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ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.9b02314 • Publication Date (Web): 15 Jul 2019

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Gold- or Indium-Catalyzed Cross-Coupling of Bromoalkynes with Allylsilanes through a Concealed Rearrangement

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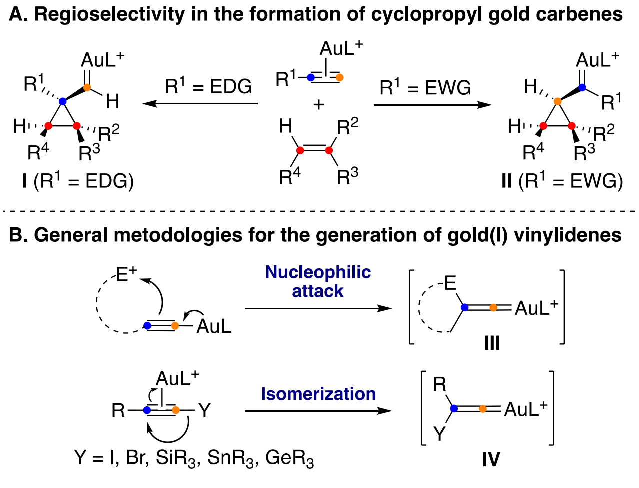
ABSTRACT: The gold(I)-catalyzed reaction of bromoalkynes with allylsilanes gives 1,4-enynes in a formal cross-coupling reaction. Mechanistic studies revealed the involvement of gold(I) vinylidenes or vinylidenephenonium gold(I) cations depending on the substituent on the bromoalkyne. In the case of bromo arylalkynes, the vinylidenephenonium gold(I) cations lead to 1,4-enynes via a 1,2-aryl rearrangement. The same reactivity has been observed in the presence of $InBr_3$.

KEYWORDS: bromoalkynes, allylsilanes, 1,4-enynes, metal vinylidene, gold catalysis, indium catalysis

INTRODUCTION

The gold(I) catalyzed intermolecular reaction of alkenes with alkynes can lead to the formation of cyclobutenes by a [2+2] cycloaddition or to 1,3 dienes via a rearrangement reaction.[1] Both reactions start with the *anti*-attack of the alkene on (η^2-alkynes)gold(I) complexes to form cyclopropyl gold(I) carbenes **I** or **II** (Scheme 1A). The regioselectivity in the generation of these intermediates mainly depends on the substitution pattern of the substrates and influences the evolution of the reaction either towards the cyclobutene formation or the rearrangement in 1,3-dienes. As a general trend, for terminal alkynes the gold(I) carbene is preferentially formed at the alkyne carbon in β-position to electron-donating groups and in α-position to electron-withdrawing groups (**I** and **II**, respectively).


A. Regioselectivity in the formation of cyclopropyl gold carbenes

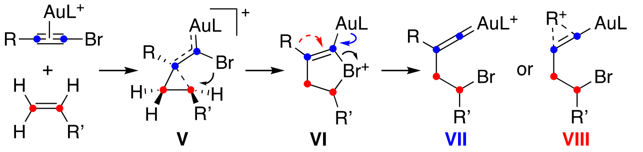
B. General metodologies for the generation of gold(I) vinylidenes

Scheme 1. Generation of cyclopropyl gold(I) carbenes and gold(I) vinylidenes.

Gold(I) vinylidenes **III**-**IV**[2] are a second fundamental group of intermediates in gold(I) catalysis, which can be generated by attack of a gold(I) acetylide to electrophiles (**III**, Scheme 1B)[3] or by an alkyne-vinylidene isomerization with 1,2-migration of a functional group (**IV**, Scheme 1B).[4,5]

The alkyne-vinylidene isomerization via 1,2-halogen migration was invoked for the intramolecular gold(I)-catalyzed hydroarylation of haloalkynes,[6] although in the case of bromoalkynes a more favorable hydroarylation/1,2-H shift/1,2-halide shift sequence was proposed for the formation of hydroarylation products.[7] Apart from the widely studied hydroarylation,[8] haloalkynes[9] are scarcely involved in gold(I)-catalyzed reactions, especially with alkenes. Only few examples of 1-bromo-1,5-enynes partaking in cycloisomerization reactions have been reported,[10] whereas chloroalkynes undergo intermolecular [2+2] cycloadditions with alkenes to form cyclobutenes[11] and react with electron-rich arenes to give (*Z*)-alkenyl chlorides in a hydroarylation reaction.[12]

We have now discovered a new mode of reactivity of bromoalkynes in the presence of gold(I). Bromoalkynes react with allyl silanes as electron-rich alkenes (R' = CH_2SiMe_3) forming the gold(I) carbenes **V** where the carbene is located in α-position to the more electron-withdrawing bromide substituent (Scheme 2). Intermediates **V** then undergo intramolecular attack of the bromine to form unprecedented cyclic bromonium intermediates **VI**[13]. Depending on the nature of the R substituent, ring opening of **VI** can generate gold(I) vinylidenes **VII** (R = alkyl) or vinylidenephenonium gold(I) cations (R = aryl). Interestingly, the same reactivity can be triggered by $InBr_3$ instead of gold(I).

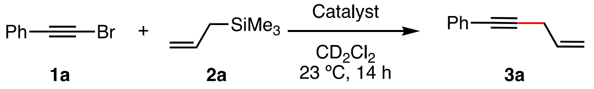


Scheme 2. Proposed evolution of cyclopropyl gold(I) carbenes into gold(I) vinylidenes.

RESULTS AND DISCUSSION

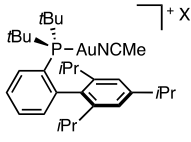
Synthesis of 1,4-Enynes. The reaction of (bromoethynyl)benzene (**1a**) with allyltrimethylsilane (**2a**) in presence of cationic gold(I) catalysts **A**-**C** led to skipped enyne **3a** in a formal cross-coupling reaction with loss of TMSBr in low to moderate yield (Table 1, entries 1-3).[14] Whereas more electrophilic phosphite-based catalyst **D**, AuCl, and $AuCl_3$ salts failed to catalyze this transformation (Table 1, entries 4-6), doubling the amount of **2a** using gold complex **B** led to **3a** in 77% yield. Among the variety of other tested Lewis acids (Table 1, entries 8-11), $InBr_3$ provided enyne **3a** in yields comparable to those obtained with cationic gold(I) catalyst **B**.

Table 1. Reaction of bromoalkyne 1a with allylsilane 2a to form 1,4-enyne 3a.

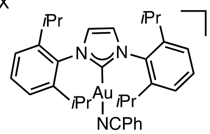


Entry	Catalyst (mol%)	1a:2a	Yield (%)[a]
1	**A** (5)	1:1	13 (7)
2	**B** (3)	1:1	50
3	**C** (5)	1:1	14
4	**D** (5)	1:1	traces
5	AuCl (5)	1:1	0
6	AuCl$_3$(5)	1:1	0
7	**B** (3)	1:2	(77)
8	PtCl$_2$ (3)	1:1	traces
9	GaCl$_3$ (3)	1:1	28-45[b]
10	InBr$_3$ (3)	1:1	50-55[b]
11	InBr$_3$ (3)	1:2	(81)

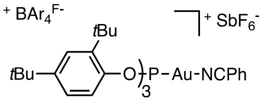
[a] Yields determined by ^{1}H NMR using mesitylene as internal standard. Isolated yields in parentheses. [b] Range of yields obtained in different runs.



A: X = SbF$_6$
B: X = BAr$_4^F$



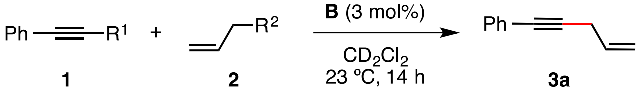
C



D

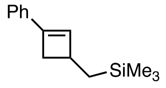
(Chloroethynyl)benzene also reacted with allyltrimethylsilane (**2a**) to give **3a** in 68% yield (Table 2, entry 2), while (iodoethynyl)benzene provided **3a** in poor yield[15] (Table 2, entry 3). Regarding the allylic partner (Table 2, entries 4-8), allyltriphenylsilyane also reacted satisfactorily with **1a** to give **3a** in 66% yield (Table 2, entry 6). Nonetheless, in the interest of the atom economy, we continued our study using allyltrimethylsilanes as substrates. The reversed reaction of alkynylsilane **1d** with allylbromide **2f** did not occur under these conditions (Table 2, entry 9).

Table 2. Optimization of the substitution pattern of the substrates to form 3a.[a]



Entry	1a-e	R^1	2a-g	R^2	Yield (%)[b]
1	**1a**	Br	**2a**	SiMe$_3$	(77)
2	**1b**	Cl	**2a**	SiMe$_3$	68[c]
3	**1c**	I	**2a**	SiMe$_3$	9
4	**1a**	Br	**2b**	Si(OMe)$_3$	21
5	**1a**	Br	**2c**	Si(*i*Pr)$_3$	23
6	**1a**	Br	**2d**	SiPh$_3$	66
7	**1a**	Br	**2e**	Bpin	16
8	**1a**	Br	**2f**	Sn(*n*Bu)$_3$	14
9	**1d**	SiMe$_3$	**2g**	Br	-[d]
10	**1e**	H	**2a**	SiMe$_3$	-[e,f]

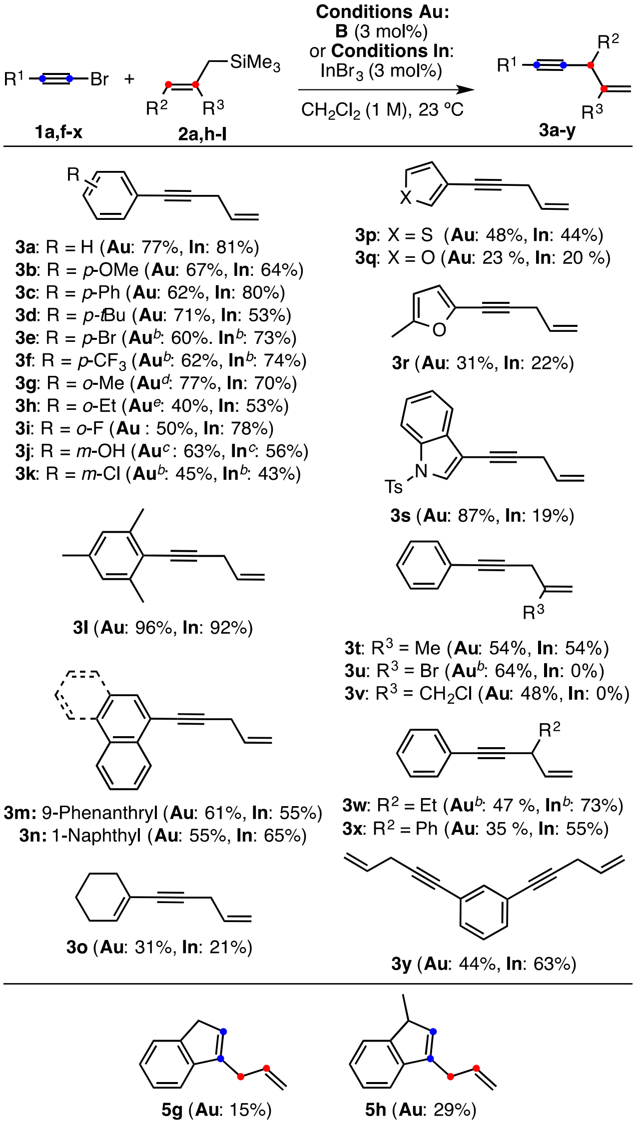
[a] Substrates **1**:**2** in a 1:2 ratio. [b] Yields determined by ^{1}H NMR using mesitylene as internal standard. Isolated yields in parentheses. [c] Reaction time was 48 h. [d] No reaction. [e] Product **4** was formed instead. [f] Reaction at 50 °C.



4 (58%)

As expected,[1] reaction between phenylacetylene **1e** and allylsilane **2a** gave cyclobutene **4** (Table 2, entry 10).

Table 3. Scope of the gold- or indium-catalyzed synthesis of skipped enynes 3a-y.[a]



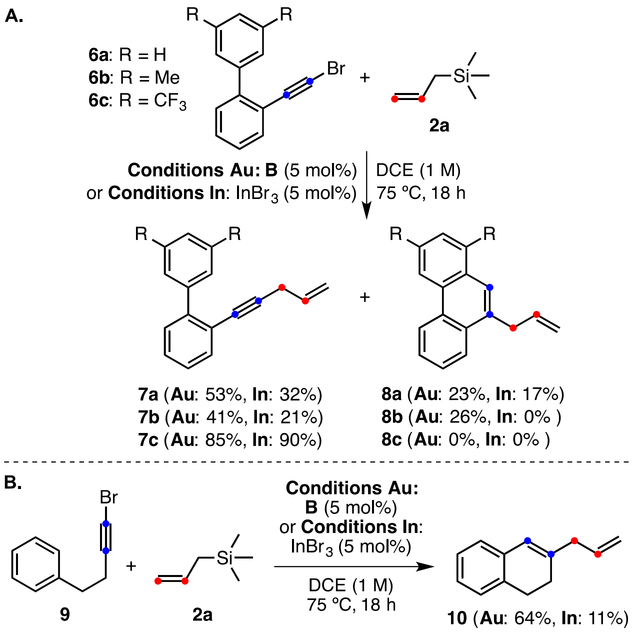
[a] Isolated yields. [b] Reaction at 50 °C. [c] Yields determined by ^{1}H NMR using mesitylene as internal standard. [d] Product **5g** was also formed. [e] Product **5h** was also formed.

We then examined the scope of the reaction between bromoalkynes **1** and allylsilanes **2** using either gold complex **B** or InBr$_3$ and, in general, comparable yields were obtained with both catalysts (Table 3). Allylsilane **2a** reacts with bromoalkynes bearing differently substituted aryl groups to give the corresponding skipped enynes **3a-n** in yields ranging from 40 to 96%. The reaction of 1-(bromoethynyl)-1-cyclohexene with **2a** gave rise to 1,6-dien-3-yne **3o**, albeit in low yields. Furyl substituted 1,4-enynes **3q,r** were also obtained in low yields, whereas thiophenyl and indolyl substituted 1,4-enynes **3p,s** were prepared in 48% and 87% yield, respectively. Diverse substituents at the 2 and 3 position of the allylsilane are tolerated, leading to skipped enynes **3t-x**.

The formation of 3-substituted 1,4-enynes **3w,x** starting from 3-substituted allylsilanes indicates that the reaction proceeds by γ-attack on the allylsilane, commonly observed in reactions with electrophiles. Moreover, 1,3-bis(bromoethynyl)benzene underwent a twofold reaction with allylsilane **2a** to afford bisallylated product **3y**.

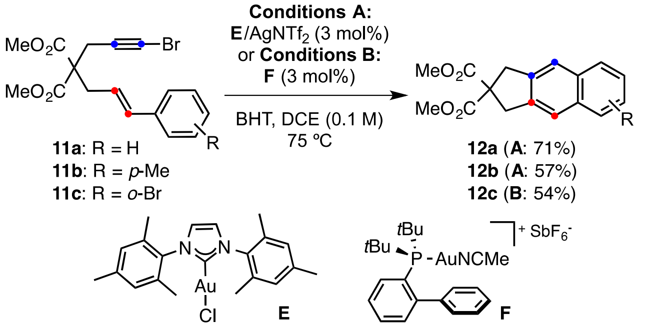
Interestingly, in the gold(I)-catalyzed reaction of *o*-methyl- or *o*-ethyl(bromoethynyl)benzene with **2a**, the 3-allylindenes **5g** and **5h** were formed together with the 1,4-enynes **3g,h**. Control experiments showed that **3g** cannot be converted into **5g** under the reaction conditions.[14] These two results suggested the involvement of gold(I) vinylidenes as reactive intermediates that undergo C−H insertion on the *o*-methyl or *o*-ethyl groups to form indenes **5g** and **5h**.

Hydroarylation Cascade. Intrigued by the hint on the involvement of gold(I) vinylidenes in the formation of **5g** and **5h**, we tested aryl substituted bromoalkynes in the reaction with allylsilanes to trigger a gold(I) vinylidene formation/hydroarylation cascade. Initially, we evaluated the reaction of allylsilane **2a** with *o*-alkynylbiaryls **6a-c** at 75 °C (Scheme 3A). Using **6a** in presence of catalyst **B**, 1,4-enyne **7a** and allylphenantrene **8a** were obtained in 53% and 23% yields, respectively. With $InBr_3$ as catalyst, both products were generated in similar ratios, although in lower yield. In the case of methyl substituted derivative **6b**, gold(I) catalyst led to the formation of **7b** and **8b** in 2:1 ratio. Importantly, the formation of phenanthrene **8b**, with differently substituted A and C rings, demonstrates that the cyclization proceeds by a process in which a formal 1,2-migration of the allyl chain takes place. No hydroarylation was observed with **6c**, which gave the skipped enyne **7c** in excellent yield with both gold and indium catalysts. In this last example, the bis(trifluoromethyl)aryl moiety in **6c** is not electron-rich enough to undergo the hydroarylation reaction. On the other hand, substrate **9** reacts with allyltrimethylsilane in the presence of catalyst **B** to give 1,2-dehydronapthalene **10** (64% yield) (Scheme 3B).



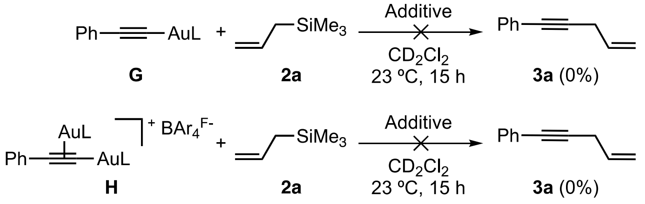
Scheme 3. Intramolecular hydroarylation reactions.

The intramolecular reaction of 1-bromo-1,6-enynes **11a-c** was also examined to test if the corresponding gold(I) vinylidenes would undergo an intramolecular hydroarylation with the aryl substituent of the alkene (Scheme 4). Thus, when **11a-c** were heated at 75 °C with gold(I) complexes **E** or **F** as catalysts, in presence of BHT,[16] 2,3-dihydro-1*H*-cyclopenta[*b*]naphthalenes **12a-c** were obtained in satisfactory yields as a result of a formal [4+2] cycloaddition.



Scheme 4. Synthesis of 2,3-dihydro-1*H*-cyclopenta[*b*]naphthalenes 12a-c from 11a-c.

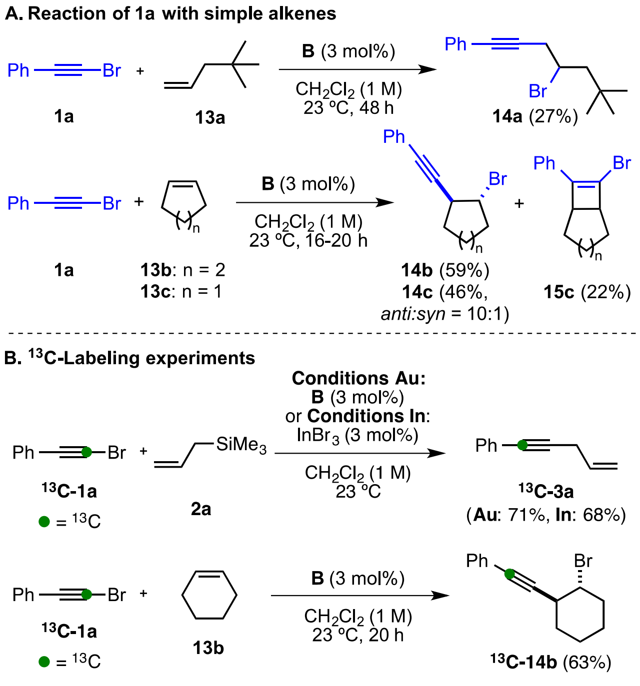
Insights into the reaction mechanism. To prove our initial hypothesis of the formation of the gold(I) vinylidene intermediate, we performed a series of mechanistic experiments and computational DFT calculations. Firstly, we investigated the possible intermediacy of gold acetylide and/or σ,π-digold(I) alkyne complexes, which has been proposed in other reactions of haloalkynes and in the formation of gold(I) vinylidenes.[17] Thus, we subjected complexes **G** and **H** to the reaction conditions, in absence or presence of the gold catalyst **B** or different bromide sources, although no reaction was detected in any case (Scheme 5).[14] Hence, we discarded possible mechanisms involving those intermediates.



L = (*t*BuXPhos); Additive: none, **B** (3 mol%),TBAB (1 equiv), LiBr (1 equiv) or TMSBr (2 equiv)

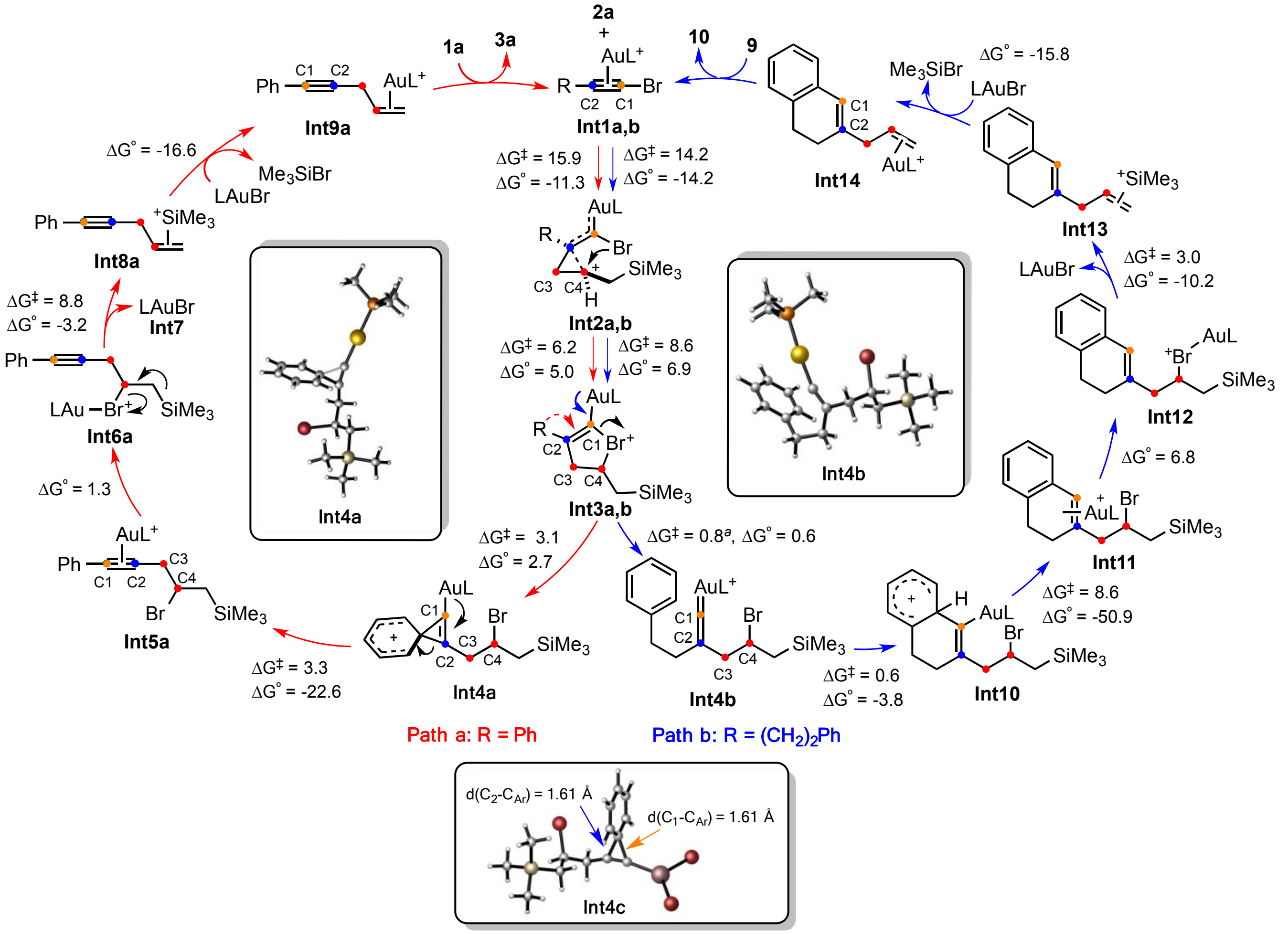
Scheme 5. Reactions with gold(I) acetylides.

To demonstrate the bromine migration, we conducted the reaction of **1a** with simple alkenes **13a-c** (Scheme 6A). In these reactions, homopropargyl bromides **14a-c** were obtained as major products as a result of a 1,2-bromoalkynylation of the alkenes. The high diasteroselectivity observed in the formation of **14b,c** suggests that the reaction occurs through a cyclic intermediate.[18] Finally, ^{13}C-labeled bromoalkyne **^{13}C-1a** was prepared and subjected to the reaction with allylsilane **2a** or alkene **13b** (Scheme 6B). Remarkably, in both **^{13}C-3a** and **^{13}C-14b** products, the ^{13}C carbon had migrated from the β- to the α-position with respect to the phenyl group.



Scheme 6. Experimental mechanistic investigations.

Considering all these experimental results, we examined the mechanism of the reactions of bromoalkynes **1a** and **9** with **2a** by means of DFT calculations (Scheme 7).[19] The most favored pathway involves the generation of cyclopropyl gold(I) carbenes **Int2a,b** (**a**: R = Ph; **b**: R = $(CH_2)_2Ph$), in which the gold(I) carbene is formed in β-position to the electron-donating R group and in α-position to electron-withdrawing bromine, in agreement with the previously observed tendency (Scheme 1A). In these intermediates, the partially cationic center at C4 is stabilized by the β-silyl group and can experience nucleophilic attack by the bromine to form cyclic bromonium intermediates **Int3a,b**. Depending on the nature of the R group, **Int3a,b** undergo ring opening to form different intermediates. The opening of **Int3a** (R = Ph) is assisted by the phenyl group to form **Int4a**, a vinylidenephenonium-gold(I) cation,[20] instead of a gold(I) vinylidene. Then, **Int4a** leads to **Int5a** in a highly exothermic step reminiscent of the Fritsch-Buttenberg-Wiechell rearrangement.[21] **Int5a** corresponds to the product of formal 1,2-bromoalkynylation of the alkene, as observed in products **14a-c** (Scheme 6A). Gold-promoted elimination of the bromide in **Int5a** *via* **Int6a** leads to bromide gold(I) complex **Int7** and skipped enyne **Int8a**, in which the trimethylsilyl group is still bound to the alkene.[14] Finally, the activation of the gold complex **Int7** with the trimethylsilyl derivative **Int8a** releases TMSBr along with (η^2-alkene)gold(I) complex **Int9a**,[14] which can turn over the catalytic cycle by ligand exchange to form **Int1a**. Thus, this reaction would afford 1,4-enyne **3a**, which is in agreement with the experimental results.



Scheme 7. Mechanism for the formation of 1,4-enyne 3a and cyclized product 10 based on DFT calculations. Free energies in kcal/mol. L = PMe_3. ^{a} The energy of $\mathbf{TS_{3b\text{-}4b}}$ was calculated by freezing the d(C1–Br). The value of this distance was taken from the previously optimized geometry of the corresponding TS with R = o-MeC_6H_4

The opening of **Int3b** (R = $(CH_2)_2Ph$) originates gold(I) vinylidene **Int4b**, which undergoes an intramolecular hydroarylation, *via* Wheland-type intermediate **Int10**, to form **Int11** (Scheme 7). Final gold(I)-promoted elimination of TMSBr *via* **Int12** gives **Int13**, and then **Int14**, which corresponds to the observed product **10** (Scheme 3B).

According to ^{13}C-labeling experiments, the indium-catalyzed transformations follow analogous mechanisms to that of the gold(I)-catalyzed reactions.[22] Indeed, DFT calculations with $InBr_2^+$ as the catalytic species show that the minimized structure for **Int4c** is even more distorted towards the vinylidenephenonium cation, with the phenyl being equidistant from C1 and C2 in a cyclopropene-like intermediate.

CONCLUSIONS

We have found that the gold(I)-catalyzed reaction of bromoalkynes with allylsilanes gives rise to 1,4-enynes by an unprecedented mechanism initiated by the formation of five-membered ring bromonium intermediates. Although this cyclic intermediate can give rise to gold(I) vinylidenes, in the case of aryl alkynes, vinylidenephenonium cations are formed and undergo a 1,2-aryl migration, bypassing the formation of gold(I) vinylidenes. These new reaction pathways could be the basis of the discovery of new transformations in electrophilic metal-catalyzed reactions of haloalkynes.

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Notes

No competing financial interests have been declared.

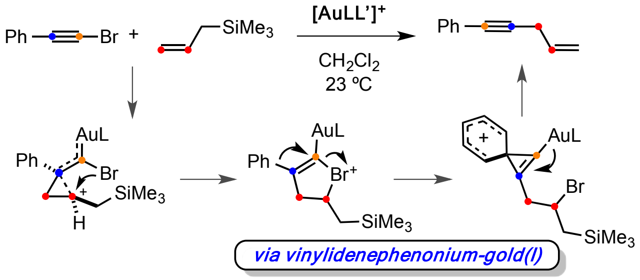
ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, characterization data, experimental and theoretical mechanistic studies (PDF).

ACKNOWLEDGMENTS

We thank the Agencia Estatal de Investigación (AEI)/FEDER, UE (CTQ2016-75960-P), Severo Ochoa Excellence Acreditation 2014-2018 (SEV-2013-0319, Severo Ochoa predoctoral fellowship to M.E.d.O. and Caixa-Severo Ochoa predoctoral fellowship to M.Z.), Juan de la Cierva postdoctoral fellowship (O.Q.), AGAUR (2017 SGR 1257) and CERCA Program/Generalitat de Catalunya for financial support.

TOC graphic



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(14) See Supporting Information for additional details.

(15) In the reaction of **1c** with **2a**, 1,4-enyne **3a** was obtained together with a mixture of 1-phenyl-2-trimethylsilylacetylene and allyliodide. This reaction did not take place in the absence of catalyst **B**. See Supporting Information for additional details.

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(18) See the Supporting Information (Scheme S4) for the mechanistic proposal.

(19) Calculations were performed with M06/6-31G(d) (C, H, P, Si) and LANL2DZ (Br, Au, In) in CH_2Cl_2 (SMD). See the Supporting Information for full computational details.

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