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Cascade Reaction

Gold(I)-Catalyzed Allene–Diene–Alkyne Coupling Reaction to Polycycles

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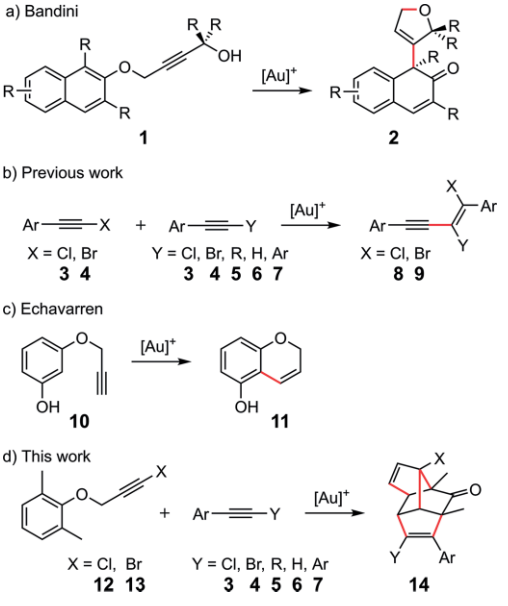
Abstract: In general, the design of complex polycycles from simple building blocks is challenging and requires many reaction steps. Herein, we present that complex polycycles can be synthesized starting from two alkyne building blocks in a one-pot reaction using gold(I) as catalyst, in yields up to 77 %. Mechanistically, the process can be described as cascade reaction in two steps: first, the allene is formed by gold(I)-catalyzed dearomatization, second, the desired product is then obtained by allene–diene–alkyne coupling. Quantum chemical investigations confirm the assumed mechanism. In sum, five new C–C bonds are built in one sweep, which is extraordinary since non-identical building blocks are combined in this reaction. The introduced new allene–diene–alkyne coupling reaction paves the way for several new syntheses of cycles and polycycles considering potential intermolecular reactions.

In organic chemistry the development of efficient and new C–C coupling reactions is highly important for the synthesis of complex molecules. Especially, catalysis by transition metals has become an important tool to design such molecules.[1] One of these transition metal-catalyzed C–C coupling reactions is the catalytic asymmetric dearomatization (CADA).[2–6] By using cheap, functionalizable and ubiquitous aromatic systems for this C–C coupling reaction it is possible to synthesize more complex polycycles.[2–6] In search of efficient transition metal catalysts to build up new C–C bonds, homogeneous gold catalysis has come to the fore.[7–11] Currently, it is possible to form up to four new C–C bonds[12] during a reaction cascade by means of homogeneous gold catalysis if the combination of identical building blocks (e.g. oligomerization) is not taken into account.[13] However, gold has been rarely used in CADA reactions compared to other transition metals.[14–17] An example of gold-catalyzed dearomatization involving one alkyne unit was shown by Bandini et al.[18] They converted naphthyl propargyl ethers **1** to naphthalene-2-one derivatives **2** (Scheme 1a). This reaction can be considered as a Claisen rearrangement with subsequent intramolecular hydroxy group addition to the newly formed allene.

Our previous work in the field of gold catalysis was focused on the conversion of haloacetylenes (Scheme 1b). The advantage of these compounds is their easy accessibility[19] and their thermal stability at standard conditions.[20–22] During the last few years we and other research groups presented haloalkynylation reactions of different alkynes[23–25] and alkenes.[26–29] Mechanistic investigations proved that the formation of products obtained by addition has to take place via rearrangement.[30] However, the restriction of previous systems is that only conjugated alkynes can be used. While attempting to transfer the concept of haloalkynylation to non-conjugated haloacetylenes, we discovered a gold(I)-catalyzed allene–diene–alkyne coupling reaction to polycycles. Herein, we describe the application range as well as mechanistical investigations of this novel type of cascade reaction.



Scheme 1. Gold(I)-catalyzed dearomatization (a), haloalkynylation (b), cyclization (c) of alkynes and allene–diene–alkyne coupling reaction (d).

In the course of studies relating to gold(I)-catalyzed reactions of non-conjugated haloacetylenes with alkynes, compound

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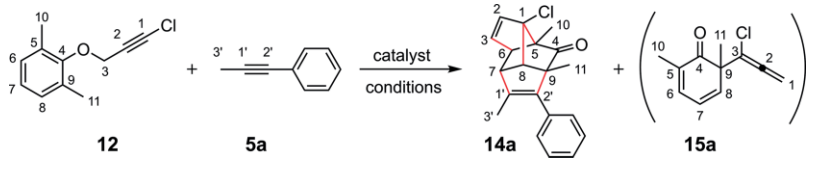
classes **12** and **13** got into our focus of interest (Scheme 1d). These molecules can be prepared in a few steps from readily accessible compounds. The use of two methyl groups in *ortho* position is necessary to avoid gold(I)-catalyzed cyclization to the corresponding 2*H*-chromene; this type of reaction has already been observed for terminal alkynes (Scheme 1c).[31–34] A similar concept was used for propargylic ethers **1** (Scheme 1a).[18] The undesired cyclization could actually be prevented and 2,5-dihydrofurans **2** emerged from gold(I)-catalyzed asymmetric dearomatization. Regarding haloacetylenes **12** and **13** adequate cyclization reactions are not expected as halogen atoms are monovalent.

As test reaction the conversion of chloroacetylene **12** with alkyne **5a** and [JohnPhosAu(NCMe)]SbF_6[35] as gold catalyst was investigated via NMR experiments in deuterated chloroform. Within only two hours at room temperature the starting material was completely consumed. Fortunately, one single main product (yield: 47 %) was obtained (see Figure S8 and Table 1). The yields of all side products amounted to less than 5 %. However, the NMR spectra showed that not the expected enyne dimer but a polycycle was formed. Structural investigations via 2D NMR spectroscopy revealed that the main product can be ascribed to tetracycle **14a** (Figures S9–S11). Analysis of the connectivity in tetracycle **14a** shows that five C–C bonds were formed in the course of the reaction. Additionally, one C–O bond was broken, and one hydrogen atom was rearranged. Until now, we are not aware of any case in which so many C–C bonds were formed by gold catalysis in one reaction cascade, if the combination of two identical building blocks (e.g. oligomerization) is not taken into account.[13]

We wanted to examine if the yield obtained in the cascade reaction can be increased. Therefore, we tested different gold catalysts in the first step (entries 1–8 in Table 1). Nevertheless, we were not able to improve the yield (47 %) that was obtained by using [JohnPhosAu(NCMe)]SbF_6. The usage of sterically demanding ligands like XPhos led to distinctly lower yields for polycycle **14a** (30 %; entry 4). If another type of phosphine ligand like trimethylphosphine was employed, no conversion was observed (entry 6). If JohnPhosAuCl was used with $NaBArF_{24}$ as counterion, the main product was no longer polycycle **14a** but the multiple unsaturated system **15a** (entry 3). This system was identified as allene by NMR spectroscopy. The use of gold(III) complex dichloro(2-picolinato)gold(III)[36] led exclusively to allene **15a** (entry 8). The use of an NHC ligand[37] ended up in a product mixture in which polycycle **14a** and allene **15a** were formed in a 2:1 ratio (entry 7). Thus, the initially applied catalyst [JohnPhosAu(NCMe)]SbF_6 turned out to be the best choice. In the next step, the equivalents of both starting materials and catalyst as well as temperatures and solvents were varied (entries 9–17). The highest yield of polycycle **14a** (52 %) was obtained, when chloroacetylene **12** was converted with 2.5 mol-% of the catalyst and two equivalents of alkyne **5a** at room temperature in chloroform.

After optimization of the reaction conditions, we evaluated the substrate scope of this reaction on a preparative scale. Therefore, we used different arylacetylenes (**3–7**; see Scheme 2) in which both triple bond substituents were varied. At first, we had a closer look at alkyl arylacetylenes **5**. The length of the alkyl chain plays no important role, if the second substituent is a phenyl group (**14a**–**c**). In all cases the yields amount to ca.

Table 1. Optimization of the reaction conditions for the gold(I)-catalyzed coupling of **12** with alkyne **5a**.[a]



12 **5a** **14a** **15a**

Entry	Catalyst	Conditions	Yield [%] cycle	allene	Conversion [%]
1	[JohnPhosAu(NCMe)]SbF_6 (5 mol-%)[35]	RT, 2 h, $CDCl_3$	47	–	100
2	JohnPhosAuCl (5 mol-%)/$AgNTf_2$ (10 mol-%)[37]	RT, 2 h, $CDCl_3$	37	–	97
3	JohnPhosAuCl (5 mol-%)/$NaBArF_{24}$ (10 mol-%)	RT, 2 h, $CDCl_3$	9	42	100
4	*t*BuXPhosAuNTf_2 (5 mol-%)[37]	RT, 2 h, $CDCl_3$	30	–	92
5	CyJohnPhosAuCl (5 mol-%)/$AgSbF_6$ (10 mol-%)	RT, 2 h, $CDCl_3$	38	–	100
6	Me_3PAuCl (5 mol-%)/$AgSbF_6$ (10 mol-%)	RT, 2 h, $CDCl_3$	–	–	0
7	IPrAuCl (5 mol-%)[37]/$AgNTf_2$ (10 mol-%)	RT, 2 h, $CDCl_3$	24	13	97
8	Dichloro(2-picolinato)gold(III) (5 mol-%)[36]	RT, 2 h, $CDCl_3$	–	98	100
9	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	RT, 2 h, $CDCl_3$	52	–	100
10	[JohnPhosAu(NCMe)]SbF_6 (1 mol-%)	RT, 2 h, $CDCl_3$	–	19	21
11	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	RT, 2 h, C_6D_6	43	–	100
12	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	RT, 2 h, DCM	40	–	100
13	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	RT, 2 h, DCE	26	–	100
14	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	–10 °C, 2 h, $CDCl_3$	37	23	100
15	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	0 °C, 2 h, $CDCl_3$	44	9	100
16[b]	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	RT, 2 h, $CDCl_3$	49	–	100
17[c]	[JohnPhosAu(NCMe)]SbF_6 (2.5 mol-%)	RT, 2 h, $CDCl_3$	34	–	100

[a] Yields were determined by ^{1}H NMR using cyclooctane as internal standard. If not stated otherwise, the concentration of alkyne **13** was 0.15 M and alkyne **5a** was added in 2 molar equivalents. [b] 3 molar equivalents of alkyne **5a** were added. [c] 1 molar equivalent of alkyne **5a** was added.

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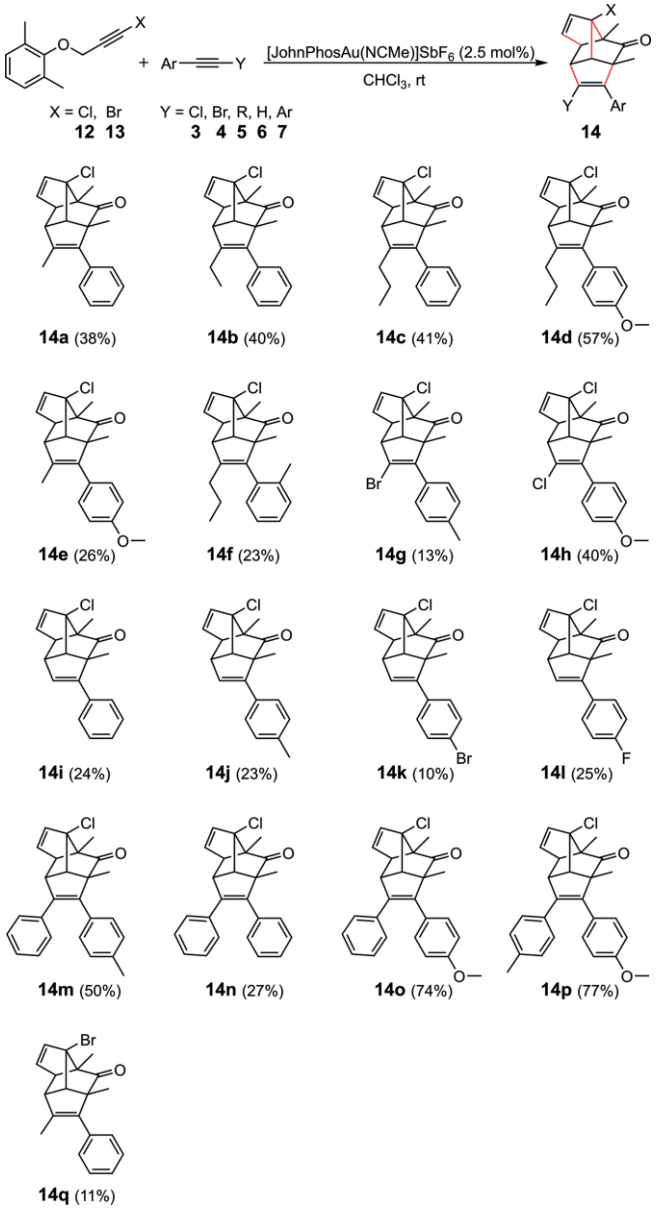
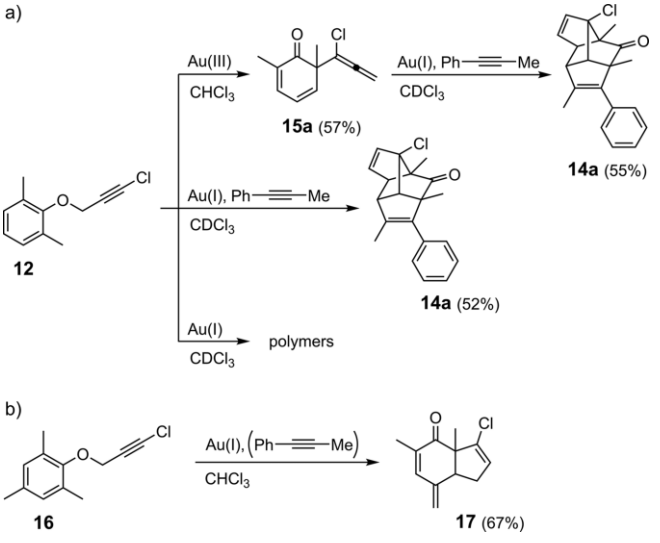
40 %. The yield was increased by a methoxy group in *para* position (57 %, **14d**), if a propyl group is attached to the triple bond as second substituent. A lower yield was found if the second substituent is a methyl group (26 %, **14e**).



Scheme 2. Evaluation of the substrate scope of the gold(I)-catalyzed coupling of haloacetylenes **12** and **13** with alkynes **3**–**7**.

A methyl group in *ortho* position lowers the yield to 23 % (**14f**). If the alkyl group in **5** is substituted by chlorine (**3a**), no significant change was observed (40 %, **14h**). The corresponding bromo derivative **14g** was isolated in 13 % yield. Terminal alkynes (**6**) are also tolerated; the corresponding products were obtained in yields of ca. 25 % (**14i**, **14j** and **14l**) and 10 % (**14k**), respectively. Diarylacetylenes (**7**) form as well polycycles with **12**. The resulting products were isolated in yields up to 77 %. In these products the more electron-rich aromatic ring is bound to the position which is closer to the carbonyl group. If bromo derivative **13** was used instead of chloroacetylene **12**, the conversion to polycycle **14q** was not complete. Even after one week at room temperature or after a few days at 40 °C, the allene and only small amounts of polycycle **14q** (11 %) were found.

Next, we wanted to elucidate the mechanism of this remarkable coupling reaction. In the first step, the role of the allene was investigated; we wanted to find out whether this allene embodies an intermediate or a side product. Therefore, we converted chloroacetylene **12** *without* alkyne **5a** using gold(III) as catalyst. The allene **15a** was isolated in 57 % yield (Scheme 3a). Afterwards, we converted **15a** under the optimized reaction conditions with [JohnPhosAu(NCMe)]SbF_6 as catalyst and **5a** by NMR experiments. Polycycle **14a** was obtained in 55 % yield. Thus, the formation of **15a** via gold-catalyzed Claisen rearrangement can be described as the first sequence of the cascade reaction.



Scheme 3. Gold(I)-catalyzed reaction of chloroacetylenes **12** and **16** in presence and absence of alkyne **5a**.

Interestingly, the NMR yield of **14a** after conversion of **15a** with alkyne **5a** (55 %) was not much higher than the NMR yield of **14a** obtained in the reaction of **12** and **5a** (52 %, Scheme 3a). This means that the one-pot cascade reaction is almost as efficient as the stepwise process. Please note, the reaction of **12** with [JohnPhosAu(NCMe)]SbF_6 as catalyst *without* alkyne **5a** led to a complete conversion (Scheme 3a), but only a variety of oligomeric compounds was formed, which could not be separated by column chromatography. Therefore, we assume that – utilizing JohnPhosAu$^+$ as catalytic species – allene **15a** (which is formed in the first step) reacts with the diene unit of the cycle. This leads to the formation of oligomeric structures due to the absence of intercepting alkynes. Another preparative mechanistic indication was achieved via conversion of **16** under the optimized reaction conditions. Bicycle **17** was obtained in 67 % yield whether alkyne **5a** was present or not. The formation of the product underlines the assumption that the allene unit is cyclized with the diene unit building a five-membered ring. The formed cation can be stabilized by deprotonation. Thus, the second sequence of the cascade reaction probably starts with the formation of a five-membered ring.

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The above-mentioned experimental indications were used to calculate the cascade reaction mechanism via quantum chemical methods. Arylacetylene **12** and alkyne **6a** were utilized as model substances. In order to optimize the geometrical parameters of all stationary points, the density functional B3LYP[38–40] together with the dispersion correction via Becke–Johnson damping[41] (D3BJ) was employed. As basis sets 6-31G(d) was applied for the elements C, H, O, P, and Cl, whereas def2-TZVP was used for Au. Furthermore, single-point calculations on the optimized structures were performed using B3LYP-D3BJ with basis sets 6-311++G(d,p) (for C, H, O, P, and Cl) and def2-TZVP (for Au). To take solvent effects into account, chloroform was considered as reaction solvent by using the SMD[42] model.

The first sequence of the cascade reaction is the formation of the allene starting with chloroacetylene **12** and JohnPhosAu$^+$ as catalytic-active species. The coordination of the gold(I) complex is accompanied by free-energy reduction amounting to 15.4 kcal/mol (Figure 1). Please note that the coordination of JohnPhosAu$^+$ to acetylene **6a** (ΔG = –16.2 kcal/mol) is energetically favored compared to the complexation of **12**. However, the reactions of the thusly formed complex with acetylenes **6a** and **12**, respectively, require high activation energies, making the complexation of **6a** a dead end (Figures S8–9). Complex **18a**, which is formed by coordination of JohnPhosAu$^+$ to acetylene **12**, was used as reference for all subsequent reaction steps. The rate-determining step of the first cascade reaction sequence (allene formation) is the cyclization to oxonium ion **20a** (10.0 kcal/mol). This ion converts into gold(I) allene complex **22a** in the second step. Therefore, a barrier of 7.4 kcal/mol needs to be overcome.

After that, two reaction paths are possible: on the one hand, decomplexation can take place leading to the catalytic species and allene **15a** (this allene formation corresponds to the end

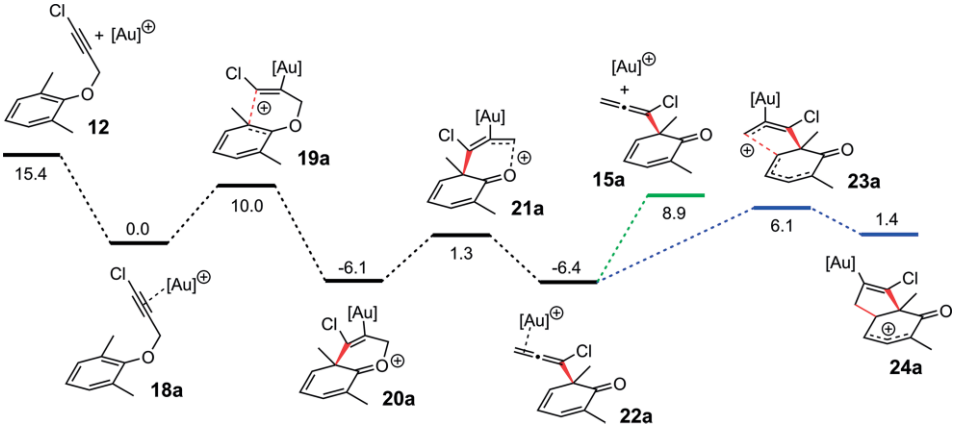

Figure 1. Reaction pathway of the gold(I)-catalyzed dearomatization of chloroacetylene **12**. The indicated free-energy values (ΔG in kcal/mol) were calculated using B3LYP-D3BJ(SMD) and are relative to gold complex **18a**. [Au]$^+$ = JohnPhosAu$^+$.

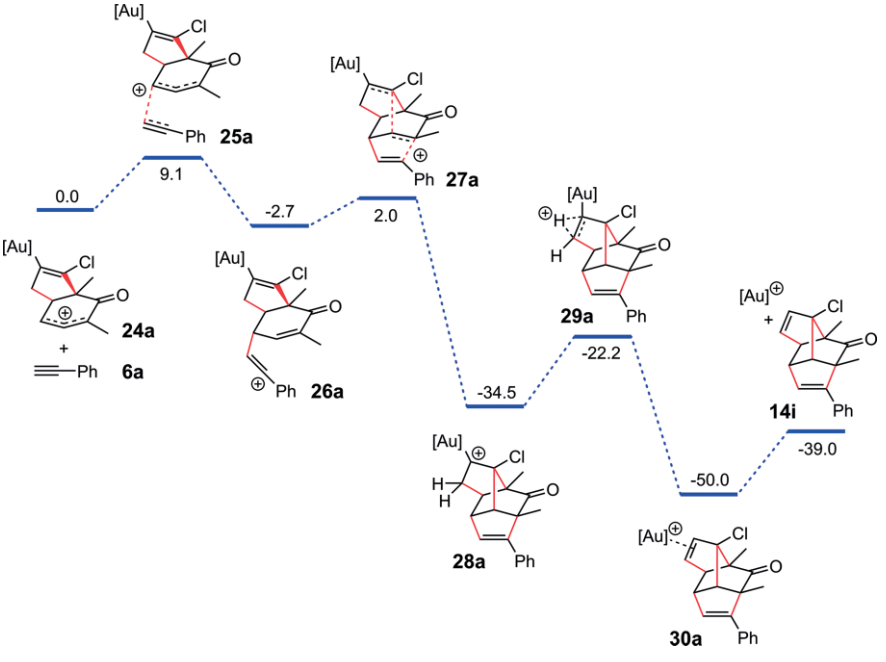

Figure 2. Reaction pathway of the addition of acetylene **6a** to cation **24a**. The indicated free-energy values (ΔG in kcal/mol) were calculated using B3LYP-D3BJ(SMD) and are relative to acetylene **6a** and cation **24a**. [Au]$^+$ = JohnPhosAu$^+$.

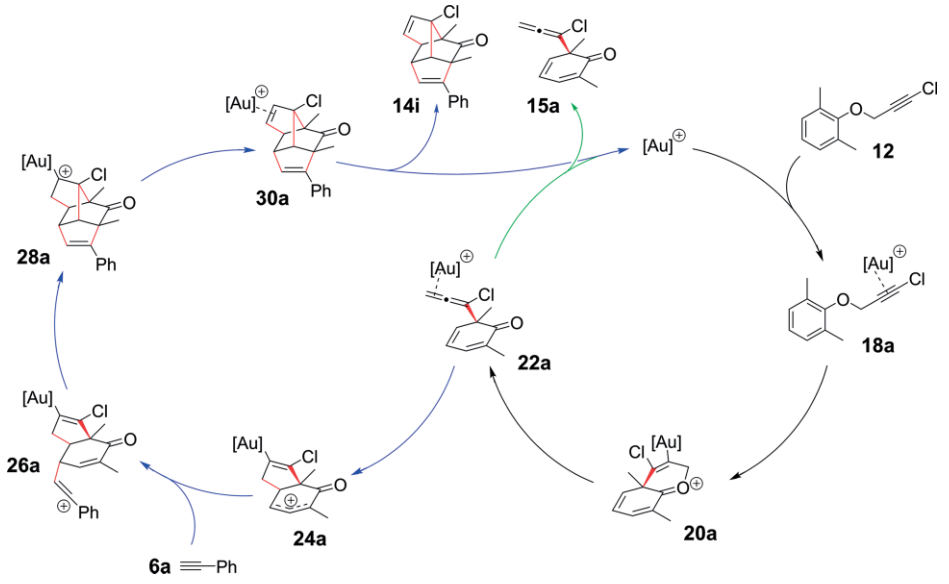

Figure 3. Possible reaction mechanism for the gold(I)-catalyzed dearomatization (black and green arrows) leading to allene **15a** and the allene–diene–alkyne coupling (blue arrows) leading to polycycle **14i**.

of the first cascade reaction sequence). On the other hand, the formation of bicyclic cation **24a** can occur initiating the second cascade reaction sequence (allene–diene–alkyne coupling). According to calculations, the second sequence (intramolecular cyclization) is more favored (12.5 kcal/mol) than the formation of free allenes (15.3 kcal/mol). This agrees well with the results showing a polymerization in case of converting **12** in absence of **5a** with JohnPhosAu$^+$ as catalytic species.

Let us now consider the second cascade reaction sequence (allene–diene–alkyne coupling): the first step is again rate-determining and corresponds to the addition of alkyne **6a** to cation **24a** with formation of vinyl cation **26a** (Figure 2). The activation energy for this step amounts to 9.1 kcal/mol. The vinyl cation is stabilized by the phenyl ring, which also explains the regioselectivity of the attack of **6a** to **24a**. A possible competing reaction to the addition of alkyne **6a** to cation **24a** is the addition of alkyne **12** to cation **24a**. However, the required activation energy for the latter reaction path is distinctly higher (15.5 kcal/mol; Figure S10). In the next step, two intramolecular C–C bonds are simultaneously formed leading to gold(I)-stabilized cation **28a**. Proceeding from this σ complex, π complex **30a** is formed by a 1,2-hydride shift. Decomplexation leads to the final product **14i**.

In Figure 3 the most important intermediates are illustrated in a catalyst cycle. The whole cycle consists of two sequences; in both gold(I) complexed allene **22a** is passed. Allene formation takes place via two-step gold-catalyzed Claisen-like rearrangement (black in Figure 3). Allene **22a** functions as origin of two branches: on the one hand, the formation of allene **15a** is enabled by decomplexation (green in Figure 3), on the other hand, the intramolecular 5-*endo*-*trig*-cyclization to **24a** is possible (blue in Figure 3). Alkyne **6a** can be added to intermediate **24a** ending up in the formation of gold complexed polycycle **30a** via two further steps. Decomplexation leads to final product **14i** and finishes the catalyst cycle.

In sum, we were able to show that polycycles can be designed from haloacetylenes and alkynes by gold(I) catalysis. In our case, the haloacetylene was an *o,o*-dimethyl-substituted propargyl ether. The reaction tolerates a wide range of alkyne substrates like alkylaryl, diaryl, halo- and terminal alkynes. The achieved preparative yields amount up to 77 %. Experimental and quantum chemical investigations showed that the mechanism can be described as cascade reaction with two sequences. The first sequence is a gold(I)-catalyzed dearomatization in which the corresponding allene is built from propargyl ether by formal Claisen rearrangement (isolation of the allene is possible). The second sequence is a new reaction type: four new C–C bonds are formed by an allene–diene–alkyne coupling leading to the corresponding polycycle. Altogether, even five C–C bonds are newly formed during the whole cascade. The described allene–diene–alkyne coupling reaction has the potential to exploit new ways of polycycle formation starting from simple building blocks. Especially, the option of expanding the reaction to obtain intermolecular products is promising and desires further exploration.

Supporting Information (see footnote on the first page of this article): Figures and Tables syntheses of the new compounds, NMR experiments, computational details, cartesian coordinates and absolute energies for all calculated compounds, ^{1}H NMR and ^{13}C NMR spectra of the new compounds.

Conflict of Interest

There is no conflict of interest to declare.

Acknowledgments

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Keywords: C–C bond formation · Cyclization · Dearomatization · DFT calculations · Gold catalysis

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