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Intermolecular Gold-Catalyzed Cycloaddition of Alkynes with Oxoalkenes

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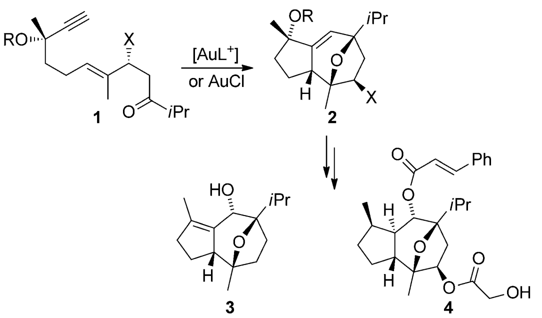
Gold(I) catalysts selectively activate alkynes in polyfunctional substrates, which triggers a wide variety of cyclizations.[1] We developed a tandem process for the simultaneous formation of two C−C bonds and one C−O bond by a gold(I)-catalyzed [2+2+2] alkyne/alkene/carbonyl cycloaddition of 1,6-enynes bearing a carbonyl group (Scheme 1).[2]



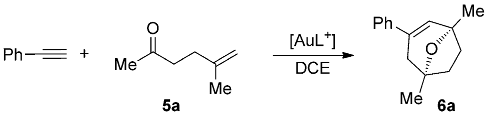
Scheme 1. Intramolecular gold(I)-catalyzed [2+2+2] alkyne/alkene/carbonyl cycloaddition of 1,6-enynes.

As has been demonstrated in many gold(I)-catalyzed reactions of enynes,[1,3] this cycloaddition is stereospecific. This is best illustrated in the cyclization of substrates **1** to form intermediates **2**, which were later transformed into oxatricyclic sesquiterpenes (+)-orientalol F (**3**)[4] and (−)-englerin A (**4**).[5,6] Cationic gold(I) complexes also catalyze the cycloisomerization of oxo-1,5-enynes[7] as well as the addition of carbonyl compounds to 1,*n*-enynes.[8]

In contrast to the large number of gold-catalyzed intramolecular cycloisomerization reactions developed over the last decade,[1] the development of gold(I)-catalyzed intermolecular reactions of alkynes with alkenes has been much more challenging.[9–11] Herein, we report the intermolecular cycloaddition reaction of terminal alkynes with 5-oxoalkenes that leads to the formation of 8-oxabicyclo[3.2.1]oct-3-enes, a structural motif present in natural products[12] and other biologically relevant compounds.[13] In addition to the major cycloaddition pathway, we have also identified a competitive process leading to the formation of 2-(arylethynyl)tetrahydrofurans. We also report a detailed mechanistic study that explains the formation of both product types by activation of the alkyne by gold(I), whereas the oxoalkenes can competitively be activated by the strong Brønsted acid generated in situ.

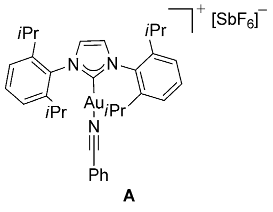
We first examined the cycloaddition between phenylacetylene and 5-methylhex-5-en-2-one (**5a**). No cycloaddition was observed using AuCl or complex **D** (Table 1, entries 1

Table 1. Optimization of the gold(I)-catalyzed intermolecular cycloaddition of alkynes with oxoalkenes (see the Supporting Information).[a]

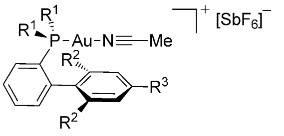


Entry	Catalyst	T [°C]	Yield [%][b]
1	AuCl	23	–
2	**A**	23	15
3	**B**	23	15
4	**C**	23	25
5	**D**	23	–
6	**E**	23	39
7	**E**	50	67
8[c]	**E**	50	46
9	**E**	80	43
10	**F**	50	63
11	**G**	50	57

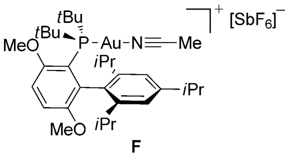
[a] Reaction conditions: 3 mol% catalyst, $c=0.5$ M, 2–5:1 phenylacetylene/**5a**, 24 h. [b] Determined by ^{1}H NMR spectroscopy by using 1,4-diacetylbenzene as internal standard. [c] $c=1$ M.



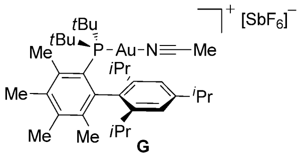
A



B: R^1 = *t*Bu, R^2 = H, R^3 = H
C: R^1 = Cy, R^2 = R^3 = *i*Pr
D: R^1 = Cy, R^2 = OMe, R^3 = H
E: R^1 = *t*Bu, R^2 = R^3 = *i*Pr



F



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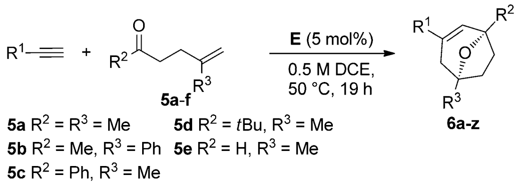
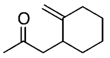
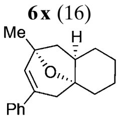
and 5), whereas other cationic gold(I) complexes **A**–**C** and **E**–**G** led to 1,5-dimethyl-3-phenyl-8-oxabicyclo[3.2.1]oct-3-ene (**6a**) in low to moderate yields. As we observed before in the intermolecular reaction of alkynes with alkenes,[9] increasing the steric bulkiness of the ligand in the gold(I) complex led to a significant improvement in the cycloaddition reaction. The best results were obtained using cationic *t*BuXPhos–gold(I) catalyst **E** in 1,2-dichloroethane (DCE) at 50 °C for 24 h (Table 1, entry 7),[14] whereas related cationic complexes [(*t*BuBrettPhos)Au(MeCN)]SbF$_6$ (**F**) and [(Me$_4$*t*BuXPhos)Au(MeCN)]SbF$_6$ (**G**)[15,16] led to slightly lower yields (Table 1, entries 10 and 11).

The cycloaddition reaction proceeds in a general manner with aryl acetylenes substituted at *ortho*, *meta*, or *para* positions and oxoalkenes **5a**–**f** to form cycloadducts **6a**–**y** in moderate to excellent yields (Table 2). Aryl acetylenes with electron-donating and -withdrawing substituents react similarly. The reaction tolerates a free phenol to form 8-oxabicyclo[3.2.1]oct-3-ene (**6p**; Table 2, entry 16), the structure of which was confirmed by X-ray diffraction (Figure 1).[17] In addition, the reaction can be carried out on a 2 mmol scale without observing a drop in the yield (see the Supporting Information). (3-Thienyl)acetylene also reacted with oxoalkene **5a** to furnish product **6t** (Table 2, entry 20). Reaction of aldehyde **5e** led to cycloadduct **6x** in low yield owing to the lower nucleophilicity of the carbonyl moiety (Table 2, entry 23). Substrate **5f** led stereoselectively to **6y** in moderate yield with a tricyclic skeleton (Table 2, entry 24). Alkyl-substituted alkynes and oxoalkenes with monosubstituted alkenes failed to form oxabicyclic products.

Table 2. Scope of the intermolecular gold(I)-catalyzed [2+2+2] cycloaddition of alkynes with oxoalkenes.



Entry	R^1	R^2	R^3	Yield [%]
1	Ph	Me	Me	**6a** (68)[a]
2	Ph	Me	Ph	**6b** (68)
3	*p*-Tol	Me	Me	**6c** (55)
4	*p*-MeOC$_6$H$_4$	Me	Me	**6d** (43)
5	*p*-FC$_6$H$_4$	Me	Me	**6e** (68)
6	*p*-FC$_6$H$_4$	Me	Ph	**6f** (65)
7	*p*-ClC$_6$H$_4$	Me	Me	**6g** (55)[a]
8	*p*-ClC$_6$H$_4$	Me	Ph	**6h** (61)
9	*p*-BrC$_6$H$_4$	Me	Me	**6i** (49)[a]
10	*p*-BrC$_6$H$_4$	Me	Ph	**6j** (70)
11	*m*-Tol	Me	Me	**6k** (70)
12	*m*-FC$_6$H$_4$	Me	Me	**6l** (49)[a]
13	*m*-FC$_6$H$_4$	Me	Ph	**6m** (59)
14	*m*-ClC$_6$H$_4$	Me	Me	**6n** (55)[a]
15	*m*-ClC$_6$H$_4$	Me	Ph	**6o** (60)
16	*m*-HOC$_6$H$_4$	Me	Me	**6p** (65)
17	*m*-MeOC$_6$H$_4$	Me	Me	**6q** (91)
18	*o*-MeC$_6$H$_4$	Me	Me	**6r** (41)
19	2-naphthyl	Me	Me	**6s** (62)
20	3-thienyl	Me	Me	**6t** (40)
21	Ph	Ph	Me	**6u** (87)
22	Ph	*t*Bu	Me	**6v** (54)
23	Ph	H	Me	**6x** (16)
24	Ph			

[a] 2,2,5-Trimethyl-5-(arylethynyl)tetrahydrofurans **7** were obtained as side products in 26–42 % yields.

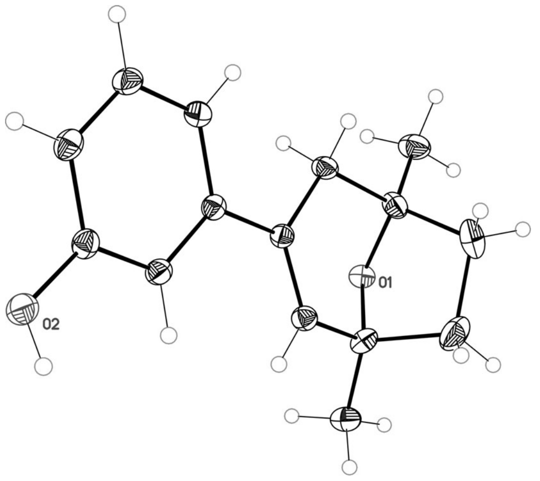
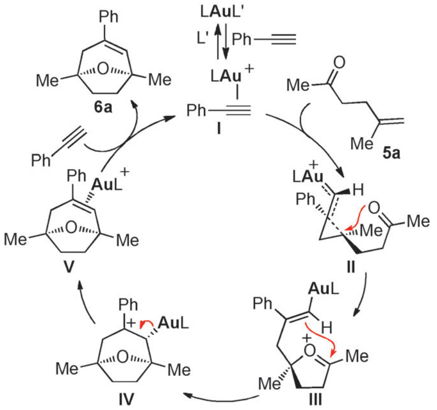
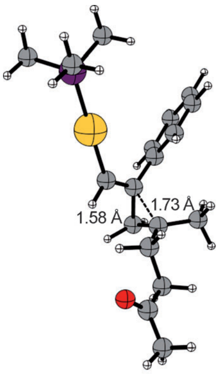


Figure 1. X-ray crystal structure of cycloadduct **6p**. ORTEP plot (50 % thermal ellipsoids).

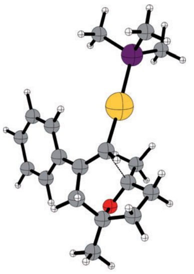
DFT calculations (M06 functional) revealed a stepwise formation of the C–C and C–O bonds (Scheme 2). The nucleophilic attack of alkene **5a** to complex **I** is the rate-determining step with free activation energy of 15.9 kcal mol^{-1} (see the Supporting Information for additional computational details). This process occurs both regio- and stereoselectively and forms intermediate **II** with a highly unsymmetrical cyclopropyl gold(I) carbene structure (new C–C bond lengths of 1.58 and 1.73 Å). Regioselective attack of the carbonyl group at the most substituted position through **TS$_{II–III}$**



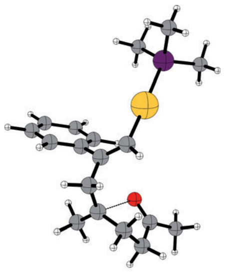
Scheme 2. Catalytic cycle for the intermolecular gold(I)-catalyzed [2+2+2] cycloaddition of alkynes with oxoalkenes based on DFT calculations (M06, 6-31G(d) (C, H, P, O) and SDD (Au), CH$_2$Cl$_2$).



II



$TS_{II–III}$



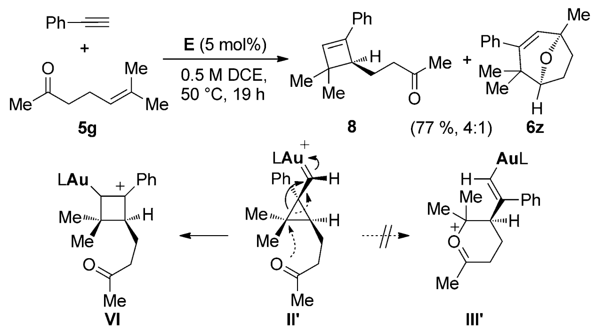
$TS_{II–IV}$

then leads to oxonium cation **III**, which undergoes a Prins reaction to close a seven-membered ring leading to benzylic cation **IV** and, finally, to **6a** by metal elimination and ligand exchange between **V** and phenyl acetylene.[18,19]

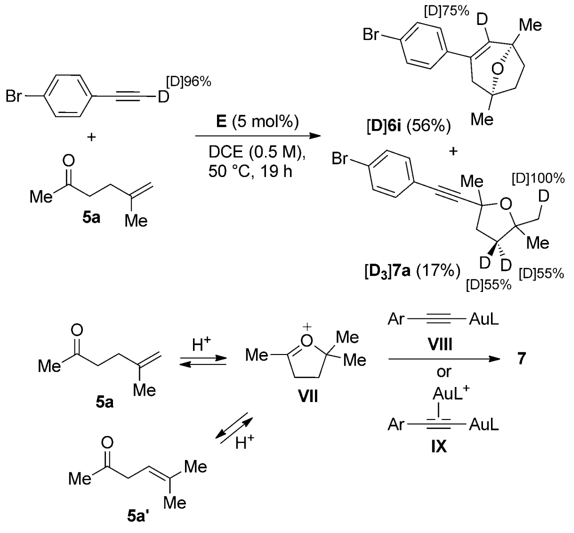
Reaction of oxoalkene **5g** with phenylacetylene led to 8-cyclobutene **8** as the major product, along with **6z** (Scheme 3). Cyclobutene **8** is formed by ring expansion of intermediate **II′** to form **VI**. The alternative opening of **II′** to form six-membered ring oxonium cation **III′** was not observed.

Tetrahydrofurans **7** were also observed as side products in some of the cycloaddition reactions. Reaction of deuterated *p*-bromophenylacetylene with **5a** led to [D]**6i** and [D_3]**7a**, which demonstrates that the tetrahydrofurans are formed by a proton-catalyzed process, presumably via oxonium cation **VII** in equilibrium with **5a**, **5a′**, and **VII′**, followed by the nucleophilic attack of alkynyl gold species **VIII** or **IX** (Scheme 4).[20–24]

Performing the reaction at −78 °C allowed monogold species **I** to be observed spectroscopically.[23,24] However, at room temperature, over the whole process, a single signal at $\delta = 65.22$ ppm was observed by ^{31}P NMR spectroscopy corresponding to digold complex **9** (=**IX**, **L**=*t*BuXPhos), which was characterized by X-ray diffraction (Figure 2).[18] Formation of **9** releases Brønsted acid $HSbF_6$. Digold complexes similar to **9** have been isolated recently and their role in catalysis has been discussed.[20,21,23–26]



Scheme 3. Intermolecular gold(I)-catalyzed reaction of phenylacetylene with oxoalkene **5g**.



Scheme 4. Isotopic labeling experiment and mechanistic proposal for the formation of 2,2,5-trimethyl-5-(arylethynyl)tetrahydrofurans.

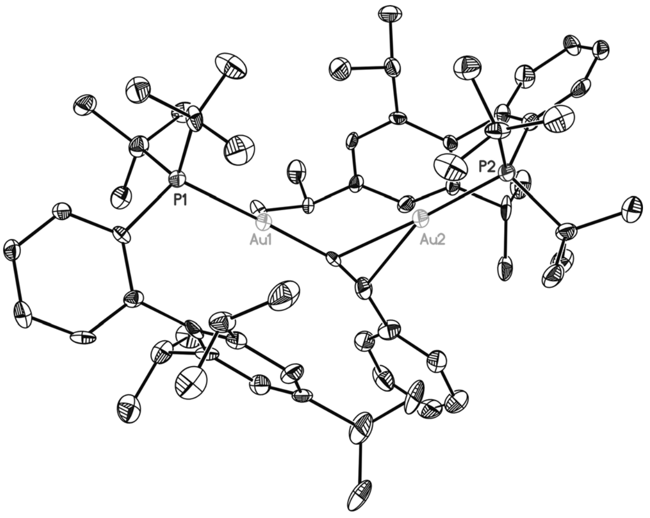
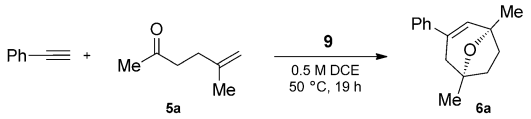


Figure 2. X-ray crystal structure of digold complex **9** (=**IX**; **L**=*t*BuXPhos). ORTEP plot (50 % thermal ellipsoids).

We decided to probe whether complex **9** was actively involved in the catalytic cycle. Our results indicate that this digold complex acts as a dead end, sequestering most of the active gold(I), since no reaction was observed between **5a** and **9** under stoichiometric conditions (Table 3, entry 1). Furthermore, under catalytic conditions using 2.5 mol % of **9**, only 9 % of **6a** was obtained after 19 h at 50 °C. Nevertheless, when $HSbF_6$ was added substoichiometrically, the equilibrium was re-established to allow the formation of the reactive species **I** and then, the reaction proceeded to give product **6a** with slightly lower yield (Table 3, entry 4). No

Table 3. Test of the catalytic activity of complex **9**.



Entry	**9** [mol %]	Alkyne/ alkene	Additive	Yield [%][a]
1	100	0:1	–	–
2[b]	2.5	3.5:1	–	9
3[c]	2.5	1:2	–	8
4	2.5	5:1[d]	$HSbF_6 \cdot 6H_2O$ (2.5 mol %)	50 (45)[e]
5	–	5:1	$HSbF_6 \cdot 6H_2O$ (2.5 mol %)	–

[a] Determined by ^1H NMR spectroscopy using 1,4-diacetylbenzene as internal standard. [b] Dimerization of the alkyne detected.[27] [c] Reaction time of 4 d. [d] Proportion of alkyne increased to account for the competitive hydration. [e] Isolated yield.

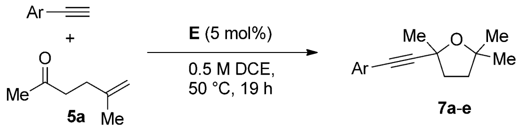
reaction was observed with $HSbF_6$ in the absence of gold complex (Table 3, entry 5). The same behavior was observed in the reaction between oxoalkene **5g** and phenylacetylene to form **8** and **6z** using **9** as the gold source (see the Supporting Information).

Computationally, the free activation energy for the key attack of oxoalkene **5a** to the phenylacetylene moiety of a model of **9** (=**IX**, Ar=Ph, **L**=PMe_3) is 10 kcal mol^{-1} higher than that corresponding to the first step (**I** to **II**) in Scheme 2 (also see the Supporting Information). Therefore, these results suggest that digold complex **9** acts as an unreactive resting state outside the catalytic cycle, which lowers the concentration of the active species [**L**Au**L**′]$^+$ and explains the rather long reaction times.

We reasoned that it would be possible to improve the formation of the arylethynyltetrahydrofurans **7**, which can be valuable synthetic intermediates,[28] by performing the reaction in the presence of a strong Brønsted acid. Indeed, tetrahydrofurans **7a–e** were obtained in 47–57 % yield by performing the reaction with **E** and TsOH as catalysts (entries 2, 4, 6, 8, and 10, Table 4).

In summary, we have developed a new intermolecular gold(I)-catalyzed reaction of terminal alkynes with functionalized alkenes that leads to 8-oxabicyclo[3.2.1]oct-3-enes by a [2+2+2] cycloaddition process in which two C–C bonds and one C–O bond are formed. Our experimental and theoretical mechanistic study sheds light into a complex scenario in which gold(I) and a Brønsted acid compete for the activation of the alkyne and the oxoalkene. This study also demonstrates that digold σ,π-acetylide species are outside the main catalytic cycle in the intermolecular cycloaddition of alkynes with functionalized alkenes. Our efforts are now focused on the development of new intermolecular gold(I)-catalyzed reactions based on these results.

Table 4. Synthesis of arylethynyltetrahydrofurans **7**.[a]



Entry	Ar	Additive[b]	Product	Yield [%]
1	p-BrC_6H_4	–	**7a**	32
2	p-BrC_6H_4	TsOH	**7a**	50
3	Ph	–	**7b**	14
4	Ph	TsOH	**7b**	50
5	p-ClC_6H_4	–	**7c**	26
6	p-ClC_6H_4	TsOH	**7c**	48
7	m-FC_6H_4	–	**7d**	31
8	m-FC_6H_4	TsOH	**7d**	47
9	m-ClC_6H_4	–	**7e**	42
10	m-ClC_6H_4	TsOH	**7e**	57

[a] Traces of oxabicycles **6** were also formed in entries 2, 4, 6, 8, and 10. [b] 10 mol %.

Acknowledgements

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Keywords: alkynes • cycloaddition • density functional calculations • gold • homogeneous catalysis

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[14] A 5:1 ratio of phenylacetylene to **5a** was used as trimerization of the alkyne was detected. When the reaction was performed in the absence of the oxoalkene, trimerization of the terminal alkynes was observed to give 1,3,5-triarylbenzenes in moderate yields. The stoichiometric formation of tris(hexamethylene)benzene by decomposition of $[Au(cot)_3]SbF_6$ (cot = cyclooctyne) has been reported. See: A. Das, C. Dash, M. Yousufuddin, M. A. Celik, G. Frenking, H. V. Rasika Dias, *Angew. Chem.* **2012**, *124*, 4006–4009; *Angew. Chem. Int. Ed.* **2012**, *51*, 3940–3943.

[15] X-ray diffraction data for [(*t*BuBrettPhos)Au(MeCN)]SbF_6 and [(Me_4*t*BuXPhos)Au(MeCN)]SbF_6: C. Obradors, D. Lebœuf, J. Aydin, A. M. Echavarren, unpublished results.

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Cycloaddition

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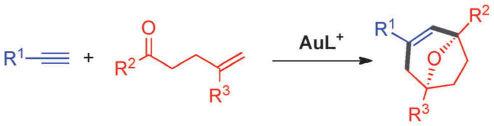
Intermolecular Gold-Catalyzed Cycloaddition of Alkynes with Oxoalkenes



As good as gold: Gold(I) catalyzes a new intermolecular reaction of terminal alkynes with functionalized alkenes that gives 8-oxabicyclo[3.2.1]oct-3-enes by a [2+2+2] cycloaddition process in which two C–C bonds and one C–O bond are formed (see scheme).