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Gold(I)-Catalyzed Cycloisomerization of Nitrogen and Oxygen-Tethered Alkylidenecyclopropanes to Tricyclic Compounds

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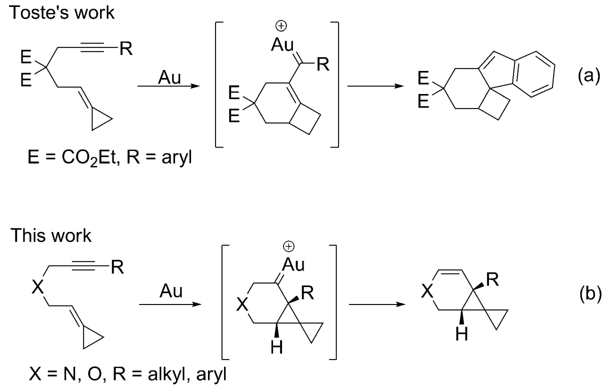
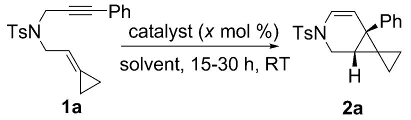
Homogeneous catalysis by gold complexes has received considerable attention in recent years.[1] Among these interesting reactions, gold-catalyzed cycloisomerization of 1,6-enynes is one of the most important strategies for the construction of functionalized cyclic structures.[2] Nitrogen- and oxygen-bridged enynes are useful starting materials for the preparation of heterocyclic building blocks. Since Blum et al. first reported the $PtCl_4$-catalyzed cyclorearrangement of allyl propynyl ether to 3-oxabicyclo[4.1.0]heptenes in 1995,[3a] this type of 6-*endo-dig* cycloisomerization has been developed by the use of transition-metal catalysts, such as platinum,[3] rhodium,[4] gold[5] and iridium.[6] For example, Chung and co-workers reported the gold-catalyzed cyclization of enynes containing an olefinic cycle to give azabicyclo[4.1.0]heptenes under mild conditions.[5c] Similar oxygen heterocycles with high diastereoselectivities have been reported by Michelet's and Chen's groups.[5f,h]

Alkylidenecyclopropanes (ACPs) containing a coordinating double bond and a strained carbocycle can undergo a number of interesting metal-assisted cycloadditions when tethered by alkenes or alkynes.[7] In this aspect, Toste's group reported a new gold-catalyzed ring-expanding enyne cycloisomerization reaction that allows for rapid preparation of complex polycyclic ring systems (Scheme 1a).[2j] Herein, we report a new construction of tricyclic compounds along with cycloisomerization from alkylidenecyclopropanes toward six-membered heterocyclic rings (Scheme 1b).



Scheme 1. Gold-catalyzed cycloisomerization of alkylidenecyclopropanes tethered by alkynes.

Table 1. Optimization of the reaction conditions for gold(I)-catalyzed intramolecular cyclization.



Entry[a]	Catalyst [*x* mol %]	Solvent	Yield [%],[b] **2a**
1	$[(PPh_3)AuCl]/AgOTf$ (5)	DCE	69
2[c]	$PtCl_2$ (5)	DCE	45
3[c]	$RhCl(CO)(PPh_3)_2/AgSbF_6$ (5)	DCE	Complex
4	$[(PPh_3)AuCl]$ (5)	DCM	NR
5	AgOTf (5)	DCM	NR
6	$[(PPh_3)AuCl]/AgOTf$ (5)	toluene	20
7	$[(PPh_3)AuCl]/AgOTf$ (5)	MeCN	NR
8	$[(PPh_3)AuCl]/AgOTf$ (5)	1,4-dioxane	37
9	$[(PPh_3)AuCl]/AgOTf$ (5)	$CHCl_3$	87
10	$[(PPh_3)AuCl]/AgOTf$ (5)	DCM	90
11	$[(PPh_3)AuCl]/AgOTf$ (10)	DCM	44
12	$[(PPh_3)AuCl]/AgSbF_6$ (5)	DCM	42
13	$[(PPh_3)AuCl]/AgBF_4$ (5)	DCM	39
14	$[(PMe_3)AuCl]/AgOTf$ (5)	DCM	47
15	$[(tBu_3P)AuCl]/AgOTf$ (5)	DCM	90
16	$[AuCl_3]/AgOTf$ (5)	DCM	3
17	$[(IPr)AuCl]/AgOTf$ (5)	DCM	58
18	$[(tBuXPhos)Au(NCMe)]SbF_6$ (5)	DCM	94

[a] All reactions were carried out by using **1a** (0.2 mmol) in the presence of catalyst (*x* mol %) in various solvents (2.0 mL) unless otherwise specified. [b] Yield of isolated product. [c] At 80 °C. NR = no reaction.

Initial studies by using alkylidenecyclopropane **1a** (0.2 mmol) as the substrate were aimed to determine the reaction outcome and subsequently optimize the reaction conditions. The results are summarized in Table 1. We found that an interesting tricyclic product **2a** was formed in 69 % yield by using $[(PPh_3)AuCl]/AgOTf$ as the catalyst (5 mol %) in 1,2-dichloroethane (DCE) at room temperature (20 °C) (Table 1, entry 1). The structure of compound

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2a was confirmed by NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).[8] Carrying out the reaction in the presence of $PtCl_2$ or $[RhCl(CO)(PPh_3)_2]/[AgSbF_6]$ (5 mol %), which were effective catalysts in other similar reactions, afforded the desired product **2a** in lower yield or complex product mixtures, respectively (Table 1, entries 2 and 3).[3b–h,j,m,4d] Control experiments indicated that by using $[(PPh_3)AuCl]$ or AgOTf alone as the catalyst did not promote the reaction (Table 1, entries 4 and 5). Further examination of solvent effects revealed that dichloromethane (DCM) was the solvent of choice, and **2a** was formed in lower yield in other organic solvents, such as toluene, MeCN, 1,4-dioxane, or $CHCl_3$ (Table 1, entries 6–10). Moreover, adding $[(PPh_3)AuCl]$/AgOTf (10 mol %) afforded **2a** in 44 % yield (Table 1, entry 11). Changing silver salt to $AgSbF_6$ or $AgBF_4$ did not improve the reaction outcomes (Table 1, entries 12 and 13). By using $[(PMe_3)AuCl]$ or $[(tBu_3P)AuCl]$ instead of $[(PPh_3)AuCl]$ as the gold catalyst gave **2a** in 47 and 90 % yields, respectively, and [(IPr)AuCl] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as well as $AuCl_3$ were not effective gold catalysts in this reaction (Table 1, entries 14–17). In the presence of $[(tBuXPhos)Au(NCMe)]SbF_6$ (Figure 1, cat. **1**), **2a** could be obtained in 94 % yield under otherwise identical conditions (Table 1, entry 18). Therefore, the optimal reaction conditions have been identified to carry out the reaction in DCM at room temperature by using $[(tBuXPhos)Au(NCMe)]SbF_6$ (5 mol %) as the catalyst.

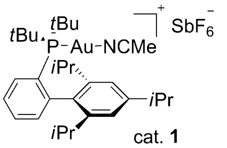
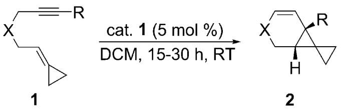


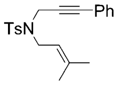
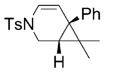
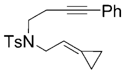
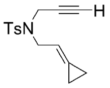
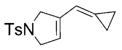
Figure 1. Structure of $[(tBuXPhos)Au(NCMe)]SbF_6$.

We next examined the substrate generality of the reaction under the optimized conditions, and the results are shown in Table 2. As can be seen, for nitrogen-tethered substrates **1b–d** with an electron-donating group on the benzene ring, such as MeO and Me groups, the reactions proceeded smoothly to give the desired products **2b–d** in 87–99 % yields (Table 2, entries 1–3). When the electron-withdrawing groups, Br or Cl, were introduced on the benzene ring (substrates **1e** and **1f**), the corresponding products **2e** and **2f** were obtained in 98 and 99 % yields, respectively (Table 2, entries 4 and 5). The aromatic group of **1** could also be a naphthyl group (substrate **1g**), giving the cycloisomerized compound **2g** in 99 % yield (Table 2, entry 6). As for substrates **1h** (R = Me) and **1i** (R = Et) with an alkyl group at the terminal of alkyne moiety, tricyclic compounds **2h** and **2i** could be formed in 73 and 87 % yields, respectively (Table 2, entries 7 and 8). In the case of other N-sulfonated amines (X = NNs or NBs), the reaction also proceeded smoothly to give the desired products **2j** and **2k** in 88–99 % yields, indicating a broad substrate scope of this reaction (Table 2, entries 9 and 10). For oxygen-tethered alkylidenecyclopropanes, such as substrates **1l** and **1m**, the reactions produced **2l** and **2m** in 71 and 80 % yields, respectively (Table 2, entries 11 and 12). Further examination of substrate **1n** revealed that the azabicyclo[4.1.0]heptene derivative **2n** could be obtained in 94 % yield, when 4 Å molecular sieves was added (Table 2, entry 13). As for 1,7-enyne **1o**, no reaction occurred under the standard conditions (Table 2, entry 14). When the terminal of alkyne moiety is a hydrogen atom (substrate **1p**), the corresponding 1,3-diene **3p** could be obtained in 71 % yield rather than the tricyclic product (Table 2, entry 15).[9] The product structures of **2b–n** were determined by NMR spectroscopic data, MS, and HRMS. The structure of compound **3p** was confirmed by NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).[10]

Table 2. Substrate scope of the gold(I)-catalyzed cycloisomerization.



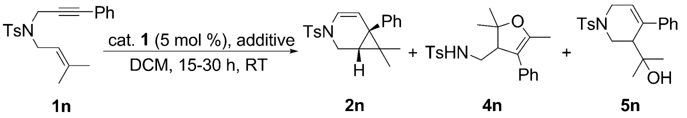
1 2

Entry[a]	1	X	R	Yield [%],[b] 2
1	**1b**	NTs	4-MeOPh	**2b**, 87
2	**1c**	NTs	4-MePh	**2c**, 95
3	**1d**	NTs	3-MePh	**2d**, 90
4	**1e**	NTs	2-BrPh	**2e**, 98
5	**1f**	NTs	4-ClPh	**2f**, 99
6	**1g**	NTs	1-naphthyl	**2g**, 99
7	**1h**	NTs	Me	**2h**, 73
8	**1i**	NTs	Et	**2i**, 87
9	**1j**	NNs	Ph	**2j**, 88
10	**1k**	NBs	Ph	**2k**, 99
11	**1l**	O	Ph	**2l**, 71
12	**1m**	O	4-ClPh	**2m**,80
13[c]	**1n**	 TsN Ph	 TsN Ph H	**2n**, 94
14	**1o**	 TsN Ph		NR
15	**1p**	 TsN H	 TsN	**3p**, 71

[a] All reactions were carried out by using **1** (0.2 mmol) in the presence of cat. **1** (5 mol %) in DCM (2.0 mL) at RT for 15–30 h. [b] Yield of isolated product. [c] Molecular sieves (4 Å, 50 mg) was added. Ts = 4-toluenesulfonyl; Ns = 4-nitrobenzenesulfonyl; Bs = 4-bromobenzenesulfonyl; NR = no reaction.

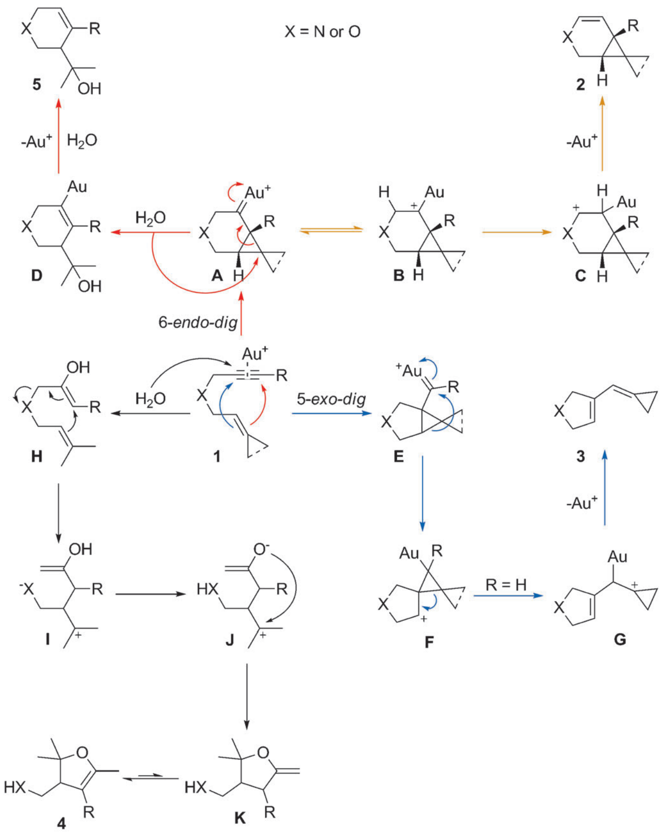
On the other hand, in the case of 1,6-enyne **1n**, under the standard conditions, the reactions produced **2n**, **4n**, and **5n**[11] in 49, 15, and 29 % yields, respectively. Then, adding molecular sieves (4 Å, 50 mg) into the reaction system, azabicyclo[4.1.0]heptene derivative **2n** could be obtained in 94 % yield as the sole product. Alcohol derivative **5n** was formed in 77 % yield along with a trace amount of 2,3-dihydrofuran derivative **4n**, when H_2O (10 equiv) was added, suggesting that products **4n** and **5n** are derived from adventitious water (Scheme 2). The structure of compound **4n** was confirmed by NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).[12]

Plausible mechanisms for these reactions are outlined in Scheme 3 on the basis of above results. Coordination of Au^I complex to the alkyne forms intermediate **1**, which evolves



Additive	Yield [%]		
none	49	15	29
molecular sieves (4Å; 50 mg)	94	–	–
H_2O (10 equiv)	–	trace	77

Scheme 2. Gold(I)-catalyzed cycloisomerization of **1n** by using different conditions.



Scheme 3. A plausible reaction mechanism.

to give the cyclopropyl Au–carbene intermediate **A** (via *6-endo-dig* cyclization) or **E** (via *5-exo-dig* cyclization), which are often observed in gold-catalyzed cycloisomerizations of 1,6-enynes. It should be also mentioned here that we did not observe any product via *6-exo-dig* cyclization as reported by Toste and co-workers.[2j] There might be an equilibrium between the intermediates **A** and **B**, intermediate **B** is expected to undergo a facile [1,2]hydride shift to generate intermediate **C**, followed by elimination of Au^I complex to give product **2** (orange arrow).[5f] Alternatively, nucleophilic attack of water on the cyclopropyl moiety of intermediate **A** gives intermediate **D**, which undergoes hydrolysis to produce alcohol derivative **5** (red arrow).[5b] On the other hand, carbenoid **E** can undergo a rearrangement to give a spiro intermediate **F**.[4b,9a] Depending on the substitution pattern, when R=H, the spiro intermediate **F** undergoes fragmentation to produce the carbocation **G**, followed by elimination of Au^I complex to give 1,3-diene **3** (blue arrow). As depicted by black arrows, activation of the alkyne moiety by Au^I complex induces a nucleophilic attack of water to give intermediate **H**. Skeletal reorganization of intermediate **H** produces enol **I**, followed by intramolecular proton transfer to form the oxo-anion intermediate **J**. Intermediate **J** undergoes intramolecular nucleophilic attack to produce tetrahydrofuran **K**, which can also further tautomerize to the corresponding 2,3-dihydrofuran derivative **4**.

In conclusion, we have developed a new gold(I)-catalyzed cycloisomerization of nitrogen and oxygen-tethered alkylidenecyclopropanes to provide an easy access to tricyclic compounds or bicyclo[4.1.0]heptene derivatives in high yields under very mild conditions. Further applications of this air- or moisture-tolerant reaction of a gold-catalyzed tandem system and more detailed mechanistic investigation are underway in our laboratory.

Experimental Section

General procedure for gold(I)-catalyzed cycloisomerization of alkylidenecyclopropanes under the standard reaction conditions: Under ambient atmosphere, an alkylidenecyclopropanes **1** (0.2 mmol, 1.0 equiv) was dissolved in DCM (2.0 mL) in an Schlenk tube, and [(*t*BuXPhos)Au(NCMe)]SbF_6 (5 mol %) was added. Then, the reaction mixture was stirred at RT until the reaction was completed. The solvent was removed under reduced pressure, and the residue was purified by a flash-column chromatography (SiO_2) to give the corresponding product **2** in moderate-to-excellent yields.

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Keywords: cyclization · cyclotrimerization · homogeneous catalysis · heterocycles · gold

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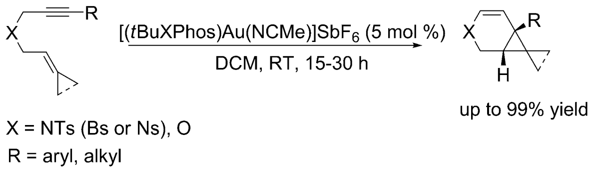

A new construction of tricyclic compounds has been developed from a gold-catalyzed cycloisomerization of alkylidenecyclopropanes tethered by alkynes, giving the corresponding nitrogen- and oxygen-containing six-membered heterocyclic compounds in high yields under very mild conditions (see scheme; Ts = 4-toluenesulfonyl, Ns = 4-nitrobenzenesulfonyl, Bs = 4-bromobenzenesulfonyl).

Hererocycles

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Gold(I)-Catalyzed Cycloisomerization of Nitrogen and Oxygen-Tethered Alkylidenecyclopropanes to Tricyclic Compounds