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Letter

Photoredox-Assisted Gold-Catalyzed Arylative Alkoxycyclization of 1,6-Enynes

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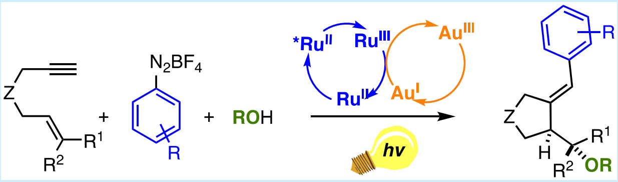
ABSTRACT: The photoredox-assisted gold-catalyzed arylative cyclization of 1,6-enynes with aryldiazonium salts gives rise to cyclization products with the opposite configuration at the alkene than that obtained by gold(I)-catalyzed alkoxycyclization. The reaction occurs under mild conditions and shows high functional group tolerance.

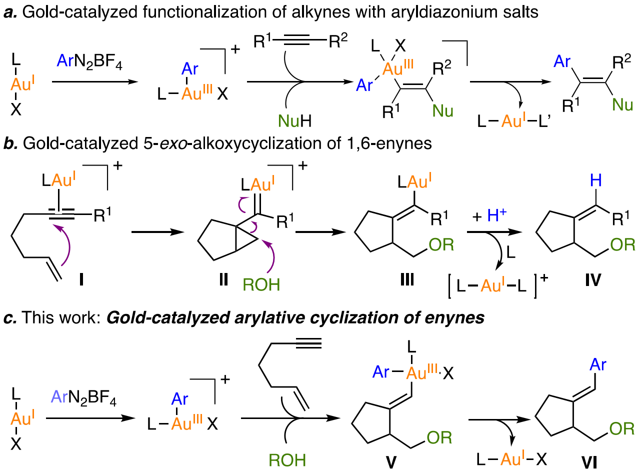


The carbophilic character of gold(I) complexes allows the selective activation of π-systems toward the attack of nucleophiles.[1] This reactivity has been widely studied and successfully applied for the construction of complex polycyclic structures including core scaffolds of natural products[2] and relevant organic materials.[3]

In the past decade, an increasing interest has emerged in employing gold complexes as catalysts for cross-coupling reactions.[4] However, the direct oxidative addition of commonly used electrophiles to gold(I) complexes is difficult, because of the relatively high redox potential of the couple (E^0(Au(I)/Au(III)) = 1.41 V).[5] This transformation can be promoted by using external oxidants, such as hypervalent iodine reagents or selectfluor, which limits the substrate scope to substrates that are stable under the oxidative conditions.[6] The Bourissou group discovered that gold(I) complexes with small-bite-angle bidentate ligands readily undergo oxidative addition of aryl halides.[7] An alternative approach was developed by the groups of Glorius and Toste, using the combination of aryldiazonium salts and a photocatalyst in the presence of visible light (Scheme 1a).[8] This catalytic system has allowed the development of several gold-catalyzed arylative reactions such as tandem rearrangement/arylations, nucleophilic addition/arylations, and cross-coupling reactions.[9] Recently, the group of Fensterbank discovered that the oxidative addition of iodoalkynes can readily happen to photosensitized gold(I) catalysts.[10]

The gold(I)-catalyzed alkoxycyclization of 1,6-enynes proceeds via the activation of the alkyne **I** the formation of a cyclopropyl gold(I) carbene intermediate **II**, the nucleophilic attack of an alcohol to form an alkenyl gold(I) complex **III**, and protodeauration to give the final product **IV** (Scheme 1b).[11] We wondered whether it would be possible to design a dual gold-catalyzed/photoredox-initiated process in which a Au(III) species generated oxidatively from Au(I) and an aryl diazonium salt, in the presence of an alcohol, would be able to activate the 1,6-enyne to form alkenyl gold(III) complex **V**, which would finally furnish product **VI** after reductive elimination (Scheme 1c).[12] To be successful, the 1,6-enyne cyclization should be faster than the previously described Sonogashira-type coupling[13] and the reductive elimination of **V** should be faster than the protodeauration.

Scheme 1. Gold-Catalyzed Functionalization of Alkynes



This strategy would expand the scope of gold-catalyzed enyne cyclizations, giving access to product **VI** with the opposite configuration at the alkene to that obtained via metal-catalyzed alkoxycyclization[11,14] and would complement other arylative cyclizations of enynes.[15]

We first screened different gold(I) catalysts for the transformation of enyne **1a** and PhN_2BF_4 into the desired

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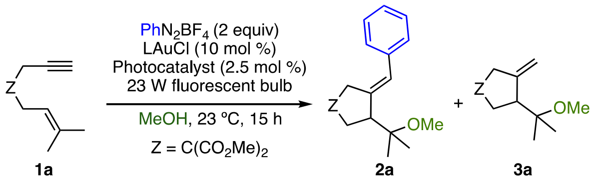
arylated product **2a** by irradiation with a 23 W fluorescent bulb in MeOH (see Table 1). Gold(I) complexes with arylphosphines in combination with $[Ru(bpm)_3]Cl_2$ as a photoredox catalyst (where bpm = 2,2′-bipyrimidine) led mainly to product **3a** of direct methoxycyclization (Table 1, entries 1−3). The selectivity toward **2a** improved by using a phosphite gold(I) complex (Table 1, entry 4), whereas IPrAuCl was ineffective (Table 1, entry 5). Interestingly, electron-rich trialkylphosphine gold(I) complexes proved to be the best catalysts for this reaction (Table 1, entries 6−13). Then, a screening of photocatalysts showed that commonly used $Ru(bpy)_3$ ($E_{1/2}^{\mathrm{III/*II}}$ = −0.81 V vs SCE) (Table 1, entries 9 and 10) worked less efficiently than the more oxidizing $Ru(bpm)_3$ ($E_{1/2}^{\mathrm{III/*II}}$ = −0.21 V vs SCE) (Table 1, entry 8) or $Ru(bpz)_3$ ($E_{1/2}^{\mathrm{III/*II}}$ = −0.26 V vs SCE) (Table 1, entry 11).[16] The optimal results were finally obtained when Me_3PAuCl and $[Ru(bpz)_3](PF_6)_2$ were used in a mixture of MeOH/ACN (1/1), at −15 °C, affording **2a** in 83% isolated yield (Table 1, entry 12).[17] Decreasing the amount of catalyst to 5 mol % led to lower yield (Table 1, entry 13).

Table 1. Formation of 2a from 1,6-Enyne 1a with Different Gold(I) Catalysts and Ru(II) Photocatalysts[a]

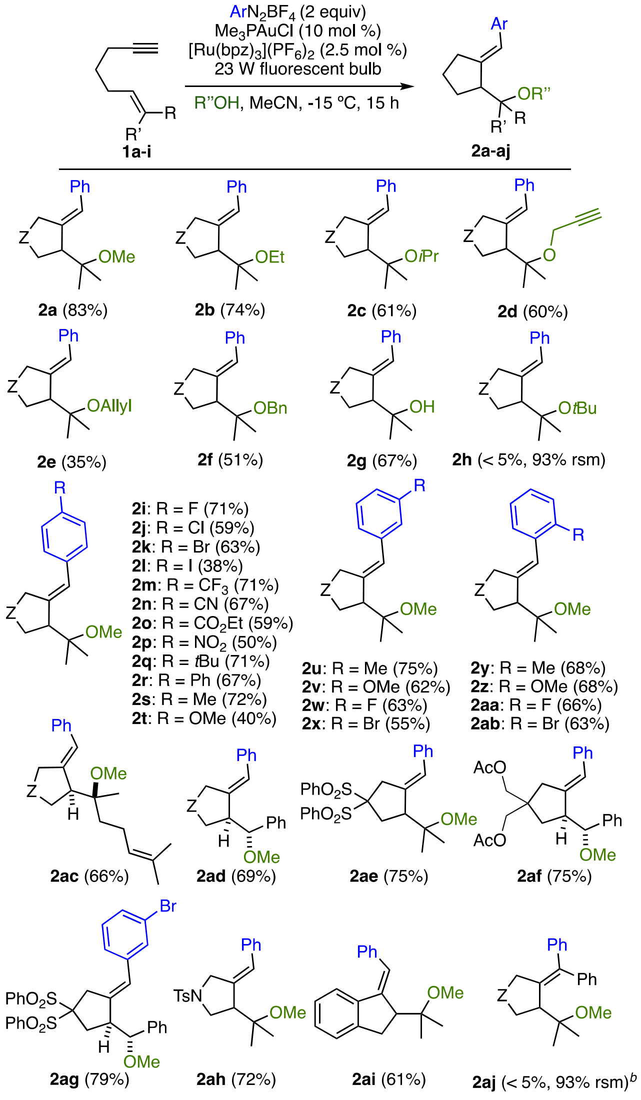


entry	catalyst	photocatalyst[b]	2a[c] (%)	3a[c] (%)
1	Ph_3PAuCl	$[Ru(bpm)_3]Cl_2$	21	46
2	$Ph_3PAuNTs_2$	$[Ru(bpm)_3]Cl_2$	24	51
3	JohnphosAuCl	$[Ru(bpm)_3]Cl_2$	−	42
4	$(MeO)_3PAuCl$	$[Ru(bpm)_3]Cl_2$	28	10
5	IPrAuCl	$[Ru(bpm)_3]Cl_2$	−	8
6	Cy_3PAuCl	$[Ru(bpm)_3]Cl_2$	54	20
7	Et_3PAuCl	$[Ru(bpm)_3]Cl_2$	68	15
8	Me_3PAuCl	$[Ru(bpm)_3]Cl_2$	70	11
9	Me_3PAuCl	$[Ru(bpy)_3]Cl_2$	61	5
10	Me_3PAuCl	$[Ru(bpy)_3](PF_6)_2$	59	14
11	Me_3PAuCl	$[Ru(bpz)_3](PF_6)_2$	72	10
12[d]	Me_3PAuCl	$[Ru(bpz)_3](PF_6)_2$	90 (83)[e]	−
13[d,f]	Me_3PAuCl	$Ru(bpz)_3](PF_6)_2$	74	3

[a] The product of Sonogashira coupling was observed by ^1H NMR (<10% yield). [b] bpm = 2,2′-bipyrimidine; bpy = 2,2′-bipyridine; bpz = 2,2′-bipyrazine. [c] Yields determined by ^1H NMR (3,5-dimethylpyrazole as internal standard). [d] Reaction under optimized conditions: 0.04 M, −15 °C, MeOH/MeCN (1:1) as a solvent. [e] Isolated yield. [f] 5 mol % of Me_3PAuCl.

Different alcohols could be used in the arylative cyclization under the optimized conditions to form products **2a**−**2f** (Scheme 2). Interestingly, the addition of propargylic alcohol led to **2d** in 60% yield, without the formation of other products from the activation of the new terminal alkyne. Reaction in the presence of water led to alcohol **2g**. The reaction is sensitive to the steric hindrance of the alcohol since *i*PrOH led to product **2c** in 61% yield, whereas only traces of **2h** could be obtained in the presence of *t*-BuOH. A range of aryldiazonium salts with electronically different substituents at the *ortho*-, *meta*-, and *para*-positions led to the corresponding products of arylation **2i**−**2ab** in 38%−75% yields. In the case of the electron-donating OMe substituent, we observed a decrease of the yield when placed at the *para*-position (**2t**, 40%), compared to its *meta* and *ortho* analogues (**2v**, 62% yield and **2z**, 68% yield, respectively).

Scheme 2. Arylative Cyclization of 1,6-Enynes 1a−1i[a]

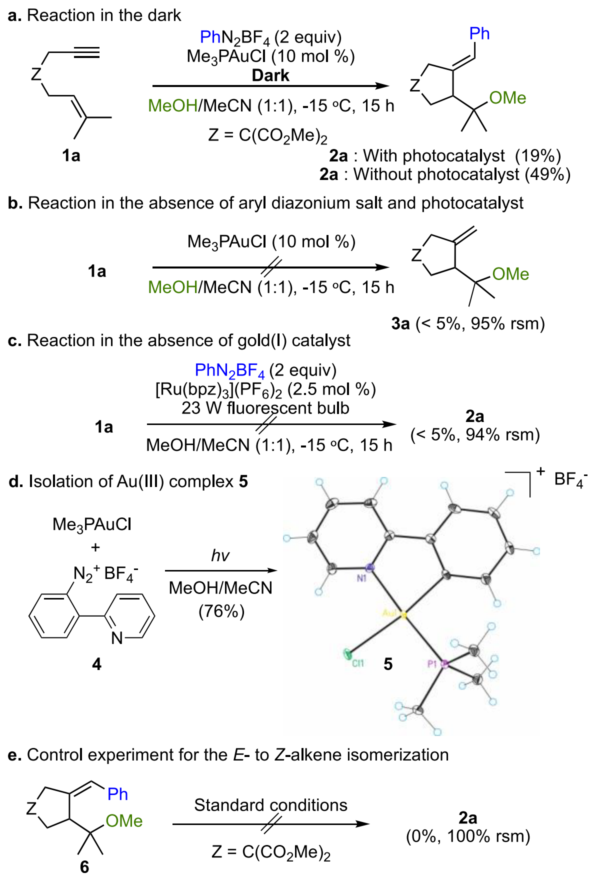


[a] Z = $C(CO_2Me)_2$. [b] Reaction at 30 °C.

Other 1,6-enynes **1b**−**1h** with differently substituted alkenes also led to the expected products **2ac**−**2ai** in 61%−79% yields (Scheme 2). However, 1,6-enyne **1i** with a phenyl-substituted internal alkyne failed to give **2aj**, even at 30 °C.

Several experiments were performed to elucidate the mechanism of the arylative cyclization (Scheme 3). First, an experiment in darkness was conducted with and without Ru(II) photocatalyst (reactions fully covered with aluminum foil) (Scheme 3a). To our surprise, product **2a** was obtained in 19% and 49% yields, respectively, showing that gold catalytic turnover could happen in the absence of the photocatalytic cycle. The thermal decomposition of diazonium salts into the corresponding aryl radicals or the direct interaction between Au(I) catalyst and the radical precursor[18] could explain these results, which are consistent with the different reports of photocatalyst-free visible-light-mediated gold-catalyzed arylations of alkynes.[19] However, all our attempts at developing a

Scheme 3. Control Experiments and Formation of Au(III) Complex 5


a. Reaction in the dark

b. Reaction in the absence of aryl diazonium salt and photocatalyst

c. Reaction in the absence of gold(I) catalyst

d. Isolation of Au(III) complex 5

e. Control experiment for the *E*- to *Z*-alkene isomerization

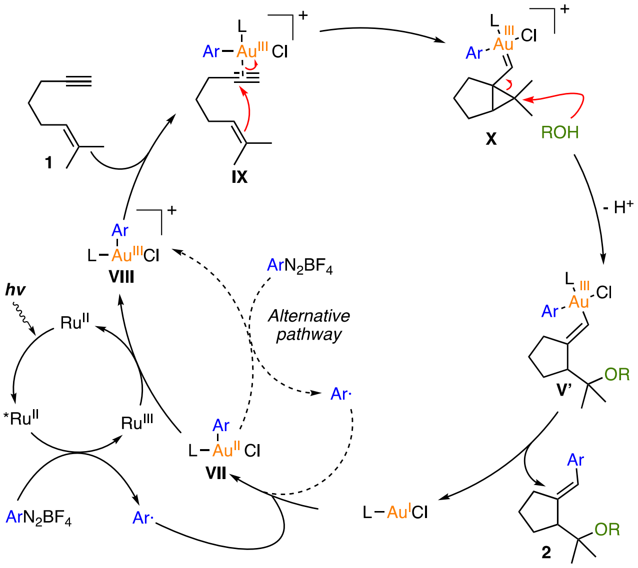
photosensitizer-free version of the reaction led to lower yields and complex reactions mixtures,[17] showing the importance of this latter concept. Furthermore, the presence of photocatalyst lowers the performance of the reaction, which could be rationalized by catalyst inactivation by coordination of gold with the basic 2,2′-bipyrazine (bpz) ligand.

Next, we examined at which stage the oxidation of gold(I) to gold(III) occurs.[20] In our system, Me_3PAuCl was not able to activate the alkyne, leading to recovered starting enyne **1a** in 95% (Scheme 3b), and, as expected, no reaction occurred in the absence of gold(I) complex (Scheme 3c). These experiments suggest that the oxidation of gold(I) precedes enyne cyclization, pointing toward the involvement of an Ar–Au(III) species as the actual catalyst of the cyclization. Indeed, reaction of Me_3PAuCl with diazonium salt **4** led to the formation of gold(III) complex **5**, whose structure was determined by X-ray diffraction (Scheme 3d).[21] This result reinforces the idea of a direct interaction between the gold catalyst and the diazo compound.

The alkoxycyclization of 1,6-enynes bearing internal alkynes occurs with Pt(II)[22] or Au(I).[11] On the other hand, the arylation of terminal alkynes with diazonium salts by dual gold/photoredox-catalyzed is a known process.[13] Therefore, we considered the possibility that our system proceeds via a Sonogashira-type coupling of the alkyne of enynes **1**, followed by a gold-catalyzed enyne alkoxycyclization and isomerization of the aryl-substituted alkene. However, compound **6** with a *Z*-configured alkene, prepared using our previously reported procedures,[11,17] did not undergo *Z* to *E* isomerization to form **2a** and was recovered quantitatively after being subjected to the optimized reaction conditions (Scheme 3e).[23]

Based on these control experiments and previous reports,[21,24] a mechanistic proposal for the gold-catalyzed arylative cyclization of enynes is depicted in Scheme 4. Thus,

Scheme 4. Proposed Mechanism for the Arylative Cyclization



the aryl radical generated upon reduction of the diazonium salt in the photoredox cycle adds to Au(I) complex to form Au(II) intermediate **VII**, which is further oxidized to Au(III) complex **VIII** through SET from the photocatalyst or another diazonium salt (radical chain pathway). Next, coordination of the 1,6-enyne **1** provides **IX**, which undergoes a 5-*exo*-dig cyclization to form **X**, followed by addition of the alcohol to generate intermediate **V′**. Finally, reductive elimination delivers the desired product **2** and regenerates the initial Au(I) complex. A similar mechanism in which the Au(III) intermediate is obtained without the need of the photocatalyst could also be considered.

In conclusion, we have developed a photoredox-initiated gold-catalyzed arylative alkoxycyclization of 1,6-enynes with aryldiazonium salts in the presence of alcohols. This three-component reaction leads to five-membered ring compounds bearing an exocyclic alkene with the opposite configuration to that obtained by gold(I)-catalyzed cyclizations. Mechanistic investigations suggest that the catalytic cycle starts with the stepwise oxidative formation of a gold(III) species, which triggers the 5-*exo*-alkoxycyclization of the 1,6-enyne.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00799.

Experimental procedures and characterization data for compounds (PDF)

Accession Codes

CCDC 1987486 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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