Information). GC-MS data obtained dissolving **22** (C₂₀H₂₄N₂) in CH₂Cl₂ show a peak at 292.19 Da in agreement with the expected molecular formula (see Fig. S41 in the supporting information). Besides bis-propargylamine **22** as final product, formation of mono propargylamine **21** (C₁₅H₁₅N) was observed as primary product from the mono A³ coupling and characterized by GC-MS data showing a peak at 209.2 Da in agreement with the expected molecular formula (see Figs. S42 in the supporting information). A plausible mechanism for the double -A³ coupling leading to **22** would be similar to that previous reported^[13] for analogous cationic copper (I) complexes as catalyst (see Fig. S43 in the supporting information).

To show the generality of the use of the this new cationic Ag (I) **11** complex as catalyst, double A³ coupling of aliphatic 1,6-heptadiyne (**23**) was also tested (Table 2) in the optimized conditions. The expected bis-propargylamine **25** was obtained as final product in good yield and excellent selectivity (see Table 2, entries 4, 5). As expected the mono propargylamine **24** was also observed as primary reaction product. Bis-propargylamine **25** was isolated as light-yellow oil and characterized by ¹H, ¹³C and DEPT NMR spectroscopy (see Figs. S44-S46 in the Supporting Information). GC-MS data obtained dissolving **25** (C₁₇H₂₆N₂) in CH₂Cl₂ show a peak at 258.2 Da in agreement with the expected molecular formula (see Fig. S47 in the supporting information). The ¹H NMR spectrum of **25** shows a coupling between the two CH₂ groups across the C≡C bond appearing at 3.25 (triplet) and 2.24 (triplet of triplet) ppm with ⁴J = 2.20 Hz (see Experimental Section and Fig. S44). On the other hand, mono propargylamine compound **24** (C₁₂H₁₇N) (see Scheme in Table 2) was characterized by GC-MS data showing a peak at 174.1 Da in agreement with the expected molecular formula (see Fig. S48 in the supporting information).

To expand the scope of cationic silver (I) complexes as catalyst and with the aim to confirm the lower activity of the neutral related complexes, neutral (phosphine)silver (I) organosulfonate complexes [(L1)AgX] (**27**) and [(L2)AgX] (**29**) were prepared. A stoichiometric (1:1) mixture of silver (I) p-tolylsulfonate **26** and L1 (**2**) or L2 (**28**) was stirred for 24 h at room temperature in CH₂Cl₂ (Scheme 8, top), followed by the subsequent careful addition of a layer of n-hexane over the resulting transparent solutions and, then, kept at -30 °C for 48 h. This procedure afforded, respectively, colourless crystals of complexes **27** and **29** in 92 % yield each (see experimental section). The structures of these stable neutral silver (I) complexes **27** and **29** could be resolved by single-crystal X-ray crystallography (Scheme 2, Bottom for ORTEPs and Tables S7 and S8 and Figs. S53 and S59 for single-crystal X-ray data and crystal packing details in the supporting information).

The neutral silver (I) complexes **27** and **29** were also characterized by combustion elemental analysis, NMR spectroscopy and ESI-MS (see the experimental section and Figs. S49-S54 for **27** and Figs. S55-S60 for **29** in the supporting information). ¹H, ¹³C, Dept and ³¹P NMR spectroscopy of solutions in CD₂Cl₂ provided evidence that the starting silver (I) p-tolylsulfonate (**26**) was completely converted into **27** or **29** (see Figs. S49-S52 for **27** and Figs. S55-S58 for **29** in the supporting information). Thus, the formation of a Ag-P bond in these complexes **27** and **29** was confirmed by the appearance in ³¹P NMR spectroscopy as two doublets due to coupling of ³¹P with the two silver isotopes of spin ½ (¹⁰⁷Ag and ¹⁰⁹Ag), respectively, at 43.93 ppm with ¹J(¹⁰⁷Ag-³¹P) = 695.07 Hz, ¹J(¹⁰⁹Ag-³¹P) = 802.18 Hz for **27** (Fig. S50 in the supporting information) and at 42.09 ppm with ¹J(¹⁰⁷Ag-³¹P) = 685.33 Hz, ¹J(¹⁰⁹Ag-³¹P) = 791.34 Hz for **29** (Fig. S56 in the supporting information). These coupling constants became smaller in the case of complex **29** with a bulky 2-di-tert-butylphosphanyl(2',4',6'-triisopropyl)biphenyl (L2) compared to the coupling constants of complex **27** with a less bulky 2-di-tert-butylphosphanylbiphenyl (L1) (Scheme 8). Formation of the neutral Ag(I) complexes **27**

and **29** was also confirmed by ESI-MS spectroscopy (For details see Fig. S54 for **27** and Fig. S60 for **29** in the supporting information).



Scheme 8. Top: Synthesis of neutral L1-Ag-(p-tolylsulfonate)(H₂O) **27** and L2-Ag-(p-tolylsulfonate) **29** silver (I) complexes. Bottom: ORTEP views of **27** and **29**; ellipsoids are given at the 30 % probability level (C-H hydrogen atoms are omitted for clarity. (single-crystal X-ray data and crystal packing details are given in Table S7 and Fig. S53 for **27** and Table S8 and Fig. S59 for **29** in the supporting information).

Analysis of the solid state structures of neutral Ag (I) complexes L1-Ag-(p-tolylsulfonate)(H₂O) **27** and L2-Ag-(p-tolylsulfonate) **29** reveals the presence of one crystallization CH_2Cl_2 molecule and an additional water co-ligand in the case of L1-Ag(I)-(H₂O)X (**27**) complex having less bulky phosphine ligand (L1) in position trans to the P atom with an P1-Ag1-O4(water) angle of 146.71 (5) ° (Scheme; third row). In the case of L2-Ag(I)-X (**29**) complex with more bulky phosphine ligand L2 no water co-ligand exists and the p-tolylsulfonate (X) is in trans position with an angle P1-

Ag1-O1(X) of 164.42 (6) ° (Scheme 8: Bottom). Selected bond lengths for Ag-O, Ag-P, Ag-C(7)_{ipso} and between Ag and the closest carbon atom (C8) of the distal phenyl ring for complex **27** (Table S7 and Fig. S53 in the supporting information) are 2.2652(18) (water) and 2.4722(18) (p-tolylsulfonate), 2.3798(6), 2.963 and 2.852(3) Å, respectively, compared to the Ag-O, Ag-P, Ag-C(7)_{ipso} bonds lengths and the distance between Ag and the closest carbon atom (C8) of the distal phenyl ring for complex **29** (Table S8 and Fig. S59 in the supporting information) that are 2.140(2), 2.3637(7), 3.029 and 2.834(3) Å, respectively.

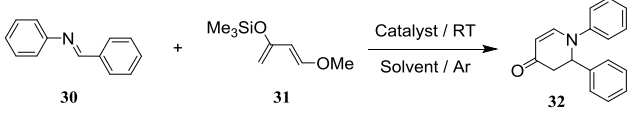
The catalytic activity of these new neutral silver (I) complexes **27** and **29** for the single Mannich A³ coupling was tested under the same condition as complex **11**, but using different solvent, confirming again that the choice of a suitable reaction solvent is crucial for the success of the process. When dioxane or CH_2Cl_2 are used instead of toluene as solvents, neutral complexes **27** and **29** become very active promoting the formation of the propargylamine **16** with very good yield and selectivity (see Table 1, entries 11-14). This high activity in dioxane or CH_2Cl_2 instead of toluene can be explained by their higher ability to dissolve the Ag (I) complexes and also with the principles of hard-soft acid-base theory, where polar solvents should make easier dissociation of sulfonate complexes L-Ag-X affording cationic [LAg]⁺ complex which is probably the catalytically active species.

It has been reported that the aza-Diels-Alder cycloaddition of Danishefsky's dienes with imines proceeds efficiently in water in the presence of substoichiometric amount of silver (I) benzenesulfonate (10 %).^[6] Aimed at developing a robust catalyst for this transformation and to shed some light into the mechanism of this catalytic reaction by isolation of possible intermediates, the catalytic activity of neutral L1Ag(p-tolylsulfonate)(H₂O) **27** and L2Ag(p-tolylsulfonate) **29** (Table 1) was tested. It was observed that complexes **27** and **29** even in lesser amounts (6 %) were considerably more active than silver benzenesulfonate. This higher activity can be attributed to the higher stability of complexes **27** and **29** provided by the bulky phosphine ligands.

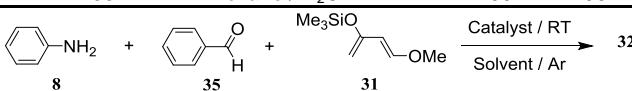
In the catalytic tests, neutral L2-Ag-(p-tolylsulfonate) **29** complex was found to be inactive as catalyst in CH_2Cl_2 or dioxane as solvent (Table 3, entries 1, 2), while in presence of mixture of dioxane/water (3/1) the reaction took place in short time (1 h) to give the corresponding 1,2-diphenyl-2,3-dihydro-4-pyridone (**32**)^[6, 12] in high yield and selectivity (Table 3, entry 3). Compound **32** was characterized by NMR and GC-MS spectroscopies (Figs. S61-S64 in the supporting information). Similarly, using neutral L1-Ag-(p-tolylsulfonate)(H₂O) **27** as catalyst under the same optimized conditions, high activation was also observed (Table 3, entry 4). For the sake of comparison, the catalytic activity of cationic Ag (I) complex **10** (L1-aniline-Ag^I) was also evaluated under these optimised conditions, observing the formation of pyridone **32** in slightly lower yield, accompanied with small amounts of aniline and benzaldehyde as byproducts resulting from the hydrolysis of starting imine **30** (Table 3, entry 5). When CH_2Cl_2 is used as solvent instead of dioxane under the same conditions, a very low conversion and yield were achieved (Table 3, entry 6). Also it

was observed that the mixture THF/H₂O is not a suitable medium since additional isomeric by-products (GC-MS: 130 Da) by reaction of THF with Danishefsky's diene (**31**) are formed.

Table 3. Aza-Diels-Alder cycloaddition of imine (**30**) and Danishefsky's diene (**31**) promoted by neutral (**27**, **29**) and cationic (**10**) Ag(I) complexes as catalysts (6 mol %).^[a]



entry	Catalyst	Solvent / H ₂ O (3/1)	Time (h)	Conv. (%) ^[b]	Yield (%) ^[b]
1	29	CH ₂ Cl ₂ / none	2	0	-
2	29	Dioxane / none	2	0	-
3	29	Dioxane / H ₂ O	1	99	94
4	27	Dioxane / H ₂ O	1	97	91
5	10	Dioxane / H ₂ O	1	94	80 ^[c]
6	10	CH ₂ Cl ₂ / H ₂ O	1	8	5
7	33	Dioxane / H ₂ O	1	99	96

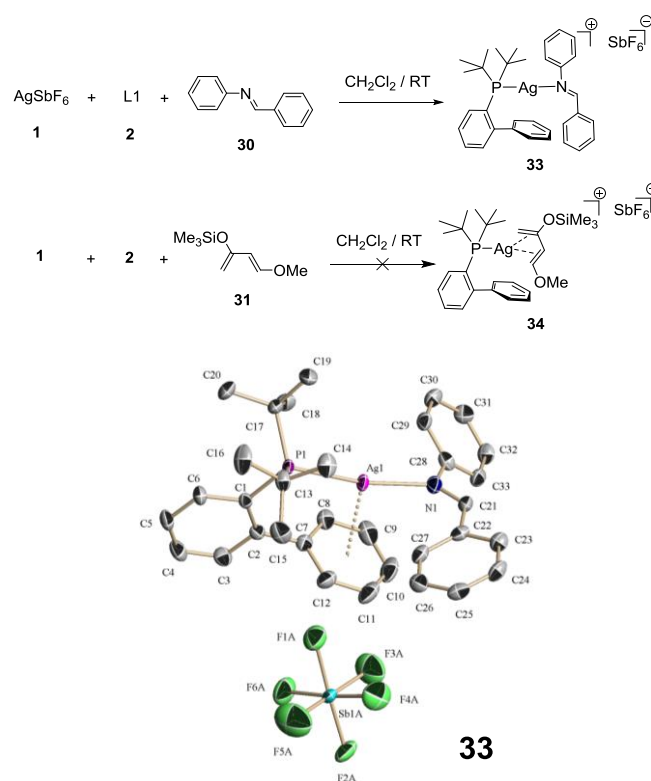


8	29	Dioxane / H ₂ O	1	99 ^[d]	50 ^[e]
9	10	Dioxane / H ₂ O	1	98 ^[d]	45 ^[e]
10	10 ^[f]	Dioxane / H ₂ O	1	98 ^[d]	86
11	33 ^[f]	Dioxane / H ₂ O	1	99 ^[d]	91
12	29 ^[f]	Dioxane / H ₂ O	1	99 ^[d]	93
13	27 ^[f]	Dioxane / H ₂ O	1	98 ^[d]	92

[a] All reactions were carried out using 0.25 mmol of imine, 0.3 mmol of Danishefsky's diene (**31**) and solvent (1.5 ml) / H₂O (0.5 ml). [b] Conversion of **30** and yield of **32** were determined by ¹H NMR spectroscopy and GC of the crude reaction mixture. [c] 7 % of aniline and 5 % of benzaldehyde are also observed. [d] Conversions of **8** determined by GC of the reaction mixture. [e] About 20 % of an unknown product with a molecular peak at 161 Da is also observed (see Fig. S57 for GC-MS data). [f] Slow addition of Danishefsky's diene (**31**) to the mixture of aniline **8** and benzaldehyde **35** over 50 min.

When the reagents of this aza-Diels-Alder cycloaddition imine (**30**) and Danishefsky's diene (**31**) were mixed with a stoichiometric amount of **1** and **2**, and then the mixture stirred for 16 h at room temperature in CH₂Cl₂ (Scheme 9), transparent solutions were obtained. In a first trial (Scheme 9, top), a layer of n-hexane was carefully added, followed by standing the mixture at -30 °C. Under these conditions colourless crystals of complex **33** were obtained in 93 % yield (see experimental section). A second experiment was aimed to isolate the silver (I)-Danishefsky's diene (**31**) (Scheme 9, middle) from the resulting yellow-red solution. However, the trial was unsuccessful and a mixture of cationic aquo-Ag^I-L1 complex **4** (see the Experimental Section, Table S1 and Figs. S3-S6 in the supporting information) and yellow-red oil that can be separated by crystallization was obtained. The [L1Ag(imine)][SbF₆] complex **33** corresponding to the complex of the Ag(I) precatalyst with the imine **30** compound was isolated and characterized on the basis of analytical and spectroscopic data (see experimental details, Figs. S65-S70, and Table S9 in the supporting information for X-ray data and crystal packing details). Combustion elemental analysis of

complex **33** was in accordance with the percentages expected for its formula. Single crystals of complex **33** of sufficient quality for X-ray crystallography studies could be obtained. Selected bond lengths for Ag(1)-N(1), Ag(1)-P(1), Ag(1)-C(7)_{ipso} and the distance between Ag and closest carbon atom (C8) of the distal phenyl ring for complex **33** are 2.180(4), 2.3669(11), 2.929 and 3.006 Å, respectively. These values are close to those determined in complexes [L1Ag(pyrrolidine)][SbF₆] (**11**) and [L1Ag(propylamine)][SbF₆] (**17**), indicating that the imine (**30**) ligand is labile, allowing operation of turnovers through the intermediary of the complex [L1Ag(imine)][SbF₆] (**33**). ORTEP view of the Ag^I complex **33** is shown in Scheme 9 (bottom) (see experimental section and Table S9 and Fig. S69 in the supporting information).



Scheme 9. Top: Synthesis of cationic silver (I) [L1Ag(imine)][SbF₆] complex **33**. Middle: Failure to isolate silver complex **34**. Bottom: ORTEP view of **33**; ellipsoids are given at the 30 % probability level (C-H hydrogen atoms are omitted for clarity). (single-crystal X-ray data and crystal packing are given in Table S9 and Fig. S69 in the supporting information).

The new cationic silver (I) complex **33** was characterized by NMR spectroscopy and ESI-MS (see the experimental section and Figs. S65-S68 and S70 in the supporting information). ¹H, ¹³C, Dept and ³¹P NMR spectroscopy of solutions in CD₂Cl₂ provided evidence that the starting AgSbF₆ (**1**) salt was completely converted into **33** by coordination of both starting free ligands phosphine (**2**) and imine (**30**) (see Figs. S65-S68 in the supporting information). Thus, the formation of a Ag-P bond in complex **33** was confirmed by the appearance of ³¹P NMR

spectra of two doublets due to coupling in the ^{31}P with the two silver isotopes of spin $\frac{1}{2}$ (^{107}Ag and ^{109}Ag) at 46.03 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) = 634.08$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 732.02$ Hz (Fig. S66 in the supporting information). Similarly, ^1H NMR spectroscopy showed new signals for the methyl groups of complex **33** at 1.29 and 1.24 ppm (Fig. S65 in the supporting information) instead of those corresponding to the initial phosphine ligand **2** at 1.11 and 1.07 ppm. ESI-MS of a solution obtained after dissolving complex **33** in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1/1) shows mainly a cluster of ions with major positive peaks at 586.2 and 588.2 Da attributable to cationic Ag (I) complex with the ^{107}Ag and ^{109}Ag isotope of $[\text{C}_{33}\text{H}_{37}\text{AgF}_6\text{NPSb}(\mathbf{33}) - \text{SbF}_6]^+$.

The measured mass distribution was in good agreement with the simulated isotopic distribution for $[\text{C}_{33}\text{H}_{38}\text{AgNP}]^+$ (see details in Fig. S70 (Top) in the supporting information). Other smaller cluster of ions with major positive peaks at 847.2 and 849.1 Da attributable to cationic Ag(I) complex $[\text{C}_{66}\text{H}_{74}\text{Ag}_2\text{F}_{12}\text{N}_2\text{P}_2\text{Sb}_2(\mathbf{33})_2 - (\text{SbF}_6)_2 - (\text{Imine})_2 + \text{Cl}]^+$ with the ^{107}Ag and ^{109}Ag isotope (see Fig. S70 (Bottom) for details in supporting information) were observed suggesting that under these conditions some CH_2Cl_2 was reacted, releasing chloride that reacted to form some neutral dichloride-bridged disilver (I) complex $[\{\text{L1-Ag}(\mu\text{-Cl})\}_2]$ **18** characterized previously. When a one chlorine atom lost from **18**, the major positive MS peaks appear at 847.2 and 849.1 Da (see detailed fragmentation of this cluster of peaks in Fig. S70 (Bottom) in the supporting information). Finally the catalytic activity of the cationic silver (I) complex **33** for the two-component aza-Diels-Alder reaction (Table 3, entry 7) was as high as that of the initial Ag (I) precatalyst complexes **29**, **27** or **10**.

Besides imine **30** a mixture of aniline **8** and benzaldehyde **35** was used as substrate, instead of imine **30**, to react with the Danishefsky's diene (**31**) in one tandem three coupling version of the aza-Diels-Alder reaction catalysed by 6 % of neutral L2-Ag-(p-tolylsulfonate) **29** or cationic L1-aniline-Ag^I (**10**) silver (I) complexes in dioxane/water (3/1) under optimized condition [Table 3, Scheme (Middle)]. Under these conditions 50 (Table 3, entry 8) and 45 % (Table 3, entry 9) of 1,2-diphenyl-2,3-dihydro-4-pyridone (**32**) was formed using **29** and **10** as catalysts, respectively, an unknown product with molecular mass at 161 Da (see Fig. S71 for GC-MS data in the supporting information) was also detected. This unknown by product was present even when all imine **30** formed in situ reacted totally (see Fig. S72 for GC-MS data of imine **30** in the supporting information). However, slow addition of Danishefsky's diene (**31**) to the mixture of aniline **8** and benzaldehyde **35** over 50 min using as catalyst cationic **10**, **33** or neutral **29** and **27** silver (I) complexes improved the yield for this three-component reaction reading values that were comparable to that of the two-component catalytic reaction (see Table 3, entries 10-13).

An alternative catalytic experiment was carried out, in which 15 mol % of silver (I) complex **7** was added to aniline (**8**) at RT and, after 1 h, the mixture was analysed by ^{31}P NMR spectroscopy showing the presence of two doublets of ^{31}P with chemical shift 47.35 ppm and $^1J(^{107}\text{Ag}-^{31}\text{P}) = 639.17$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 738.97$ Hz characteristic of (L1-aniline-Ag^I) complex **10** instead of two doublets of ^{31}P with 45.59 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) =$

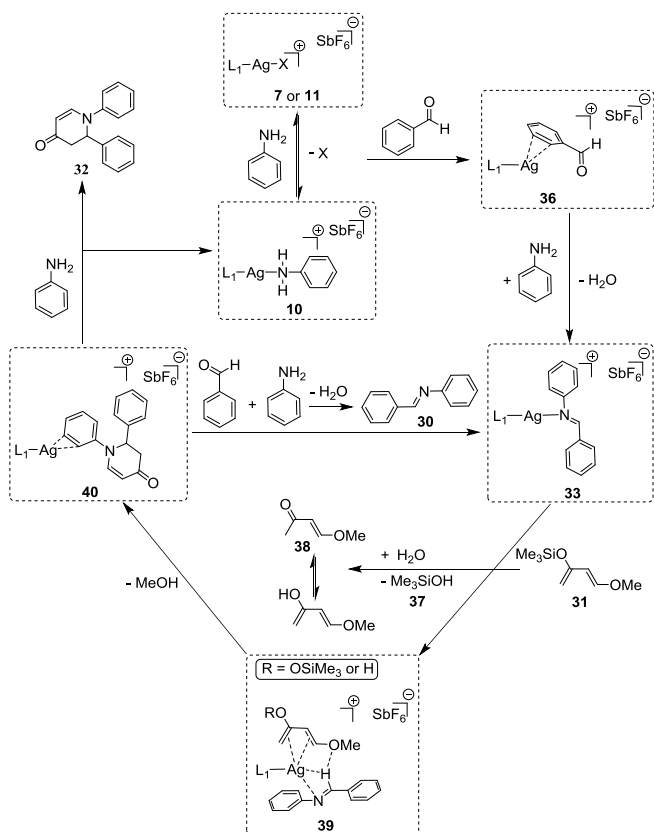
691.53 Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 798.39$ Hz characteristic of (L1-toluene-Ag^I) complex **7** (see Figs. S73 and S9 in the supporting information). At this time an excess of benzaldehyde (**35**, 1.5 equiv) with respect to the starting aniline (**8**) was added at RT and, after 1 h, the ^{31}P NMR spectrum was recorded again. It was observed that complex **10** (dd, 47.35 ppm) was completely consumed and complex (L1-imine-Ag^I) **33** was formed based on the presence of two doublets of ^{31}P with 46.03 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) = 634.08$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 732.02$ Hz (see Fig. S74 in the supporting information). After observation of the complete formation of **33**, at RT an excess of Danishefsky's diene (**31**, 2 equiv) with respect to the starting aniline (**8**) was added and, after 30 min, the ^{31}P NMR spectrum was recorded again. It was observed that complex **33** (dd, 46.03 ppm) was totally consumed and two new doublets of ^{31}P with 47.21 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) = 671.09$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 773.94$ Hz, attributable to presumed (L1-dihydropyridin-4-one-Ag^I) complex **40** appear together with two doublet signals of (L1-aniline-Ag^I) complex **10** (Fig. S75 in the supporting information). For detailed measurements of these coupling constants see respectively Figs. S76 and S77 in the supporting information). Over the time (2 h), the peaks corresponding to **40** and **10** were consumed with the concomitant formation of 1,2-diphenyl-2,3-dihydro-4-pyridone (**32**). At final reaction time the only silver (I) complex present in the mixture was the cationic aquo-silver (I) complex **4** as confirmed by the appearance in the ^{31}P NMR spectra of two doublets at 46.08 ppm with $^1J(^{107}\text{Ag}-^{31}\text{P}) = 714.28$ Hz and $^1J(^{109}\text{Ag}-^{31}\text{P}) = 824.42$ Hz (see Fig. S78 in the supporting information) due to the conditions for this experiment in dioxane/water (3/1), in which excess of Danishefsky's diene (**31**, 2 equiv) and benzaldehyde (**35**, 1.5 equiv) versus aniline (**8**) was used.

According to these experimental results, a reaction mechanism for the three coupling with $[\text{Ag}(\text{L1})(\text{toluene})][\text{SbF}_6]$ (**7**) or $[\text{Ag}(\text{L1})(\text{pyrrolidine})][\text{SbF}_6]$ (**11**) as precatalysts in dioxane/water (3/1) is proposed (Scheme 10). The main point of this mechanism is the coordination of Ag (I) complexes **7** or **11** with aniline (**8**) leading to the isolated intermediate $[\text{Ag}(\text{L1})(\text{aniline})][\text{SbF}_6]$ (**10**) and the presumed formation of π -complex intermediate (**36**) between silver and benzaldehyde (**35**).^[17] The condensation between benzaldehyde and aniline takes place leading to the formation of isolated silver (I) imine complex **33** and the release of one molecule of water. The partial hydrolysis of Danishefsky's diene (**31**) leads to the formation of trimethylsilanol (**37**) and 4-methoxy-3-buten-2-one (**38**) that could be characterized by GC-MS (see Fig. S79 for **37** and Fig. S80 for **38** in the supporting information). The presumed formation of π -complex intermediate (**39**) between silver (I) complex **33** and silyl enol ether (**31**) followed by cyclisation of the six membered ring would lead to the formation of intermediate L1-dihydropyridin-4-one-Ag^I complex **40** (see Scheme 10 and Fig. S75 for NMR spectra experiment in the supporting information). Release of 1,2-diphenyl-2,3-dihydro-4-pyridone (**32**) from the coordination sphere of the metal ion by replacement with free aniline (**8**) or imine (**30**) (see Fig. S41 for GC-MS characterization of **30** in the supporting information) will initiate a new catalytic cycle.

Experimental Section

General

Experimental Details of preparation, isolation and full characterization of silver (I) complexes **4** and **7**;^[3] new silver (I) complexes **10**, **11**, **17**, **18**, **27**, **29** and **33**; phosphonium salt **5**; mono- **16**, **21**, **24** and bis- **22**, **25** propargylamines compounds; as well as compound **32**,^[12] including NMR spectroscopy, ESI-MS, GC-MS spectra, combustion analysis and single-crystal X-ray crystallography data are provided in the supporting information. CCDC-1414010 (**4**), 1414011 (**7**), 1414012 (**10**), 1414013 (**11**), 1414014 (**17**), 1414015 (**18**), 1414016 (**27**), 1414017 (**29**) and 1414018 (**33**) contain the supplementary crystallographic data for this paper. These data can also be obtained free of charge from The Cambridge Crystallographic Data centre via http://www.ccdc.cam.ac.uk/data_request/cif. All reactions were carried out under Ar atmosphere in dried solvent using a commercial solvent purification system. ¹H NMR spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts of ¹H signals are reported in ppm using the solvent peak as the internal standard (CH₂Cl₂: 5.27 ppm). Data are reported as follows: chemical shift, integral, multiplicity (s = singlet, br = broad, d = doublet, dd = doublet of doublets, t = triplet, tt = triplet of triplets, sept = septuplet, m = multiplet), coupling constants (Hz) and assignment. Chemical shifts of ¹³C are reported also in ppm using the solvent peak as the internal standard (CD₂Cl₂: 53.84 ppm). ³¹P spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts are reported in ppm and coupling constants in Hz. Gas chromatography (GC) was performed in a Varian 3900 apparatus equipped with an TRB-5MS column (5% phenyl, 95% polymethylsiloxane, 30 m, 0.25 mm x 0.25 μm, Teknokroma). GC-MS analyses were performed on an Agilent spectrometer (5973N-6890N) equipped with the same column as the GC and operated under the same conditions. ESI-MS were performed on an Agilent Esquire 6000 instrument. Elemental analyses were performed on an EuroEA Elemental Analyser Eurovector.



Scheme 10. Mechanistic proposal for the three-coupling aza-Diels-Alder cycloaddition leading to 1,2-diphenyl-2,3-dihydro-4-pyridone (**32**) using as precatalyst cationic Ag (I) complexes **7** or **11** in dioxane/water (1/1). Intermediates silver (I) complexes **10** and **33** have been isolated, compounds **37** and **38** have been characterized and intermediates silver (I) complexes **36**, **39** and **40** are proposed.

Conclusions

The present study provides an easy access to a series of cationic and neutral silver (I) complexes with Buchwald-type phosphane ligands and an additional ligand exhibiting varied electronic and steric properties. These cationic and neutral silver (I) complexes exhibit higher activity than analogous copper (I) and gold (I) complexes as catalyst for the single and double Mannich A³-coupling and aza-Diels-Alder two and three - coupling reactions. A strong influence of the solvent on the performance attributable to their limited complex solubility or decomposition has been observed. Isolation of some silver (I) complexes that are likely to be reaction intermediates has allowed shedding light on the reaction mechanism and understanding the different stability of Ag (I) compared to Cu (I) and Au (I). The mechanism of A³ couplings using Ag (I) complexes as catalysts presents similarities to that of Cu (I) and differences with Au (I).

Isolation of cationic [Ag(L1)(H₂O)][SbF₆] complex (**4**)

A mixture of [Ag]⁺[SbF₆]⁻ (**1**) salt (0.086 g, 0.25 mmol) and 2-di-tert-butylphosphinobiphenyl (L1) (**2**) (0.075 g, 0.25 mmol) was dissolved in dried-dichloromethane (2 ml). The solution was stirred at RT under argon atmosphere for 8 h. Then, the solvent was removed under reduced pressure. Followed by crystallization in a mixture of non-dried dichloromethane/n-hexane (1/3) at -30 °C for 24 h. Silver(I)(2-biphenyl)di-tert-butylphosphane-water hexafluoroantimonate complex (**4**) was collected (0.139 g, 84 % yield) as colourless crystals suitable for X-ray crystallography (see Table S1 and Fig. S6 for details). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 7.88 (t, 1 H; ArH); 7.66-7.44 (m, 5 H; ArH), 7.35-7.16 (m, 3 H; ArH), 2.80 (br, 2 H; H₂O), 1.29 (s, 9 H; *tert*-butyl CH₃), 1.24 (s, 9 H; *tert*-butyl CH₃) (see Fig. S3 for details). ³¹P NMR (CD₂Cl₂): δ (ppm) = 46.08 (dd, ¹J(¹⁰⁷Ag-³¹P) = 714.28 Hz and ¹J(¹⁰⁹Ag-³¹P) = 824.42 Hz). (see Fig. S4 for details). ESI-MS (+MS) *m/z* 463.1 amu for [C₂₀H₂₈AgF₆OPSb (**4**) - SbF₆⁻ + K]⁺ and 405.1 amu for [C₂₀H₂₈AgF₆OPSb (**4**) - SbF₆⁻ - H₂O]⁺ with the ¹⁰⁷Ag and ¹⁰⁹Ag isotopos (see Fig. S5 for details). ESI-MS (-MS) *m/z* 234.9 and 236.7 amu for counter anion [SbF₆]⁻ of complex **4** with the ¹²¹Sb and ¹²³Sb isotopos. Elemental analysis, calc. for C₂₀H₂₈AgF₆OPSb (**4**) (%): C, 36.45; H, 4.28. Found: C, 36.56; H, 4.35.

Isolation of cationic [Ag(L1)(H₂O)][SbF₆] complex (**7**)

A mixture of $[\text{Ag}]^+[\text{SbF}_6]^-$ (**1**) salt (0.086 g, 0.25 mmol) and 2-di-tert-butylphosphinobiphenyl (L1) (**2**) (0.075 g, 0.25 mmol) was dissolved in dried-dichloromethane (2 ml). The solution was stirred at RT under argon atmosphere for 8 h. Then, the solvent was removed under reduced pressure. Followed by crystallization in a mixture of dried-dichloromethane/toluene (1/2) at RT for 48 h. Silver(I)(2-biphenyl)di-tert-butylphosphane-toluene hexafluoroantimonate complex (**7**) was collected (0.162 g, 88 % yield) as colourless crystals suitable for X-ray crystallography (see Table S2 and Fig. S7 for details). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.85 (t, 1 H; ArH); 7.70-7.45 (m, 5 H; ArH), 7.35-7.00 (m, 7 H; ArH), 2.30 (s, 3 H; CH_3 of toluene), 1.23 (s, 9 H; *tert*-butyl CH_3), 1.17 (s, 9 H; *tert*-butyl CH_3) (see Fig. S8 for details). ^{31}P NMR (CD_2Cl_2): δ (ppm) = 45.59 (dd, $^1J(^{107}\text{Ag}-^{31}\text{P}) = 691.531$ Hz and $^1J(^{109}\text{Ag}-^{31}\text{P}) = 798.389$ Hz). (see Fig. S9 for details). Elemental analysis, calc. for $\text{C}_{27}\text{H}_{35}\text{AgF}_6\text{P}_2\text{Sb}$ (**7**) (%): C, 44.17; H, 4.81. Found: C, 44.33; H, 4.90.

Isolation of cationic $[\text{Ag}(\text{L1})(\text{H}_2\text{NPh})][\text{SbF}_6]$ complex (**10**)

A mixture of $[\text{Ag}]^+[\text{SbF}_6]^-$ (**1**) salt (0.086 g, 0.25 mmol) and 2-di-tert-butylphosphinobiphenyl (L1) (**2**) (0.075 g, 0.25 mmol) and aniline (**8**) (0.025 g, 0.27 mmol) was dissolved in dichloromethane (2 ml). The solution was stirred at RT for 18 h under argon atmosphere. Then, the resulting mixture was diluted with additional 2 ml of CH_2Cl_2 , filtered and the supernatant was covered carefully with a layer of 2 ml of n-pentane. Colourless crystals of **10** suitable for X-ray crystallography (see Table S3 and Fig. S10 for details) were obtained by standing for 48 h at -30 °C, which were collected by filtration, washed with cold n-pentane and dried under vacuum to yield the corresponding complex silver(I)(2-biphenyl)di-tert-butylphosphane-aniline hexafluoroantimonate (**10**) (0.164 g, 89 % yield). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.85 (t, 1 H; ArH); 7.62-7.40 (m, 5 H; ArH); 7.38-7.14 (m, 5 H; ArH), 7.02 (t, 1 H; ArH), 6.93-6.81 (m, 2 H; ArH), 4.20 (s, 2 H; H_2NPh), 1.20 (s, 9 H; *tert*-butyl CH_3), 1.15 (s, 9 H; *tert*-butyl CH_3) (see Fig. S11 for details). ^{31}P NMR (CD_2Cl_2): δ (ppm) = 47.35 (dd, $^1J(^{107}\text{Ag}-^{31}\text{P}) = 639.171$ Hz and $^1J(^{109}\text{Ag}-^{31}\text{P}) = 738.974$ Hz). (see Fig. S12 for details). ^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) = 149.45 (d), 149.20 (d), 143.03 (d), 142.91 (d), 141.81, 134.10 (d), 132.49 (d), 131.38 (d), 130.12, 129.99, 129.46, 128.15 (two ds), 127.90, 126.73 (d), 126.33 (d), 124.56, 119.89, 35.65 (d), 35.46 (d), 30.88 (d), 30.75 (d) (see Fig. S13 for details). ^{13}C Dept-135 NMR (75 MHz, CD_2Cl_2): δ (ppm) = Negative Signals: none; Positive Signals: 134.10 (d), 132.49 (d), 131.38 (d), 130.12, 129.99, 129.47, 128.15 (d), 127.90, 124.56, 119.89, 30.88 (d), 30.75 (d) (see fig. S14). ESI-MS (+MS) m/z 405.1 and 407.1 amu for $[\text{C}_{26}\text{H}_{33}\text{AgF}_6\text{NPSb}(\text{10}) - \text{SbF}_6]^-$ and - aniline] $^+$ and 437.2 amu for $[\text{C}_{26}\text{H}_{33}\text{AgF}_6\text{NPSb}(\text{10}) - \text{SbF}_6]^-$ - aniline and + $\text{MeOH}]^+$ with the ^{107}Ag and ^{109}Ag isotopos (see Fig. S15 for details). ESI-MS (-MS) m/z 234.9 and 236.7 amu for counter anion $[\text{SbF}_6]^-$ of complex **10** with the ^{121}Sb and ^{123}Sb isotopos (see Fig. S15 for details). Elemental analysis, calc. for $\text{C}_{26}\text{H}_{33}\text{AgF}_6\text{NPSb}$ (**10**) (%): C, 42.54; H, 4.53; N, 1.91. Found: C, 42.76; H, 4.80; N, 2.1.

Isolation of cationic $[\text{Ag}(\text{L1})(\text{pyrrolidine})][\text{SbF}_6]$ complex (**11**)

A mixture of $[\text{Ag}]^+[\text{SbF}_6]^-$ (**1**) salt (0.086 g, 0.25 mmol) and 2-di-tert-butylphosphinobiphenyl (L1) (**2**) (0.075 g, 0.25 mmol) and pyrrolidine (**9**) (0.019 g, 0.27 mmol) was suspended in toluene (2 ml). The solution was stirred at RT for 18 h under argon atmosphere. Then, the precipitate formed in the resulting mixture was dissolved by adding 2 ml of dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$), filtered and then a layer of n-pentane was carefully added. Colourless crystals of **11** suitable for X-ray

crystallography (see Table S4 and Fig. S16 for details) were obtained by slow evaporation at RT, which were collected by filtration, washed with cold n-pentane and dried under vacuum to yield the corresponding complex silver(I)(2-biphenyl)di-tert-butylphosphane-pyrrolidine hexafluoroantimonate (**11**) (0.163 g, 91 % yield). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.87 (t, 1 H; ArH); 7.64-7.46 (m, 5 H; ArH); 7.30-7.18 (m, 3 H; ArH), 2.82 (m, 4 H; CH_2 -pyrrolidine), 2.34 (br, 1 H; NH -pyrrolidine), 1.71 (m, 4 H; CH_2 -pyrrolidine), 1.29 (s, 9 H; *tert*-butyl CH_3), 1.24 (s, 9 H; *tert*-butyl CH_3) (see Fig. S17 for details). ^{31}P NMR (CD_2Cl_2): δ (ppm) = 45.50 (dd, $^1J(^{107}\text{Ag}-^{31}\text{P}) = 608.486$ Hz and $^1J(^{109}\text{Ag}-^{31}\text{P}) = 701.649$ Hz). (see Fig. S18 for details). ^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) = 149.55 (d), 149.30 (d), 142.85 (d), 142.73 (d), 134.09 (d), 132.49 (d), 131.44 (d), 129.77, 129.54, 128.20, 128.13 (d), 126.49 (d), 126.08 (d), 50.95, 35.67 (d), 35.51 (d), 31.11 (d), 30.98 (d), 24.45 (see Fig. S19 for details). ^{13}C Dept-135 NMR (75 MHz, CD_2Cl_2): δ (ppm) = Negative Signals: 50.95 and 24.45 for (CH_2 , pyrrolidine); Positive Signals: 134.10 (d), 132.49 (d), 131.44 (d), 129.77, 129.54, 128.20, 128.14 (d), 50.95, 31.11 (d), 30.98 (d), 24.45 (see fig. S20). Elemental analysis, calc. for $\text{C}_{24}\text{H}_{36}\text{AgF}_6\text{NPSb}$ (**11**) (%): C, 40.42; H, 5.29; N, 1.96. Found: C, 40.60; H, 5.51; N, 2.03.

General Procedure for single Mannich A³-Coupling

Preparation of propargylamine (16): A mixture of phenylacetylene (0.25 mmol), pyrrolidine (0.35 mmol), formaldehyde (aq. 37%, 0.7 mmol) and silver(I) complexes **7**, **10**, **11**, **17**, **27** or **29** (0.015 mmol) as catalyst (Ag/alkynes ratio 6 mol%) was suspended in toluene or CH_2Cl_2 (1 ml). Then the flask was evacuated under vacuum and refilled with argon. The evacuation/refilling cycle was repeated three times (pressure 2 bar). The mixture was stirred at RT for 3-6 min to obtain the maximum yield of **16** (see Table 1). Then, cold n-hexane was added to the cold reaction mixture, filtered and the solvents were removed under reduced pressure at 50 °C to provide propargylamine **16** 98 % in yield as light-yellow oil. The structure and purity of propargylamine **16** was confirmed by ^1H , ^{13}C -NMR spectroscopy and GC-MS analysis:

Compound **16**: ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.40-7.20 (m, 5 H; C_6H_5), 3.54 (s, 2 H; CH_2), 2.59 (m, 4 H; CH_2 -pyrrolidine), 1.74 (m, 4 H; CH_2 -pyrrolidine) (see Fig. S21). ^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) = 131.97, 128.67, 128.33, 123.79, 86.32, 84.25, 52.94, 44.04, 24.24 (see Fig. S22). GC-MS m/z : 185.2 amu for $[\text{C}_{13}\text{H}_{15}\text{N}(\text{16})]$ (see Fig. S23 for details).

Isolation of cationic $[\text{Ag}(\text{L1})(\text{propargylamine})][\text{SbF}_6]$ complex (**17**)

A mixture of $[\text{Ag}]^+[\text{SbF}_6]^-$ (**1**) salt (0.086 g, 0.25 mmol), 2-di-tert-butylphosphinobiphenyl (L1) (**2**) (0.075 g, 0.25 mmol), pyrrolidine (**9**) (0.019 g, 0.27 mmol), formaldehyde (**15**) (aq. 37%) [0.024 g, 0.30 mmol] and phenylacetylene (**3**) (0.025 g, 0.25 mmol) was suspended in toluene (2 ml). The mixture was stirred at RT for 20 h under argon atmosphere. Then, the precipitate formed in the resulting mixture was dissolved by adding 3 ml of dichloroethane/dichloromethane (1/2), filtered and then allowed to evaporate slowly at RT. Colourless crystals of **17** suitable for X-ray crystallography (see Table S5 and Fig. S28 for details) were collected by filtration, washed with cold n-pentane and dried under vacuum to yield the corresponding complex silver(I)(2-biphenyl)di-tert-butylphosphane-propargylamine hexafluoroantimonate (**17**) (0.186 g, 90 % yield). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.84 (t, 1 H; ArH); 7.69-7.45 (m, 5 H; ArH), 7.42-7.17 (m, 8 H; ArH), 3.59 (m, 2 H; CH_2),

2.88 (m, 4 H; (CH₂)-pyrrolidine), 1.86 (m, 4 H; (CH₂)-pyrrolidine), 1.20 (s, 9 H; *tert*-butyl CH₃), 1.15 (s, 9 H; *tert*-butyl CH₃) (see Fig. S24 for details). ³¹P NMR (CD₂Cl₂): δ (ppm) = 45.53 (dd, ¹J(¹⁰⁷Ag-³¹P) = 628.632 Hz and ¹J(¹⁰⁹Ag-³¹P) = 725.041 Hz). (see Fig. S25 for details). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 149.35 (d), 142.79 (d), 134.15 (d), 132.66 (d), 132.43, 131.51, 129.92, 129.70, 129.41, 129.04, 128.56, 128.45, 128.16, 125.64, 121.70, 88.17, 84.07, 58.80, 48.73, 35.72 (d), 35.74 (d), 31.04 (d), 30.90 (d), 23.36 (see Fig. S26 for details). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): δ (ppm) = Negative Signals: 58.87 and 23.36 for (CH₂, pyrrolidine), 48.79 for (CH₂, group); Positive Signals: 134.16 (d), 132.66 (d), 132.44, 131.51, 129.95, 129.71, 129.40, 129.06, 128.47, 128.19, 128.17, 30.98 (d) (see fig. S27). Elemental analysis, calc. for C₃₃H₄₂AgF₆NPSb (17) (%): C, 47.91; H, 5.12; N, 1.69. Found: C, 47.98; H, 5.26; N, 1.75.

Isolation of neutral [(L1-Ag(μ-Cl))₂] complex (18)

To a suspension of AgCl (0.043 g, 0.3 mmol) in dichloromethane (4 ml), the ligand (L1) 2-di-*tert*-butylphosphinobiphenyl (2) (0.074 g, 0.25 mmol) was added. The suspension was stirred for 48 h at 50 °C, filtered to remove unreacted AgCl and after evaporation of the solvent under reduced pressure at 45 °C, the solid residue was washed with cold pentane (3 x 2 ml) and dried to afford the product as colorless solid (0.195 g, 88 %). Colourless crystals of **18** suitable for X-ray crystallography (see Table S6 and Fig. S37 for details) were obtained by slow evaporation of the resulting mixture in dichloromethane after standing for 4 h at RT. ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 7.87 (t, 2 H; ArH); 7.55-7.40 (m, 10 H; ArH), 7.30-7.21 (m, 2 H; ArH), 7.19-7.10 (m, 4 H; ArH), 1.30 (s, 18 H; *tert*-butyl CH₃), 1.25 (s, 18 H; *tert*-butyl CH₃) (see Fig. S33 for details). ³¹P NMR (CD₂Cl₂): δ (ppm) = 43.68 (dd, ¹J(¹⁰⁷Ag-³¹P) = 605.605 Hz and ¹J(¹⁰⁹Ag-³¹P) = 698.304 Hz). (see Fig. S34 for details). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 150.56 (d), 150.30 (d), 142.08 (d), 141.97 (d), 134.15 (d), 132.51 (d), 130.87 (d), 129.81, 128.89, 128.83, 127.66 (d), 127.51 (two ds), 127.29 (d), 35.66 (d), 35.51 (d), 31.18 (d), 31.05 (d) (see Fig. S35 for details). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): δ (ppm) = Negative Signals: none; Positive Signals: 134.25 (d), 132.52 (d), 130.87 (d), 129.81, 128.89, 128.83, 127.51 (two ds), 31.19 (d), 31.05 (d) (see fig. S36). Elemental analysis, calc. for C₄₀H₅₄Ag₂Cl₂P₂ (18) (%): C, 54.38; H, 6.16. Found: C, 54.42; H, 6.25.

General Procedure for Mannich double A³-coupling

Preparation of bis-propargylamines 22 and 25: A mixture of 1,4-diethynylbenzene (20) or 1,6-heptadiyne (23) (0.25 mmol), pyrrolidine (0.70 mmol), formaldehyde (aq. 37%, 1.4 mmol) and Ag(I) complex **11** (0.015 mmol) as catalyst (Ag/alkyne ratio 6 mol%) was suspended in CH₂Cl₂ (1 ml), then the flask was evacuated under vacuum and refilled with argon. The evacuation/refilling cycle was repeated three times (pressure 2 bar). The mixture was stirred at RT for the required time to obtain the maximum yield of **22** or **25** (see Table 2). Then cold n-hexane was added to the cold reaction mixture, filtered and the solvents removed under reduced pressure at 50 °C to provide higher than 90 % in yield of bis-propargylamines as light-yellow solid for **22** and light-yellow oils for **25**. The structure and purity of bis-propargylamines **22** and **25** were confirmed by ¹H, ¹³C, ¹³C Dept-135 NMR spectroscopies and GC-MS analysis. Also the corresponding primary mono adducts intermediates **21** and **24** were detected and characterized in the reaction mixture by GC-MS of the crude reactions:

Compound 22: ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 7.30 (s, 4 H; C₆H₄), 3.56 (s, 4 H; CH₂), 2.61 (m, 8 H; CH₂-pyrrolidine), 1.75 (m, 8 H; CH₂-pyrrolidine) (see fig. S38). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 131.89, 123.33, 87.78, 84.14, 52.85, 43.99, 24.25 (see fig. S39). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): δ (ppm) = Negative Signal: 131 for (CH, C₆H₄); Positive Signals: 52.85 and 24.25 for (CH₂, pyrrolidine), 43.99 for (CH₂, group) (see fig. S40). GC-MS *m/z*: 292.2 amu for [C₂₀H₂₄N₂ (22)] (see fig. S41 for details). Elemental analysis, calculated for (22) C₂₀H₂₄N₂·H₂O (%): C, 77.38; H, 8.44; N, 9.02. Found: C, 76.74; H, 8.63; N, 8.67.

Single coupling intermediate 21: GC-MS *m/z*: 209.2 amu for [C₁₅H₁₅N (21)] (see fig. S42 for details).

Compound 25: ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 3.25 (t, *J*^d = 2.20 Hz, 4 H; CH₂^a), 2.48 (m, 8 H; CH₂-pyrrolidine), 2.24 (tt, *J*^d = 2.20 and *J*^e = 7.03 Hz, 4 H; CH₂^b), 1.69 (m, 4 H; CH₂-Pyrrolidine), 1.61 (quin, 2 H; CH₂^c), 0.83 (see fig. S44). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 83.40, 76.85, 52.81, 43.62, 28.67, 24.16, 18.09 (see fig. S45). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): Positive Signals: δ (ppm) = 52.81, 43.62, 28.66, 24.16, 18.09 (CH₂, groups) (see Fig. S46). GC-MS *m/z*: 258.2 amu for [C₁₇H₂₆N₂ (25)] (see Fig. S47 for details).

Single adduct intermediate 24: GC-MS *m/z*: 175.2 amu for [C₁₂H₁₇N (24)] (see fig. S48 for details).

Isolation of neutral [Ag(L1)(p-tolylsulfonate)(H₂O)] complex (27)

A mixture of Ag-p-tolylsulfonate (26) (0.056 g, 0.25 mmol) and 2-di-*tert*-butylphosphinobiphenyl (L1) (2) (0.075 g, 0.25 mmol) was dissolved in dichloromethane (2 ml). The mixture was stirred at RT for 24 h under argon atmosphere. Then, the resulting mixture was diluted by adding 2 ml of dichloromethane (2 ml), filtered and then the supernatant was layered carefully by 2 ml of n-hexane. Colourless crystals of **27** suitable for X-ray crystallography (see Table S7 and Fig. S53 for details) were obtained by standing for 48 h at -30 °C. The crystals were collected by filtration, dried under vacuum to yield the corresponding complex silver(I) (2-biphenyl)di-*tert*-butylphosphane(p-tolylsulfonate)(H₂O) (27) (0.133 g, 92 % yield). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 7.86 (t, 1 H; ArH); 7.68-7.23 (m, 8 H; ArH), 7.22-7.12 (m, 4 H; ArH), 2.33 (s, 3 H; CH₃), 1.59 (s, 2 H; H₂O), 1.27 (s, 9 H; *tert*-butyl CH₃), 1.22 (s, 9 H; *tert*-butyl CH₃) (see Fig. S49 for details). ³¹P NMR (CD₂Cl₂): δ (ppm) = 43.93 (dd, ¹J(¹⁰⁷Ag-³¹P) = 695.077 Hz and ¹J(¹⁰⁹Ag-³¹P) = 802.180 Hz). (see Fig. S50 for details). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 150.15 (d), 149.90 (d), 142.38, 141.85 (d), 141.73 (d), 140.82, 134.12 (d), 132.28 (d), 131.02 (d), 129.62, 129.14, 128.91, 128.57, 127.70 (two ds), 127.27 (d), 126.89 (d), 126.42, 35.66 (d), 35.52 (d), 30.98 (d), 30.85 (d), 21.45 (see Fig. S51 for details). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): δ (ppm) = Negative Signals: none; Positive Signals: 134.12 (d), 132.28 (d), 131.02 (d), 129.61, 129.14, 128.90, 128.57, 127.70 (two ds), 126.41, 30.97 (d), 30.84 (d), 21.45 (see fig. S52). ESI-MS (+MS) *m/z*: 405.1 and 407.1 amu for [C₂₇H₃₄AgO₃PS (27) - (OTf)]⁺ with the ¹⁰⁷Ag and ¹⁰⁹Ag isotopes (see Fig. S54 for details). ESI-MS (-MS) *m/z*: 170.08 amu for counter anion 4-methylbenzenesulfonate [C₇H₇O₃S (OTf)]⁻ of complex **27** (see Fig. S54 for details). Elemental analysis, calc. for [C₂₇H₃₆AgO₄PS].CH₂Cl₂ (27) (%): C, 49.43; H, 5.63; S, 4.71. Found: C, 49.54; H, 5.69; S, 4.56.

Isolation of neutral [Ag(L2)(p-tolylsulfonate)] complex (29)

A mixture of Ag-p-tolylsulfonate (**26**) (0.056 g, 0.25 mmol) and 2-di-tert-butylphosphanyl(2',4',6'-triisopropyl)-biphenyl (L2) (**28**) (0.106 g, 0.25 mmol) was dissolved in dichloromethane (2 ml). The mixture was stirred at RT for 24 h under argon atmosphere. Then, the resulting mixture was diluted by adding 2 ml of dichloromethane (2 ml), filtered and then the supernatant layered carefully by 2 ml of n-hexane. Colourless crystals of **29** suitable for X-ray crystallography (see Table S8 and Fig. S59 for details) were obtained by standing for 48 h at -30 °C. The crystals were collected by filtration, dried under vacuum to yield the corresponding complex silver(I) (2-di-tert-butylphosphanyl(2',4',6'-triisopropyl)-biphenyl(p-tolylsulfonate) (**29**) (0.161 g, 92 % yield). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 7.86 (t, 1 H; ArH); 7.64-7.55 (m, 2 H; ArH), 7.54-7.42 (m, 2 H; ArH), 7.35-7.25 (m, 1 H; ArH), 7.16-7.06 (m, 4 H; ArH), 2.78 (sept, 1 H; CH-isopropyl), 2.33 (sept, 2 H; CH-isopropyl), 2.31 (s, 3 H; CH₃-Ar), 1.28 (s, 9 H; tert-butyl CH₃), 1.24 (d, 6 H; CH₃-isopropyl), 1.23 (s, 9 H; tert-butyl CH₃), 1.19 (d, 6 H; CH₃-isopropyl), 0.87 (d, 6 H; CH₃-isopropyl), (see Fig. S55 for details). ³¹P NMR (CD₂Cl₂): δ (ppm) = 42.09 (dd, ¹J(¹⁰⁷Ag-³¹P) = 685.329 Hz and ¹J(¹⁰⁹Ag-³¹P) = 791.345 Hz). (see Fig. S56 for details). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 150.84, 147.91 (d), 147.65 (d), 146.11, 142.54, 140.55, 135.15 (d), 134.49 (d), 134.37 (d), 130.65 (d), 128.99, 127.43 (two ds), 126.44, 122.61, 31.38, 31.29 (d), 31.16 (d), 26.51, 23.85, 23.12, 21.42 (see Fig. S57 for details). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): δ (ppm) = Negative Signals: none; Positive Signals: 135.14 (d), 133.91 (d), 130.64 (d), 128.99, 127.43 (two ds), 126.43, 122.60, 34.37, 31.38, 31.28 (d), 31.16 (d), 26.51, 23.85, 23.12, 21.42 (see fig. S58 for details). ESI-MS (+MS) *m/z*: [C₃₆H₅₂AgO₃PS (**29**) + 2 MeOH]⁺ and 531.4 and 533.2 amu for [C₃₆H₅₂AgO₃PS (**29**) - (OTf)]⁺ with the ¹⁰⁷Ag and ¹⁰⁹Ag isotopes (see Fig. S60 for details). Elemental analysis, calc. for C₃₆H₅₂AgO₃PS (**29**) (%): C, 61.45; H, 7.45; S, 4.56. Found: C, 61.49; H, 7.53; S, 4.50.

General Procedure for aza-Diels-Alder two- and three-coupling

Preparation of 1,2-diphenyl-2,3-dihydro-4-pyridone (32): two - Coupling: A mixture of imine (**30**) (0.25 mmol) and Danishefsky's diene (**31**) (0.3 mmol) suspended in dioxane/H₂O (3/1) (2 ml). **three -coupling:** Slow addition of Danishefsky's diene (**31**) dissolved in 1 ml of dioxane to the mixture of aniline (**8**) (0.25 mmol) and benzaldehyde (0.25 mmol) (**35**) suspended in dioxane/H₂O (1/1) (1 ml) over 50 min. In both cases Ag(I) complexes **27**, **29** or **33** (0.015 mmol) were used as catalysts (Ag/alkyne ratio 6 mol%) then the flask was evacuated under vacuum and refilled with argon. The evacuation/refilling cycle was repeated three times (pressure 2 bar). The mixtures were stirred at RT for the required time to obtain the maximum yield of **32** (see Table 3). Then the solvents were removed under reduced pressure at 60 °C. The reaction mixture was diluted with water and the organic material was extracted with CH₂Cl₂ to provide 1,2-diphenyl-2,3-dihydro-4-pyridone (**32**) in yield higher than 90 %. The structure and purity of **32** were confirmed by ¹H, ¹³C, ¹³C Dept-135 NMR spectroscopies and GC-MS spectrometry analysis.

Compound **32**: ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 7.80 (d, *J* = 1.2 Hz, 1 H), 7.38-7.10 (m, 10 H), 7.08-6.98 (m, 3H), 5.26 (dd, *J* = 0.9, 7.8 Hz, 2H), 3.26 (dd, *J* = 7.2, 16.5 Hz, 1H), 2.70 (ddd, 1H) (see Fig. S61 for details). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 190.83, 150.46, 144.80, 138.16, 129.95, 129.38, 128.34, 126.58, 125.32, 119.41, 101.98, 62.07, 43.52 (see Fig. S62). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): δ (ppm) = Negative Signals: 43.48; Positive Signals: 150.48, 129.95, 129.38, 128.37, 126.58, 125.31, 119.40, 102.00, 62.07 (see fig. S63 for details). GC-MS *m/z*: 249.12 amu for [C₁₇H₁₅NO (**32**)] (see Fig. S64 for details).

Isolation of cationic [Ag(L1(imine))[SbF₆]] complex (33)

A mixture of [Ag]⁺[SbF₆]⁻ salt (0.086 g, 0.25 mmol), 2-di-tert-butylphosphinobiphenyl (L1) (**2**) (0.075 g, 0.25 mmol) and imine (**30**) (0.045 g, 0.25 mmol) was suspended in dried dichloromethane (2 ml). The mixture was stirred at RT for 16 h under argon atmosphere. Then, the transparent resulting solution was carefully layered with n-pentane, followed by standing 48 h at -30 °C affording colourless crystals of complex **33** suitable for X-ray crystallography (see Table S9 and Fig. S69 for details). These crystals were collected by filtration, washed with cold n-pentane and dried under vacuum to yield the corresponding complex silver(I) (2-biphenyl)di-tert-butylphosphane-imine hexafluoroantimonate (**33**) (0.191 g, 93 % yield). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 8.68 (s, 1 H; (N=CH)-imine), 7.96-7.87 (m, 1 H; ArH); 7.81-7.64 (m, 3 H; ArH), 7.61-7.37 (m, 7 H; ArH), 7.28-7.05 (m, 6 H; ArH), 7.03-6.92 (m, 2 H; ArH), 1.29 (s, 9 H; tert-butyl CH₃), 1.24 (s, 9 H; tert-butyl CH₃) (see Fig. S65 for details). ³¹P NMR (CD₂Cl₂): δ (ppm) = 46.03 (dd, ¹J(¹⁰⁷Ag-³¹P) = 634.082 Hz and ¹J(¹⁰⁹Ag-³¹P) = 732.025 Hz). (see Fig. S66 for details). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) = 168.84, 149.82, 149.34 (d), 149.08, 142.73 (d), 142.62, 142.60, 134.73, 134.53, 134.03 (d), 132.73 (d), 131.68 (d), 130.51, 130.31, 129.82, 129.22, 128.87, 128.79, 128.42, 128.32, 126.07 (d), 125.65 (d), 122.58, 36.01 (d), 35.85 (d), 31.06 (d), 30.93 (d) (see Fig. S67 for details). ¹³C Dept-135 NMR (75 MHz, CD₂Cl₂): δ (ppm) = Negative Signals: none; Positive Signals: 168.82, 134.72, 134.00 (d), 132.70 (d), 131.66 (d), 130.48, 130.28, 129.79, 129.19, 128.84, 128.76, 128.30, 122.56, 31.02 (d), 30.89 (d) (see Fig. S68 for details). Elemental analysis, calc. for C₃₃H₃₇AgF₆NPSb (**33**) (%): C, 48.20; H, 4.54; N, 1.70. Found: C, 48.28; H, 4.61; N, 1.75.

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Keywords: coordination chemistry • silver intermediates • homogeneous catalysis • Mannich reaction • Aza-Diels-Alder reaction

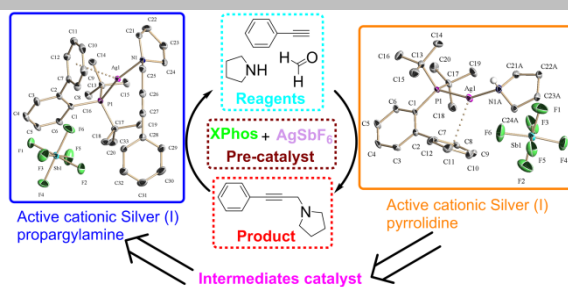
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Layout 1:

FULL PAPER

Cationic and neutral Ag(I) XPhos complexes with N co-ligands and organosulfonate are extremely active homogenous catalysts far more active than analogous Cu(I) and Au(I) complexes to promote Mannich and aza-Diels-Alder Couplings. Isolation of some Ag(I) complexes has allowed to shed light into reaction mechanism.



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Cationic and Neutral Silver(I) XPhos Complexes with N ligands and Organosulfonate: Synthesis, Characterization, Catalytic Activity and Mechanistic Insights for Mannich and Aza-Diels-Alder Couplings complexes