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The Reactivity of 4-Hydroxy- and 4-Silyloxy-1,5-allenynes with Homogeneous Gold(I) Catalysts

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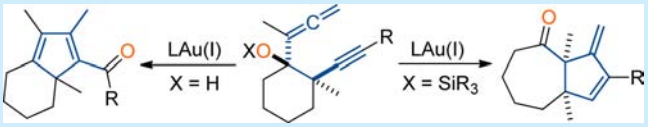
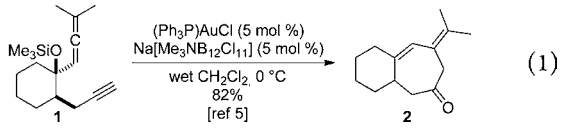
Supporting Information

ABSTRACT: Two new gold(I)-catalyzed cascade reactions of 4-hydroxy- and 4-silyloxy-1,5-allenynes are disclosed, offering access to a variety of mono- and bicyclic, polyunsaturated carbonyl compounds. The diverse reactivity observed for the investigated allenyne system is controlled by the nature of the unsaturated substrate: Allenynes bearing a free hydroxyl group engage in what is likely an oxycyclization/allene-ene carbocyclization cascade, while their silylated analogues are converted through a carbocyclization/pinacol-type rearrangement process.



The manipulation of allenynes has emerged as a useful tool in the synthesis of complex small molecules as their diverse reactivity is being exploited in an ever-growing spectrum of transformations. Thus, allenynes are being widely employed as substrates in cycloaddition[1,2] as well as other carbocyclization reactions,[3] including cycloisomerization processes catalyzed by platinum or gold π-acid catalysts that allow elegant access to a variety of valuable (poly)cyclic structures.[4]

We recently embarked on an investigation of transition-metal-catalyzed transformations of silyloxy-1,6-allenynes, in the course of which we found that a gold(I) catalyst can effect the reaction of 1,6-allenynes such as **1** (eq 1).[5] Coinciding with these studies,

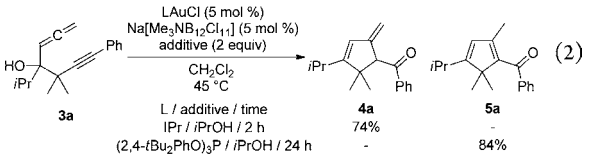


(1)

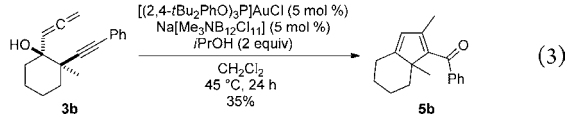
the sodium salt of the *closo*-dodecaborate $[Me_3NB_{12}Cl_{11}]^-$ was introduced as an effective reagent for the *in situ* activation of ligated gold(I) chlorides.[5,6] Due to the fact that this reagent circumvents general issues associated with common silver salt activators[7] and proved highly reliable in a broad spectrum of reactions, we continue to employ it as a standard means of activation in gold(I)-catalyzed reactions, as we did in the work herein.

Following our results with 1,6-allenynes, we next turned the focus to the catalyzed cyclization of 1,5-allenynes bearing either hydroxyl or silyloxy groups. Hydroxylated 1,5-allenynes have previously been engaged in several catalyzed transformations such as cycloisomerizations[4k] and a cascade process involving a Heck reaction;[8] in addition, they have been used as precursors for benzene derivatives.[9] In this paper, we report two previously undisclosed transformations of synthetic value: (a) 1,5-allenynes bearing a free hydroxyl group can be converted through an oxycyclization/carbocyclization cascade, and (b) their silylated analogues are converted through a carbocyclization/pinacol-type rearrangement process.

In our initial experiments with 1,5-allenynes, we found that, when subjecting allenyne **3a** to $(Ph_3P)AuCl$ and $Na[Me_3NB_{12}Cl_{11}]$ in boiling CH_2Cl_2, an inseparable mixture of cyclopentene isomers **4a** and **5a** bearing a benzoyl group was slowly formed (eq 2). Further screening revealed that, using



(2)



(3)

(IPr)AuCl as a precatalyst in the presence of *i*PrOH, full conversion was reached after 2 h under the exclusive formation of product **4a** featuring an exocyclic double bond in 74% yield. In comparison, when $[(2,4\text{-}tBu_2PO)_3P]AuCl$ was employed under otherwise identical conditions, cyclopentadiene **5a** could be obtained as the only product in 84% yield after 24 h. More details on the optimization are given in the Supporting Information. We note that performing this reaction with a reduced catalyst loading of 1.5 mol % $[(2,4\text{-}tBu_2PO)_3P]AuCl$ resulted in complete conversion after 24 h and isolation of the cyclization product in 91% yield, but as a mixture of isomers **4a** and **5a**.

As eq 3 shows, it was found that the phosphite-ligated gold(I) precatalyst effects the direct formation of [3,4]-fused cyclopentadiene **5b** in moderate 35% yield starting from cyclic allenyne **3b**.[10] However, using the (IPr)Au(I) precatalyst proved far more effective; as outlined in Scheme 1, allenynes **3b**–**d** could be reacted to the corresponding cyclopentenes **4b**–**d**, and in all cases as a single diastereomer. The relative configuration was

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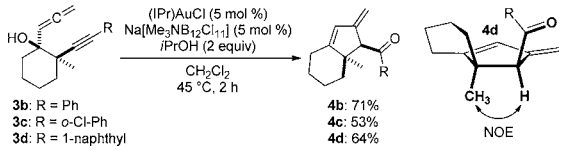
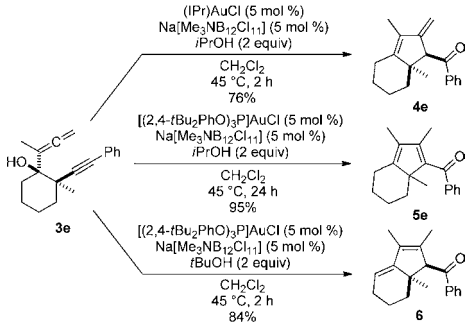
Scheme 1. Reaction of Cyclic Substrates 3b–d



unequivocally confirmed by NOESY-NMR experiments with the example of **4d**; **4b** and **4c** were assigned accordingly.

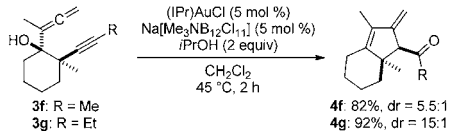
When subjecting substrate **3e**, which bears an additional methyl substituent on the allene moiety, to different reaction conditions, we found that even three different double bond isomers of the cyclization product can be accessed in a fully controlled way (Scheme 2). The expected products **4e** and **5e** are

Scheme 2. Reaction of Allenyne 3e to Various Cyclopentene Double Bond Isomers



formed under the respective conditions established above; however, using the phosphite-ligated gold(I) precatalyst in the presence of *t*BuOH gave the unexpected isomer **6**.

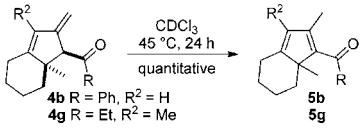
This reaction is not limited to substrates with aryl substituents on the alkyne moiety (eq 4). By use of **3f** and **3g**, the bicyclics **4f**



(4)

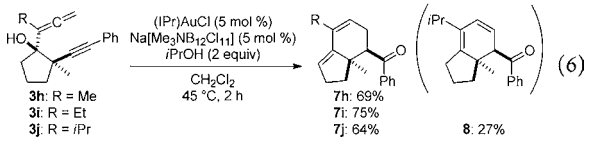
and **4g** respectively carrying acetyl and propionyl groups were formed; however, in both instances we observed the formation of an additional minor diastereomer, significantly so only in the case of the acetylated product **4f** (dr = 5.5:1).

It merits note that cyclopentadienes **5** can generally be accessed from cyclopentenes **4** by simple isomerization. This was demonstrated by stirring isolated cyclization products **4b** and **4g** in $CDCl_3$ at 45 °C for 24 h (eq 5). In both cases, [3,4]-fused cyclopentadienes **5b** and **5g**, respectively, were formed in quantitative yields as evidenced by ^{1}H NMR.



(5)

We were surprised to find that the reaction of cyclic substrates **3h–j** bearing five-membered rings did *not* provide cyclopentadiene or cyclopentene products. Instead, cyclohexenes **7h–j** were formed in good yields (eq 6). In the instances of substrates **3h** and **3i**, traces of a byproduct were observed but never isolated; in the case of substrate **3j**, however, this

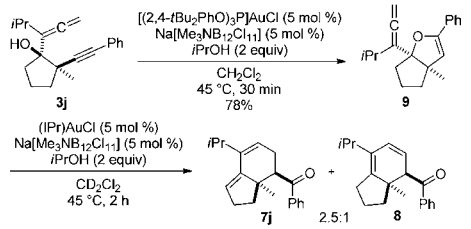


(6)

byproduct was formed in more significant amounts (27% compared to 64% of the major product) and, upon isolation, could be identified as cyclohexadiene **8**. Prolonged stirring of the reaction mixture revealed that no isomerization toward either product takes place.

An apparent key intermediate in these transformations was discovered when we reacted allenyne **3j** with the [(2,4-*t*Bu$_2$PO)$_3$P]Au(I) catalyst: The substrate was quickly consumed, and heterocyclization product **9** could be isolated in 78% yield (Scheme 3). An extended period of stirring under these

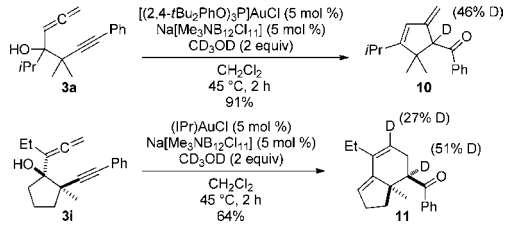
Scheme 3. Isolation of Intermediate 9 and Subsequent Cyclization to 7j and 8



conditions led to further consumption of dihydrofuran **9**, and cyclohexene **7j** could be isolated, albeit in poor yield. However, subjecting dihydrofuran **9** to the (IPr)Au(I) catalyst in an NMR experiment revealed a clean formation of **7j** and **8** as the only products, confirming dihydrofuran **9** as a likely intermediate in the direct reaction **3j** → **7j**/**8**.

To gain further understanding regarding the mechanism, we conducted deuteration experiments with **3a** and **3i** by employing deuterated methanol (Scheme 4). In the case of **3a**, deuterium

Scheme 4. Deuteration Experiments



was only found incorporated in the α-position of the ketone functionality of **10**. In contrast, the cyclization product **11** obtained from **3i** in the presence of a deuterium source exhibited deuteration at two different positions, with an additional deuterium found at the vinylic site of the newly formed cyclohexene ring.

Based on those findings we propose for these transformations to proceed via an oxycyclization/allene-ene carbocyclization cascade as summarized in Scheme 5. First, the alkyne moiety of allenyne **A** is activated by the gold catalyst toward an intramolecular attack of the hydroxyl group, which, after protodemetalation of vinylic gold species **B**, furnishes dihydrofuran **C**. Then the gold catalyst activates the allene, and subsequent carbocyclization can proceed via either 5-*exo* or 6-*endo* mode to species **D** or **G**, depending on conformational restraints. In both instances, this is followed by formation of the acylated

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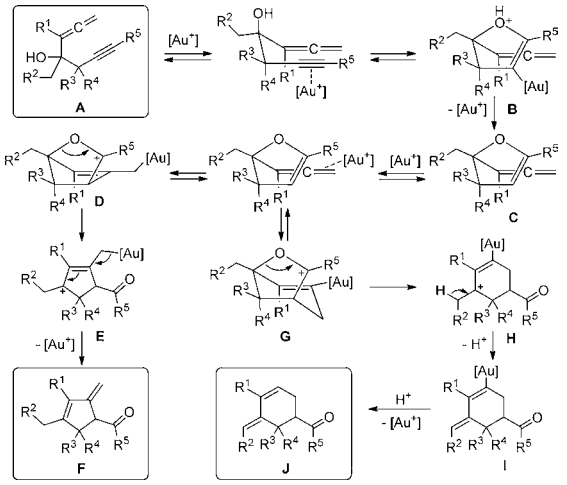
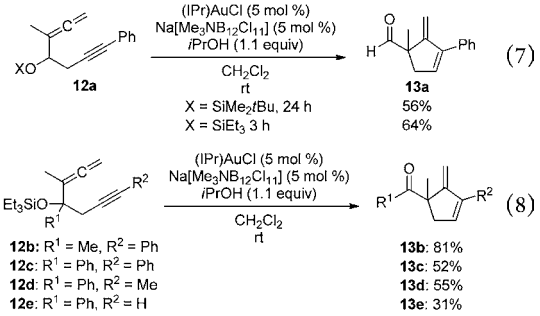
Scheme 5. Proposed Mechanism for the Formation of Carbocycles F and J



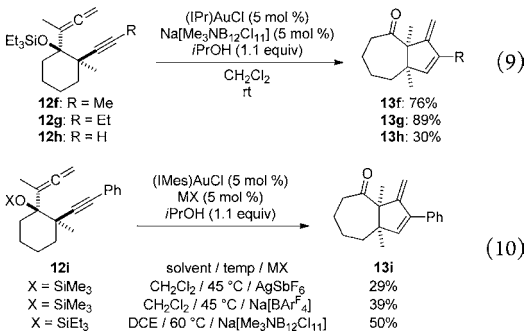
carbocycles **E** and **H**, while the former can then collapse under liberation of the catalyst to form product **F**; the latter has to undergo a deprotonation/protodemetalation step via vinylic gold species **I** to give product **J**.

Apart from the above transformations, further investigation revealed that an even wider range of products can be accessed from the allenyne system studied herein: A complete change of reactivity is observed when the hydroxyl functionalities of the allenyne substrates are simply protected as silyl ethers. As shown in eq 7, the reaction of silyloxy-allenynes **12a** with the



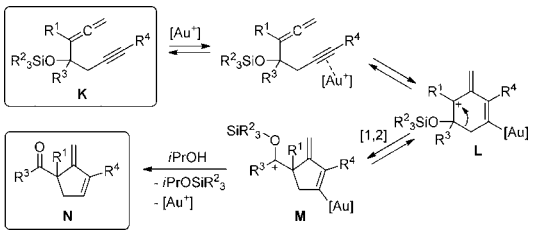
(IPr)Au(I) catalyst at room temperature furnishes aldehyde **13a**, generating a quaternary carbon center (for optimization details, see Supporting Information). Tertiary silyl ethers **12b−e** reacted in an analogous fashion giving ketones **13b−e** in very good to moderate yields, with terminal alkyne **12e** performing not as well as internal alkynes (eq 8).

Cyclic substrates **12f−h** could also be converted in good yields and with total diastereoselectivity to the predicted bicyclic ketones **13f−h** which feature a valuable hydroazulene skeleton[11] *cis*-fused at two quaternary carbon centers (eq 9). Since allenyne **12i** with a phenyl group attached to the alkyne moiety gave the corresponding product **13i** only in disappointing yields and in an impure form under the standard conditions, a further screening was conducted (eq 10 and Supporting Information). In this particular instance, (IMes)AuCl was the only precatalyst that led to any clean formation of the desired product. Using $Na[BAr^F{}_4]$ as an *in situ* activator proved to be quite effective compared to common silver salts.[12] However, our best yields for **13i** were obtained by returning to $Na[Me_3NB_{12}Cl_{11}]$ at 60 °C in 1,2-dichloroethane (DCE).

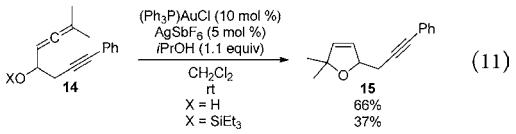


In analogy to our previous works on the cyclization of silyloxy-enynes,[13] we assume that the formation of carbonyl compounds **N** from allenynes **K** can be explained by a cascade reaction consisting of a 6-*endo* carbocyclization to cationic intermediate **L**, followed by a pinacol-type rearrangement and subsequent collapse of species **M** to product **N** (Scheme 6).

Scheme 6. Probable Mechanism for the Cyclization of Silyloxy-allenynes K



It is notable that in both of the two transformations reported above we were only able to obtain the desired products from substrates carrying two hydrogens on the terminal allene carbon. We found that allenes bearing alkyl substituents at that position are highly susceptible to an internal attack from the hydroxyl,[14] as demonstrated in eq 11 with the reaction of allenyne **14** to



dihydrofuran **15**, which was the only product isolated for both the free alcohol as well as the silyl ether under various conditions with gold and copper catalysts.

In conclusion, we have reported new cascade reactions of 4-hydroxy- and 4-silyloxy-1,5-allenynes that allow access to a variety of complex mono- and bicyclic carbonyl compounds, which includes cyclopentadienes featuring a highly unusual substitution pattern. As future contributions by our group will show, the diastereoselectivity of these transformations and the presence of functionality in the generated cycles in the form of multiple double bonds offer useful solutions to problems posed in the synthesis of small natural products.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures for all compounds with analytical data, copies of ^1H and ^{13}C NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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