Gold Catalysis Hot Paper

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Cyclization of Gold Acetylides: Synthesis of Vinyl Sulfonates via Gold Vinylidene Complexes**

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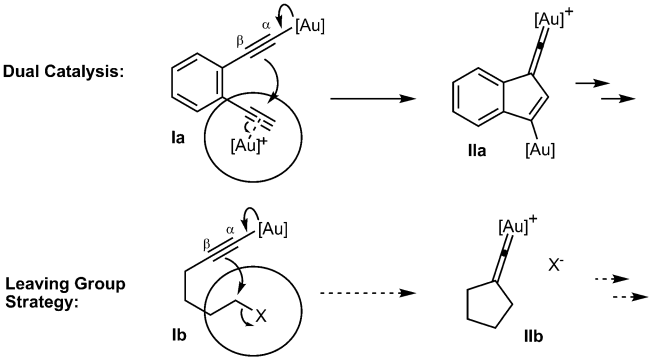
Abstract: *Differently substituted terminal alkynes that bear sulfonate leaving groups at an appropriate distance were converted in the presence of a propynyl gold(I) precatalyst. After initial formation of a gold acetylide, a cyclization takes place at the β-carbon atom of this species. Mechanistic studies support a mechanism that is related to that of dual gold-catalyzed reactions, but for the new substrates, only one gold atom is needed for substrate activation. After formation of a gold vinylidene complex, which forms a tight contact ion pair with the sulfonate leaving group, recombination of the two parts delivers vinyl sulfonates, which are valuable targets that can serve as precursors for cross-coupling reactions, for example.*

Homogeneous gold catalysis is dominated by the electrophilic π-activation of a multiple bond as the initial step. Based on this principle, numerous fruitful reports contributed to an enormous boom in gold catalysis.[1]

Significantly less examples exist for the nucleophilic activation of alkynes. Thus far, this reactivity was mostly studied with gold acetylides, which reacted in a Grignard-like fashion at their α-carbon atom.[2] Recently, Zhang's and our group independently discovered a new reactivity pattern, which is based on a dual activation principle.[3] This approach uses diyne systems, such as **Ia**, in which one of the alkyne moieties is electrophilically activated by π-coordination, while the second alkyne is activated by σ-coordination, which leads to an enhanced nucleophilicity. Depending on the backbone, this synergy allows the formation of vinylidene or carbene intermediates that enable a rich follow-up chemistry, which gives access to interesting polycyclic structures (Scheme 1).



Scheme 1. Dual activation pathway leading to vinylidenes (top) and strategy for the synthesis of vinylidenes based on acetylides and a leaving group (bottom).

Inspired by these findings, we wondered whether the π-activated alkyne could be replaced with suitable other electrophiles. This should enable a completely new access to gold vinylidene complexes. As a leaving group replaces the π-activated alkyne in this approach, we assumed that no cationic gold source should be necessary for the generation of vinylidenes of type **IIb**. Related transformations are known for X = I or X = OSO_2Ar and are either initiated by the formation of ate complexes of boron[4] or zinc[5] or by the formation of lithium acetylides.[6] Because of the high reactivity of the applied precursors, these reactions have to be performed in dry solvents, and nucleophilic addition of the starting metal acetylides onto the intermediates can lead to undesired side reactions. Herein, we report the first cyclization of gold acetylides into gold vinylidene intermediates that does not rely on the principle of dual activation. Owing to the properties of the gold catalyst, the reactions can be performed in air, and they are insensitive to moisture.

Inspired by the work of Harada and co-workers, who could cyclize a variety of hexynyl tosylates, such as **1a**, via the corresponding lithium acetylides,[6a] we used **1a** as a test system for a possible gold-catalyzed process. As mentioned earlier, only the σ-activation should be addressed by the gold catalyst; therefore, we used gold propyne acetylides as precursors that do not form cationic gold complexes. After ligand exchange with the starting material, a σ-activated substrate should be formed along with propyne as a volatile and labile throw-away ligand. Indeed, heating **1a** in benzene at reflux in the presence of [IPrAu(propynyl)] **3a** (5 mol%; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) efficiently delivered vinyl tosylate **2a** (Scheme 2).

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[+] Crystallographic investigation.

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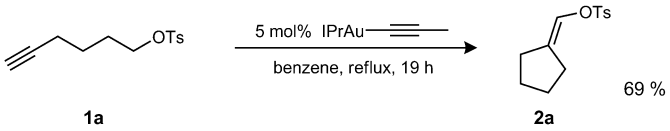
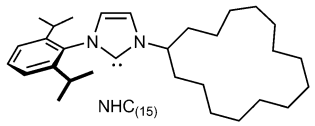


Scheme 2. Transformation of tosylate **1a** in the presence of [IPrAu(propynyl)] (**3a**; 5 mol%). Ts = tosyl = 4-toluenesulfonyl.

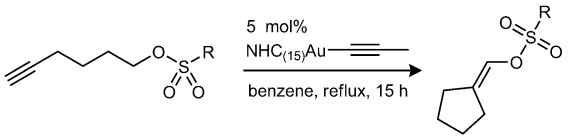
An optimization of the reaction conditions[7] revealed that gold propyne acetylide **3a** was superior to the corresponding methyl or phenyl gold complexes as well as to [IPrAuOH].[8] Next, we performed a ligand screening; unsaturated $NHC_{(15)}$



ligand **3b**[9] turned out to be the best candidate (NHC = N-heterocyclic carbene; $NHC_{(15)}$ bears a cyclopentadecyl substituent on one of the nitrogen atoms). Different solvents were screened, but the yields dropped significantly in other reaction media. A control experiment without any catalyst showed no conversion; the addition of catalytic amounts of *p*-TsOH also led to no reaction. A radical pathway can be excluded as no drop in reactivity was observed when 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) was added as a radical inhibitor.[7]

With the optimized conditions in hand (5 mol% **3b**, benzene, reflux), we set out to investigate the scope of this transformation. First, we tested different sulfonate moieties. As shown in Table 1, sulfonates with aromatic substituents

Table 1: Gold-catalyzed cyclization of hexynyl sulfonates.[a]



Entry	R	Starting material	Product	Yield [%]
1	*p*-MeC_6H_4	**1a**	**2a**	92
2	*p*-BrC_6H_4	**1b**	**2b**	88
3	*p*-$NO_2C_6H_4$	**1c**	**2c**	53
4	*p*-$MeOC_6H_4$	**1d**	**2d**	84
5	mesityl	**1e**	**2e**	93
6	Me	**1f**	**2f**	72

[a] All reactions were performed in benzene (150 mM) at reflux with **3b** (5 mol%). All yields refer to isolated products.

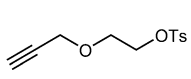
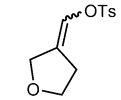
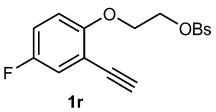
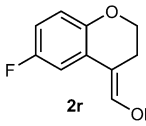
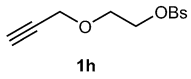
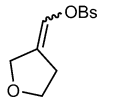
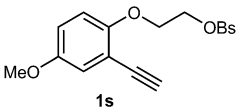
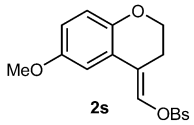
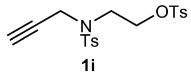
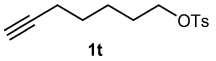
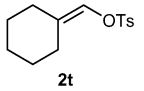
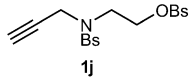
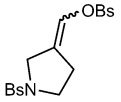
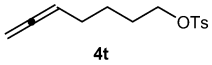
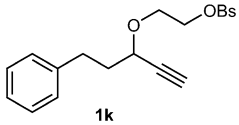
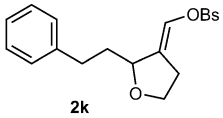
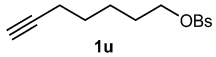
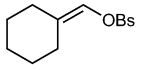
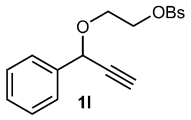
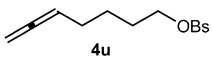
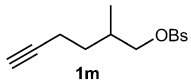
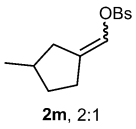
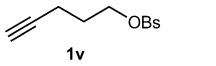
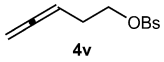
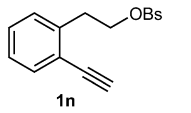
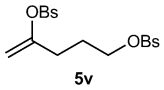
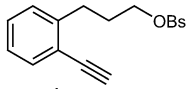
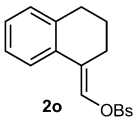
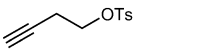
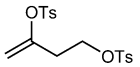
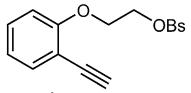
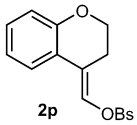
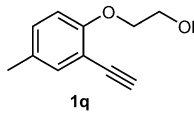
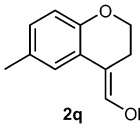
delivered the corresponding products in good to excellent yields, only a *p*-NO_2 substituent resulted in a slightly lower yield (entry 3). Mesylate (OMs = methanesulfonate) as an aliphatic substituent was also suitable, and the corresponding product **2f** could be obtained in 72% yield (entry 6).

For product **2b**, single crystals that were suitable for X-ray crystallography[7,10] could be obtained; therefore, the structural assignment of a cyclopentylidene ring with an exocyclic double bond could be confirmed. Unfortunately, attempts to perform this reaction with halides as the leaving group were unsuccessful.

Next, we tested differently substituted alkynyl sulfonates (Table 2). With ether derivatives instead of the alkyl tethers, longer reaction times were observed, and the yields were only moderate (entries 1 and 2). As the presence of the ether linkage breaks the symmetry of the cyclopentylidene ring, the products were obtained as mixtures of diastereoisomers, favoring the *E* isomers (assigned by $^1H,^1H$ NOESY NMR spectroscopy). The corresponding substrates with a sulfonamide group in the chain were also investigated. Whereas no reactivity was observed with the tosyl-substituted substrate **1i** (entry 3), switching to the brosylate (OBs = *para*-bromobenzenesulfonate) leaving group delivered the desired product **2j** in 83% yield as a 4:1 mixture of diastereoisomers (entry 4). Based on the higher reactivity that was observed for the brosylate substrates, we performed further studies with this leaving group. As a next step, we investigated substrates with an additional substituent at the propargylic position. A phenethyl substituent not only increased the reaction rate and yield, but also led to the exclusive formation of the sterically less hindered *E* isomer (entry 5). It is noteworthy that the competing CH insertion reaction was not observed. A completely different picture was obtained with a directly attached phenyl group. Most probably because of the highly activated propargylic/benzylic ether position, decomposition of the starting material was observed under the reaction conditions (entry 6). The branched alkyl substrate **1m**, which does not bear additional heteroatoms, was also investigated. The cyclized product **2m** was obtained in good yield, but again as a mixture of diastereoisomers (entry 7). Next, we evaluated whether this transformation would be possible for systems with aromatic moieties as part of the tether. Unfortunately, substrate **1n**, which bears a tether with six carbon atoms, was not converted into the analogous annulated cyclopentylidene, and only incomplete conversion was observed, along with an unselective transformation (entry 8). Whereas the expected reactivity was restored by increasing the chain length, problems still occurred with unfunctionalized substrate **1o** (entry 9). Aside from incomplete conversion, the final product turned out to be fairly unstable. Fortunately, the introduction of an oxygen atom into the phenolic substrates **1p**–**1s** delivered the stable products **2p**–**2s**, which could be isolated in good yields (entries 10–13). Crystal structure analysis of compound **2p** confirmed the constitution of the target compound as well as the *E* geometry of the exocyclic double bond.[7,10]

Finally, we tested different chain lengths for the open-chain substrates as well (entries 14–17). The formation of six-membered rings was possible, but longer reaction times were required than for the formation of the corresponding cyclopentylidene rings. For both leaving groups, allenes **4t** and **4u** were isolated as side products in small amounts (entries 14 and 15). Derivative **1v** did not undergo cyclization; instead, allene **4v**, along with the HOBs addition product **5v**,[11] was obtained (entry 16). The structure of **5v** could be confirmed by X-ray crystal structure analysis.[7,10] A similar result was obtained for butynyl derivative **1w** (entry 17). In this case, the analogous HOTs addition product **5w** was isolated together

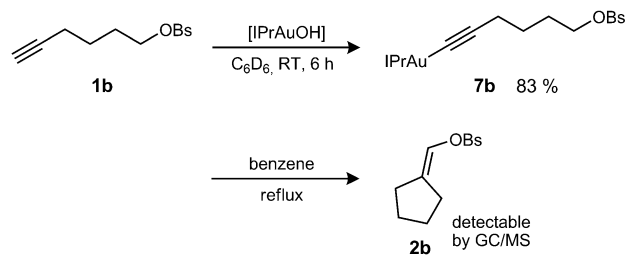
Table 2: Gold-catalyzed cyclization of substituted 1,*n*-yne sulfonates.[a]

Entry	Starting material	Product	*t*	Yield [%]	Entry	Starting material	Product	*t*	Yield [%]
1	 **1g**	 **2g**, *E*/*Z* 2.5:1	6 days	21	12	 **1r**	 **2r**	48 h	77
2	 **1h**	 **2h**, *E*/*Z* 2.5:1	39 h	53	13	 **1s**	 **2s**	15 h	78
3	 **1i**	**2i** not formed	15 h	–	14	 **1t**	 **2t**	87 h	49
4	 **1j**	 **2j**, *E*/*Z* 4:1	39 h	83			 **4t**	87 h	12
5	 **1k**	 **2k**	15 h	65	15	 **1u**	 **2u**	63 h	54
6	 **1l**	decomposition, **2l** not formed	15 h	–			 **4u**	63 h	12
7	 **1m**	 **2m**, 2:1	15 h	79	16	 **1v**	 **4v**	21 h	22
8	 **1n**	incomplete conversion into **2n**, unselective	64 h	–			 **5v**	21 h	32
9	 **1o**	 **2o**	64 h	25[b]	17	 **1w**	 **5w**	15 h	33
10	 **1p**	 **2p**	15 h	82			 **6w**	15 h	16
11	 **1q**	 **2q**	15 h	85					

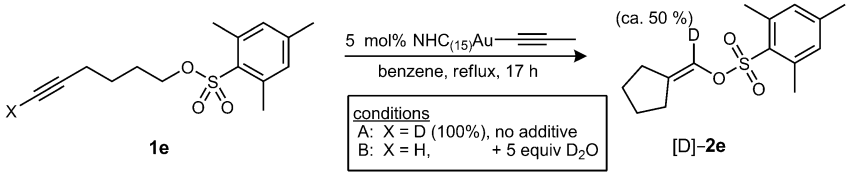
[a] All reactions were performed in benzene (150 mM) at reflux with **3b** (5 mol%). All yields refer to isolated products. [b] 16% of the starting material could be re-isolated.

with diene **6w**, which was most probably formed by elimination of the tosylate group of compound **5w**.

Our next experiments were aimed at investigating the reaction mechanism. First, we isolated acetylide **7b** by reacting substrate **1b** with [IPrAuOH] (1 equiv) at room temperature (see the Supporting Information for the solid-state molecular structure).[8a,10] Heating of **7b** to 80 °C indeed resulted in the formation of product **2b,** which was confirmed by GC/MS and thin-layer chromatography (TLC). Unfortunately, no aurated intermediate could be isolated, and the stoichiometric reaction turned out to be less selective than the catalytic process (Scheme 3).



Scheme 3. Stoichiometric reaction of gold acetylide **7b**.



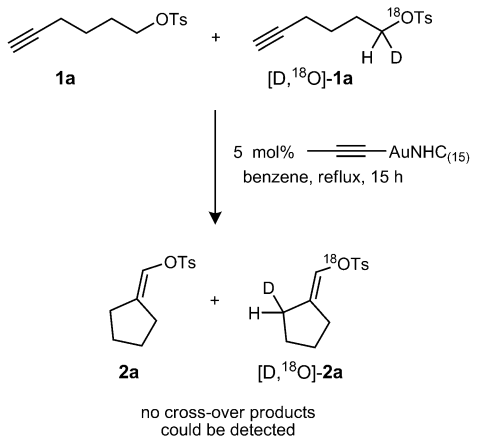
Scheme 4. Labeling experiments.

Next, we synthesized substrate [D]-**1e** with a deuterium label at the terminal alkyne position (Scheme 4, conditions A). After conversion under the optimized conditions, 50% of the deuterium had been transferred to the vinylic position of the product. This indicates that after the cyclization, a vinyl gold complex is formed, which then transfers the catalyst onto the next substrate molecule with simultaneous release of the product.[3b] A control experiment with non-deuterated substrate **1e** in the presence of D_2O (5 equiv) also led to a deuterium incorporation of 50% at the vinylic position (Scheme 4, conditions B). This uptake of deuterium can be rationalized by exchange processes that take place at the terminal alkyne position prior to cyclization. It is also possible that protodeauration of the vinyl gold intermediate by traces of water competes with the catalyst transfer.

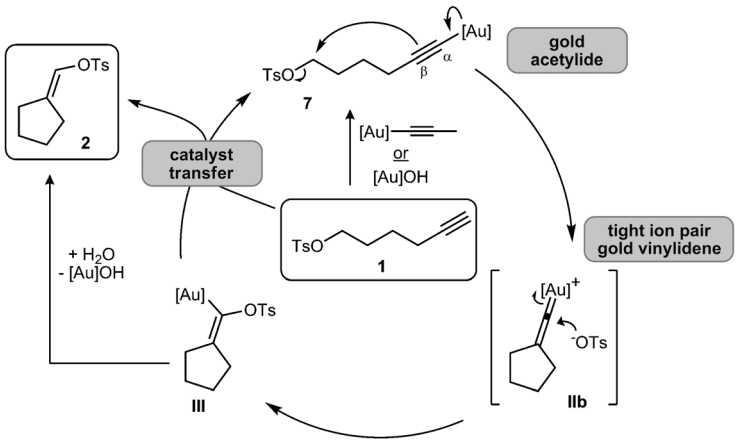
A cross-over experiment was conducted to investigate whether the recombination of the sulfonate anion with the gold vinylidene species is an inter- or an intramolecular process. We therefore synthesized substrate [D,^{18}O]-**1a** with deuterium and ^{18}O labels.

The complete conversion of a 1:1 mixture of labeled compound [D,^{18}O]-**1a** and non-labeled **1a** under the optimized conditions was confirmed by TLC and GC/MS analysis. The absence of cross-over products was affirmed by mass spectrometry (EI(+)/MS; Scheme 5). This indicates that the sulfonate counterion and the respective gold vinylidene complex must be in close contact during the reaction. This could either be due to the formation of a tight ion pair in the hydrocarbon solvent or arise from the fact that when the C–O bond of the starting material is broken, the sulfonate group directly rebinds to the forming vinylidene complex in an intramolecular fashion through one of its sulfonyl oxygen atoms. However, the latter possibility could be ruled out by the transformation of ^{18}O-labeled substrate [^{18}O]-**1a**, which resulted in the scrambling of the ^{18}O label in the product (see the Supporting Information, Scheme S1).

Based on these findings, our proposed mechanism for the cyclization is depicted in Scheme 6. Some of the key elementary steps parallel those from Zhang's and our work on the dual activation mode.[3a,b] The reaction cascade is initiated by catalyst transfer from the gold propyne acetylide onto the starting material. The resulting acetylide **7** then cyclizes through substitution of the sulfonate leaving group by its β-carbon atom, which leads to gold vinylidene intermediate **IIb**. The so-formed contact ion pair of the gold vinylidene complex and the sulfonate counterion then recombines, forming the vinyl gold species **III**. The catalytic cycle is completed either by another catalyst transfer onto the next substrate molecule (which places a deuterium at the vinylic position when a deuterated alkyne is used as the starting material) or, as water is not excluded, by protodeauration to form product **2** and a gold hydroxide complex,



Scheme 5. Cross-over experiment.



Scheme 6. Proposed reaction mechanism. OTs is used as a representative for the sulfonate leaving groups.

which then initiates another cycle by reformation of acetylide **7**. The formation of allenes in a side reaction remains unclear. Attempts to obtain the allenes by elimination from the HOBs addition product **4v** were unsuccessful,[7] which excludes a trivial explanation. Further investigations concerning the allene formation are ongoing in our laboratories.

The potential of the obtained products as synthetic building blocks for cross-coupling reactions was quickly demonstrated by a Suzuki coupling of vinyl tosylate **2a** with phenylboronic acid, which delivered the desired coupling product in an acceptable yield of 61% without any optimization.

In summary, we could demonstrate that the formation of gold vinylidene intermediates is also possible by the cyclization of gold acetylides alone and therefore not strictly dependent on a dual activation mode. The cyclization presented herein works well for a range of differently substituted sulfonates and leads to interesting products with a vinyl sulfonate moiety, which allows for further functionalization by cross-coupling reactions. Further investigations concerning the mechanism as well as the formation of the observed side products are currently underway.

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