

Silver-Catalyzed Amidiniumation of Alkynes: Isolation of a Silver Intermediate, Synthesis of Enamine Amido Carbene Precursors, and an Unprecedented Umpolung of Propiolamide

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Abstract: A silver-catalyzed amidiniumation of *N*-propiolic formamidines for the synthesis of novel enamine amido carbene precursors is reported. Isolation of a first silver intermediate in silver-catalyzed amidiniumation of alkynes and other organogold intermediates supports our proposed mechanisms. Several control experiments reveal the unexpected effects of both HOTf and substrate substituents on the choice of either a π or σ,π silver activation mode and the cyclization fashion. Bis(hydroxyimidazolium) salts were obtained through an unprecedented umpolung of propiolamides. The byproduct Ag_2O as either an oxidant or silver source promotes the syntheses of *N*-heterocyclic carbene (NHC) precursors or Ag/NHC complexes.

Over the last twenty years, *N*-heterocyclic carbenes (NHCs) have attracted much attention because of their widespread and spectacular applications as ligands in organometallic catalysis and as organocatalysts.^[1] Besides the versatile applications of NHCs in catalysis, Bertrand and co-workers discovered cyclic alkyl amino carbenes are capable of either activating H_2 and NH_3 , or fixing carbon monoxide (CO).^[2] Shortly after the initial results, several groups proved that the incorporation of carbonyl moieties into the NHC backbone could largely influence its electronic properties and reactivity.^[3–6] Bielawski and co-workers reported that the six-membered diamidocarbene (DAC) **I** was more electrophilic compared to typical NHCs (Figure 1), and favored N–H and C–H bond activation, reversibly fixing CO , coupling to isonitriles, and [2+1] cycloaddition of olefins, aldehydes, alkynes, and nitriles.^[4] The five-membered DAC **II**, reported by the groups of Bielawski^[4b] and Ganter,^[5a–c] and the six-membered amino-acrylamido carbene **III**, reported by Hudnall and co-workers,^[6a] also display similar electrophilic properties. We envision that decorating NHCs with a conjugated backbone containing an α,β -unsaturated carbonyl moiety would provide the NHC with additional stability and exhibit unprecedented electronic properties, thereby showing

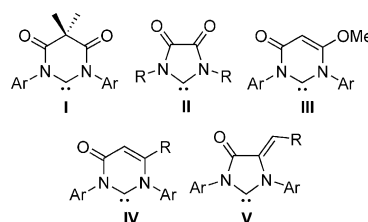


Figure 1. Selected amido NHCs I–III and targeted NHCs IV and V.

distinct reactivity behavior. Keeping this thought in mind, we designed the enamine amido carbenes **IV** and **V**. (Figure 1) The electron density in **IV** and **V** would be localized on the π^* orbitals of both the olefin and carbonyl group attached directly to the nitrogen atoms, thus rendering them less nucleophilic.

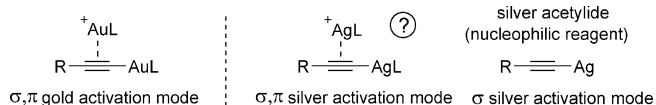
Since 2011, we have developed several methodologies for the preparation of various azolium salts as NHC precursors, starting from functionalized formamidines.^[7] Aiming at construction the scaffolds of **IV** and **V**, we expected a metal-catalyzed intramolecular amidiniumation of *N*-propiolic formamidines could probably be a practical method. Although transition-metal-catalyzed intramolecular hydroamination and hydroamidation of alkynes^[8] have been well-established, the cyclization of *N*-alkynyl formamidines to afford cyclic formamidinium salts, the direct precursors of NHCs, is unknown. In the past ten years, gold-^[9] and silver-catalyzed^[10] reactions of alkynes have attracted considerable interest because of their high selectivity and mild reaction conditions. Besides π and σ gold activation modes,^[9] the presence of a σ,π activation mode was first proposed by Toste, Houk et al. for gold-catalyzed reactions of terminal alkynes,^[11] and this dual-activation concept has been applied in a variety of cyclization reactions by several groups.^[12] Compared with the analogous gold species,^[13] the silver intermediates are highly reactive. Because the Ag–C bonds in silver intermediates are vulnerable to attack by electrophiles—mostly protons, they are rarely isolated because of the presence of a trace amount of water in the reaction mixture. Partially because of the lack of the isolable organosilver intermediate, the reaction mechanism for silver-catalyzed transformations is much less investigated, and its general reaction mode remains little understood compared to that for the gold-catalyzed reaction. Generally, under a π silver activation mode, the activated alkyne becomes prone to nucleophilic attack. For a terminal or a silylated alkyne, the silver π complex could be converted into silver acetylide.^[10,14] Unlike its gold acetylide analogue, silver acetylide is commonly studied and used to date as

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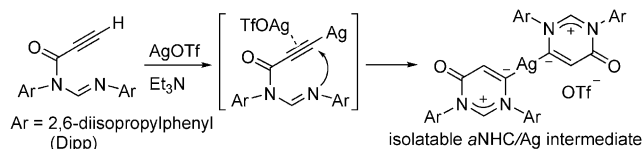
a nucleophile to react with various electrophiles or as the transmetalation intermediate in cross-coupling reactions. So we were wondering if silver acetylides could undergo π activation by another silver salt and then undergo attack by nucleophiles, as do σ,π gold activated alkynes (Scheme 1).



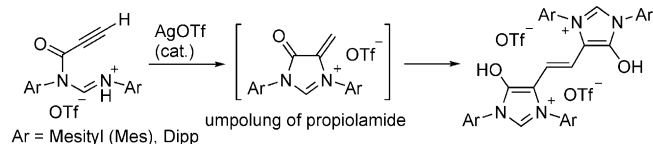
Scheme 1. Selected gold and silver activation modes in alkyne activation.

Herein, we report the first silver-catalyzed regioselective synthesis of enamine amido carbene precursors through amidiniumation of *N*-propiolic formamidines, and describe the unexpected effects of both HOTf and substrate substituents on the choice of either the π - or σ,π silver activation mode. Isolation of the first organosilver intermediate in silver-catalyzed amidiniumation of alkynes, an unprecedented umpolung of propiolamide, and the reuse of the byproduct Ag_2O to promote another reaction in a one-pot reaction are also reported (Scheme 2).

a) Silver-mediated 6-*endo*-dig cyclization: isolation of an aNHC-Ag intermediate



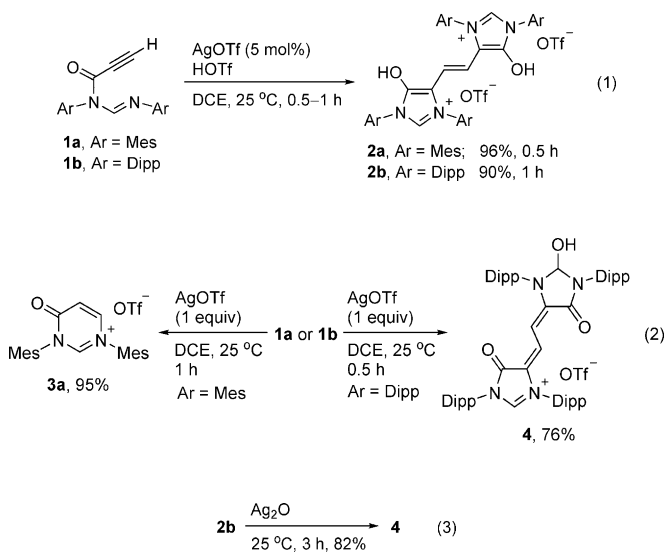
b) HOTf-mediated silver-catalyzed 5-*exo*-dig cyclization: umpolung of propiolamide



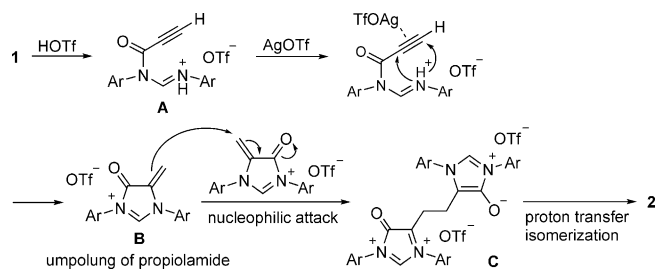
Scheme 2. Regiodivergent silver-catalyzed amidiniumation of *N*-propiolic formamidines and isolation of a key silver intermediate. Tf = trifluoromethanesulfonyl.

Various *N*-propiolic formamidines were prepared by the acylation of the *N,N'*-diarylformamidine with various substituted propiolic acids, in the presence of *N,N'*-dicyclohexylcarbodiimide, in 42–74% yield (see Scheme S1 in the Supporting Information). First, the formamidines **1a** and **1b**, bearing a terminal alkyne, were investigated in the silver-activated amidiniumation. Surprisingly, both **1a** and **1b**, in the presence of HOTf (1 equiv) and AgOTf (5 mol %), underwent cyclization to afford the *trans*-vinylene-bridged bis-(hydroxyimidazolium) salts **2a** and **2b**, respectively, with excellent yields [Eq. (1)]. ^1H NMR analysis of **2a** and **2b** shows only one set of proton signals in the aromatic region and one signal for the vinylic proton at $\delta = 6.29$ ppm for **2a** and at $\delta = 6.41$ ppm for **2b**, thus indicating a symmetric structure for both **2a** and **2b**. By using a stoichiometric amount of AgOTf, **1a** underwent 6-*endo*-dig cyclization to

form the six-membered formamidinium salt **3a**, while cyclization of **1b**, having bulkier *N*-Dipp substituents, afforded the asymmetric formamidinium salt **4** containing an imidazolone ring and an imidazolidinone ring with a hydroxy group attached [Eq. (2)]. The structures of **2b** and **4** have been unequivocally confirmed by X-ray diffraction analysis (see Figures S3 and S4 in the Supporting Information).^[15] Delightfully, **2b** could be transformed into **4** by treatment with Ag_2O at room temperature [Eq. (3); DCE = 1,2-dichloroethane]. Ag_2O , a byproduct of such AgOTf-mediated amidiniumations (see below), probably served as the oxidant for the oxidation of **2b** into **4**. The hydroxy group in **4** probably contributes to the attack of H_2O at the formamidinium carbon atom.



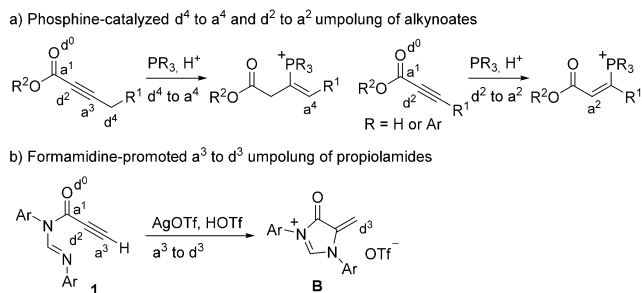
The regiochemistries observed here are quite intriguing, and further efforts have been focused on the investigation of the mechanism. Based on our observations, we proposed plausible mechanisms for these divergent transformations. In the catalytic mode, the addition of HOTf first leads to the formation of the formamidinium salt **A** (Scheme 3). Upon activation by AgOTf, **A** undergoes hydroamidiniumation in a 5-*exo*-dig fashion, and subsequent hydrolysis offers the five-membered formamidinium salt **B**, which is highly reactive and represents a rare example of the umpolung of propiolamide. Consequent nucleophilic attack by **B** on another molecule of **B** leads to the formation of the intermediate **C**, which



Scheme 3. Proposed mechanism for the formation of **2** in the presence of HOTf.

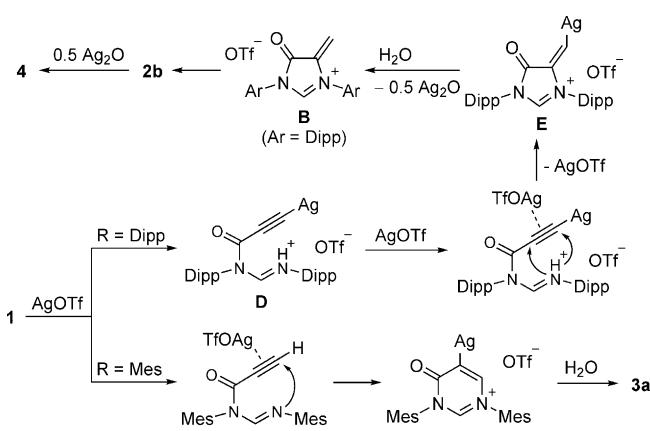
undergoes proton transfer and isomerization to generate the bis(hydroxyimidazol)ium salt **2**.

Phosphine-catalyzed d^4 to a^4 and d^2 to a^2 umpolung of alkynoates^[16] and phosphine-catalyzed d^2 to a^2 umpolung of alkynoates^[17] bearing a hydrogen atom or an aromatic ring have been reported, and the resulting vinyl phosphonium intermediates can undergo an attack by various nucleophiles (Scheme 4a).^[18] A 5-*exo*-dig cyclization of **1** catalyzed by AgOTf allows transfer of the nucleophilic property at the β -carbon atom, thereby forming a five-membered intermediate (**B**), which represents an unprecedented a^3 to d^3 umpolung of propiolamide (Scheme 4b).



Scheme 4. Examples of umpolung of propiolic acid derivative.

It is known that treating a terminal alkyne with a silver salt first generates a π complex intermediate, which, upon addition of bases such as amines, immediately undergoes deprotonation to afford the silver acetylide.^[10,14] Despite being quite stable, silver acetylide could undergo hydrolysis upon addition of strong acids, such as either HCl, HNO₃, or HOTf. Therefore, we speculate that, in the stoichiometric reaction, the imine moiety in **1b** could react as a base to promote the generation of silver acetylide and subsequently release HOTf, and subsequent protonation affords the alkynyl silver intermediate **D** (Scheme 5). Upon activation with a silver salt, **D** undergoes 5-*exo*-dig cyclization to generate the silver intermediate **E**, which is hydrolyzed to offer **B** and release Ag₂O.



Scheme 5. Proposed mechanism for the formation of **3a** and **4**.

Finally, **2b** generated from **B** is oxidized by the resulting Ag₂O to give **4**. Compared to **1a**, **1b** has more electron density on N because the twist, imposed by the two bulkier *ortho*-isopropyl substituents, of the Ar–N bond results in smaller electron delocalization into the aryl ring.^[7a] Therefore, **1a** bearing a less basic imino moiety preferred to directly undergo 6-*endo*-dig cyclization through a π silver activation mode to form the silver intermediate **F**, instead of generating the N-Mes counterpart of the alkynyl silver intermediate **D**. Choice of a 6-*endo*-dig cyclization mode for **1a** is probably due to there being a positive charge on the β -carbon atom (C6). Subsequent hydrolysis of **F** offers the six-membered formamidinium salt **3a**.

To prove that the catalytic pathway involves the formation of **B**, and that **B** also could be generated from its silver counterpart **E** in a stoichiometric pathway, the reactivity of a gold salt toward the amidination reaction was examined. Delightfully, reacting IPrAuOTf [IPr = 2,6-bis(diisopropylphenyl)imidazol-2-ylidene] with **1b** offered a stable five-membered gold species (**5**), a gold counterpart to **E** [Eq. (4)]. The formation of **5** was unequivocally confirmed by X-ray crystallography (Figure 2).^[15] In **5**, the Au1–C16 bond [2.004–

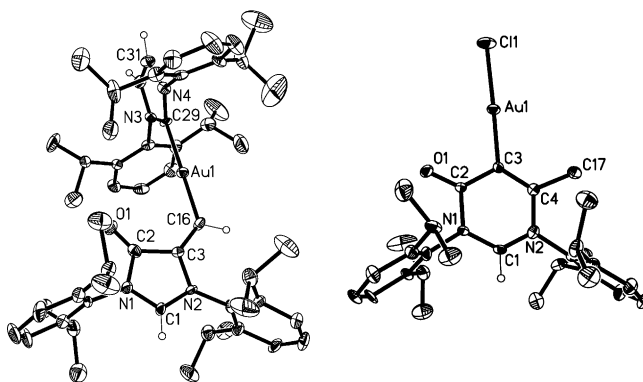
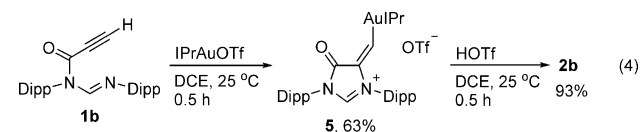


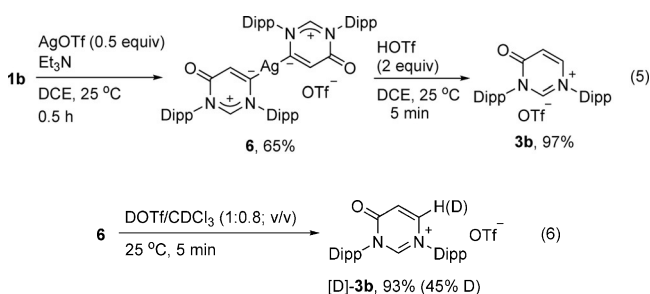
Figure 2. Molecular structures of **5** (left) and **11** (right; only one of the two independent molecules shown) with thermal ellipsoids shown at 30% probability. The counterion (OTf[−]) in **5** and H atoms of the aryl rings have been omitted for clarity.

(9 Å)] formed through amidination is shorter than the Au1–C29 bond [2.060(7) Å] in the IPrAu moiety. The gold species **5** represents a rare gold intermediate in gold-catalyzed *exo*-dig cyclization of terminal alkynes. Only one isolable vinyl gold species derived from a terminal alkyne was reported by Hashmi and co-workers before.^[20a] Interestingly, hydrolysis of **5** with HOTf can immediately afford the bis(hydroxyimidazol)ium salt **2b** with excellent yield, thus indicating the formation of **B** during the process [Eq. (4)].

Considering that protonation of the imino moiety by HOTf, released during the generation of alkynyl silver, led to

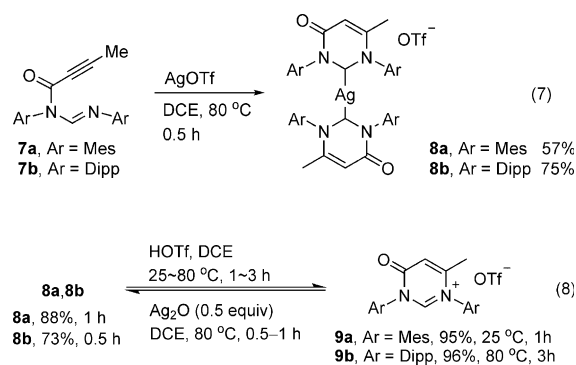


a 5-*exo*-dig amidiniumation, we designed a control experiment with addition of a base to preclude the protonation of imino moiety in the stoichiometric AgOTf-promoted cyclization of **1b**. Addition of a base could also slow down the protodemetalation to conserve the organometal species, which Hashmi et al. used to obtain the vinylgold intermediates.^[19a] Delightfully, in the presence of Et₃N as a base, a stable silver species (**6**) was isolated through a 6-*endo*-dig cyclization [Eq. (5)]. Further hydrolysis of **6** afforded the corresponding six-membered formamidinium salt **3b**. The formation of **3b** was further confirmed by X-ray crystallography (see Figure S5 in the Supporting Information).^[15] Formation of **6** was confirmed by the disappearance of the signal for the β-carbon (C6) proton in **3b** at δ = 8.17 ppm and an upfield shift of the signal for the α-carbon (C5) proton (from δ = 7.19 ppm in **3b** to δ = 6.41 ppm in **6**) and the formamidine (C2) proton (from δ = 9.90 ppm in **3b** to δ = 8.97 ppm in **6**), thus suggesting the loss of cationic character. HRMS evidence indicates one silver atom is associated with two cyclic formamidine rings in **6**. Based on the above observation, we assume that **6** is a bis(*a*NHC) silver complex, where its carbenic atom is at β-carbon (C6) position. The silver species **6** represents the first isolable silver intermediate in silver-catalyzed amination of alkynes. Compared to other highly sensitive vinyl silver complexes, the increased stability of **6** is probably attributed to the formation of an *a*NHC ring during the cyclization and the presence of a bulky N-Dipp adjacent to the carbenic atom. Upon treatment of **6** with a large excess of DOTf, deuterium incorporation (45 % D) was observed at the 6-position of [D]-**3b** [Eq. (6)].

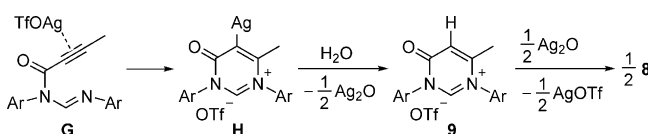


Next, the formamidines **7a** and **7b**, having an internal alkyne, were examined. Surprisingly, reaction of **7a** with 1 equivalent AgOTf for 30 minutes at 80 °C or for 3 hours at 15 °C in DCE led to the formation of a stable cationic bis(NHC) silver complex (**8a**) in 57% yield, instead of the expected cyclic formamidinium salt [Eq. (7)]. **8a** contains two six-membered ring NHCs, which were formed through a 6-*endo*-dig cyclization. Both the loss of the characteristic formamidinium proton signal in the ¹H NMR spectrum, and the X-ray diffraction analysis (see Figure S6 in the Supporting Information)^[15] confirmed the formation of **8a**. Under the same reaction conditions, the bulkier **7b** also underwent cyclization to afford the corresponding bis(NHC) silver complex **8b** in 75% yield.

Several control experiments were designed to gain mechanistic insight into the unexpected formation of **8a** and



8b. Treatment of **8a** and **8b** with HOTf gave the expected cyclic formamidinium salts **9a** and **9b**, respectively [Eq. (8)]. The structure of **9b** was secured by X-ray diffraction analysis (see Figure S7 in the Supporting Information).^[15] Further reaction of **9a** and **9b** with Ag₂O at room temperature in DCE afforded **8a** and **8b**, respectively, in good yields, whereas AgOTf failed to promote the transformation under the same reaction conditions. Additionally, in situ ¹H NMR spectroscopy showed that when AgOTf was treated with 1 equivalent of **7b** in CDCl₃ at room temperature for 2 minutes, the two sets of signals assigned to the isomers of **7b** disappeared, and only one set of signals was observed. The signals appear to have one characteristic formamidine proton signal at δ = 8.52 ppm and are close to the signals at δ = 8.83 and 8.88 ppm for the two isomers of **7b**, thus indicating a ligated silver complex (**G**) is probably formed (Scheme 6). After

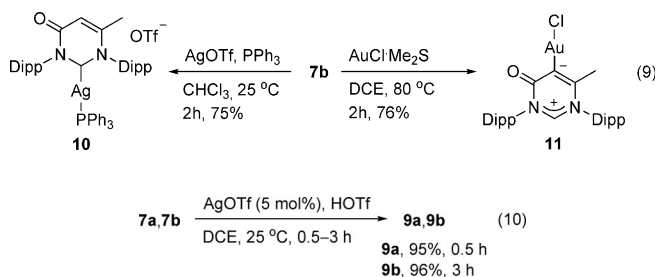


Scheme 6. Proposed mechanism of the formation of the bis(NHC) silver complex **8**.

heating the solution of **7b** and AgOTf (1 equiv) in CDCl₃ at 45 °C for 25 minutes, the signals of **9b** and **8b** began to show up in a ratio of 0.54:1 in 50.5% yield (NMR; see Scheme S2 in the Supporting Information). About a 100% conversion of **G** into **9b** and **8b** was achieved within 65 minutes with a ratio of 0.11:1. Based on the above observation, we speculate that the coordination of the triple bond in **7** to AgOTf forms **G**, and subsequent attack of the nitrogen atom at the triple bond leads to the highly active silver intermediate **H**, which rapidly undergoes protonolysis to yield **9**, and simultaneously releases Ag₂O. Then **9** reacts with the byproduct Ag₂O to generate **8** (Scheme 6).

By using this method, the mono-NHC silver complex **10** could also be obtained, in the presence of PPh₃, in high yield [Eq. (9)]. The formation of **10** was confirmed by X-ray crystallography (see Figure S8 in the Supporting Information).^[15] The process provides a novel route for direct synthesis of silver carbene complexes and does not necessitate the preparation of a carbene precursor salt in advance. To

gain more mechanistic insight, the aurated species **11** was prepared from the stoichiometric reaction of AuCl-Me₂S with **7b** [Eq. (9)]. X-ray crystallography undoubtedly confirmed the formation of **11** (Figure 2).^[15] The Au–C bond [2.005(8) Å] is similar to that observed for the abnormal thiazol-5-ylidene gold complex [2.005(14) Å]^[20] and shorter than those in vinyl gold complexes (2.04–2.06 Å),^[19] thus indicating that **11** is more like an abnormal carbene (*a*NHC) complex than a vinyl gold complex. The aurated species **11** represents a scarce example of a nonheteroatom-substituted carbene coinage-metal complex.^[21] In the presence of 5 mol % of AgOTf and HOTf, the formamidinium salts **9a** and **9b** could be catalytically synthesized through cyclization of **7a** and **7b**, respectively, with excellent yields [Eq. (10)]. In the absence of AgOTf, only trace amounts of **9a** and **9b** were observed at 25 °C after 8 hours.



In summary, we have developed a silver-catalyzed amidinium of N-propionic formamidines for the synthesis of novel enamine amido carbene precursors. Isolation of a first organosilver intermediate and organogold intermediates support our proposed mechanisms. Several control experiments reveal the unexpected effects of both HOTf and substrate substituents on the choice of either a π - or σ,π silver activation mode and the reaction process (5-*exo*-dig or 6-*endo*-dig). An unprecedented umpolung of propiolamide is also developed for the dimerization of the cyclization product.

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