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Formal Lewis acidic character of gold nanocluster catalyst*

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Abstract: Gold nanoclusters (NCs) stabilized by the poly(*N*-vinyl-2-pyrrolidone) hydrophilic polymer (Au:PVP) behave not only as aerobic oxidation catalyst but also formal Lewis acid catalyst, which promotes the intramolecular heterocyclization of γ-hydroxyalkenes and γ-aminoalkenes.

Keywords: aerobic oxidation; gold nanoclusters; heterocyclization; hydroamination; Lewis acid.

INTRODUCTION

Two decades have passed since Haruta's breakthrough that the nanosized Au clusters supported on metal oxide showed a catalytic activity toward the aerobic oxidation of CO to CO_2 [1]. Oxidation reactions have always been a central issue in this area in contrast with the cationic Au(I) complex chemistry focused on the soft Lewis acid catalyst [2]. In 2004, Tsukuda's group and our group started the collaborative works of *quasi*-homogeneous Au nanocluster (NC) chemistry mainly for the purpose of elucidating the real catalytic activity and essence of the size effect without metal oxide support. We have also been interested in researching the novel reactivity of Au clusters applicable to synthetic organic chemistry. In a series of publications, we showed that Au NCs stabilized by poly(*N*-vinyl-2-pyrrolidone) (**Au:PVP**) exhibit high catalytic activity for aerobic oxidation reactions such as oxidation of alcohols [3], oxygenation of benzylic ketones [4], and generation of hydrogen peroxide [5], but only when the diameter is reduced to less than ca. 2 nm. It was proposed that a superoxo-like molecular oxygen species generated on the cluster surface plays a key role in these oxidation reactions. We also observed that **Au:PVP** catalyzed homocoupling reactions of arylboron compounds under aerobic conditions [6]. This result hints at the possibility that an electron-deficient site at the cluster surface, generated by adsorption of O_2, behaves as a formal Lewis acid and provides a site for transmetalation of aryl moieties.

Intramolecular heterocyclization of γ-hydroxyalkenes and γ-aminoalkenes, which are conventionally promoted by Lewis acid catalyst, are suitable targets to study the possibility whether Au NCs in aqueous media under aerobic conditions act as a Lewis acid catalyst.

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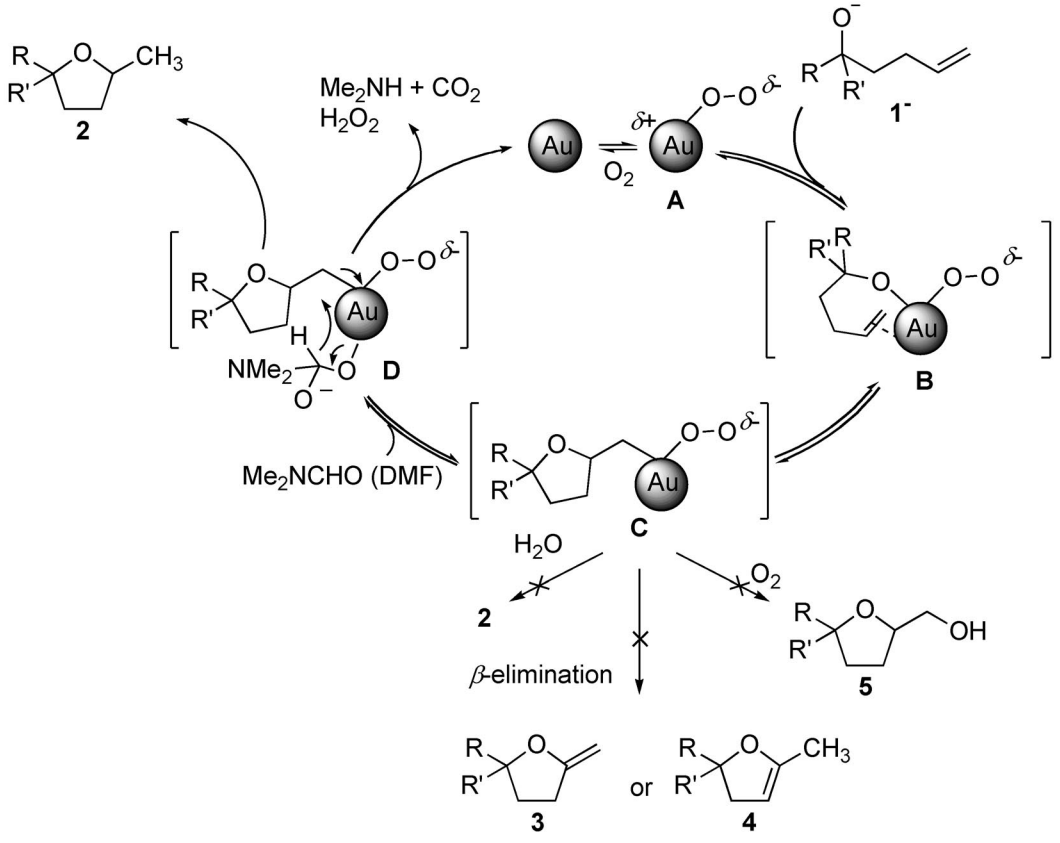
RESULTS AND DISCUSSION

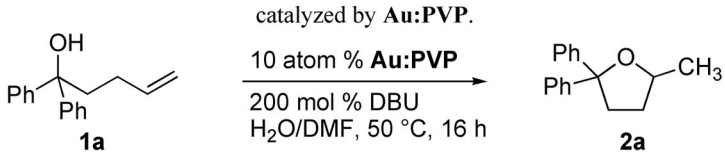
Intramolecular heterocyclization of γ-hydroxyalkenes [7]

Under aerobic oxidation conditions, γ-hydroxyalkenes generally undergo Wacker-type oxidation [8] or oxygenation [9] (Scheme 1). In contrast, when 1,1-diphenyl-4-penten-1-ol (**1a**) was treated with 10 atom % of **Au:PVP** (mean size: 1.3 nm) and 200 mol % of DBU at 50 °C for 16 h in H_2O/DMF mixed solvent under air, **2a** was obtained in 87 % yield without the formation of Wacker-type products **3a**, **4a** or oxygenation product **5a** (entry 1, Table 1). Cyclization did not occur under carefully degassed conditions (entry 2), or using a catalyst of greater cluster diameter [**Au:PVP**(9.5)]; the latter showed no catalytic activity for aerobic oxidation (entry 3) [3]. These results indicate that molecular oxygen does not act as an oxidant but plays an essential role in the reaction. The catalytic behavior of **Au:PVP** appears to be similar to that of Au(I) and Au(III) compounds, which are applied as Lewis acid catalysts particularly for activation of alkenes [10]. It is thought that molecular oxygen generates a reaction center with Lewis acid character on the Au NC surface; the constituent atoms of Au NCs are formally in a zero-valence state.



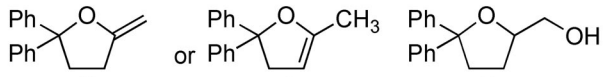
Scheme 1 Possible mechanism of **Au:PVP**-catalyzed heterocyclization of γ-hydroxyalkenes.

Table 1 The role of O_2 in **Au:PVP**-catalyzed reaction of 1,1-diphenyl-4-penten-1-ol (**1a**) catalyzed by **Au:PVP**.



1a **2a**

Entry	Catalyst	Conditions	Yield, %
1	**Au:PVP**(1.3)	under air	87
2	**Au:PVP**(1.3)	under degassed conditions	0
3	**Au:PVP**(9.5)	under air	0



3a **4a** **5a**

Results of the cyclization from γ-hydroxyalkenes catalyzed by **Au:PVP** are summarized in Table 2. The reactivity of tertiary alcohols was dependent to a remarkable extent on the substituents at the α-position of the alcohols, as shown in entries 1–3. Although cyclization proceeded smoothly in the reaction with **1a** (entry 1; also Table 1, entry 1), no reaction occurred with phenyl-methyl derivative **1b** (entry 2). In contrast, cyclization did occur with the α-naphthyl-methyl derivative **1c** to afford **2c** in 62 % yield (entry 3). The efficiency of reaction was also sensitive to substitution at the alkene moiety. The introduction of other substituents at the internal and/or terminal alkenic carbon decreased the yields of the products (entries 4–6), probably due to steric hindrance. The reactions with primary and secondary alcohols were investigated. It was anticipated that cycloaddition would compete with alcohol oxidation because the reaction was conducted under conditions similar to those for aerobic oxidation [3]. However, cyclization took place predominantly for the aliphatic alcohols, giving the corresponding tetrahydrofuran derivatives (entries 7–9). In contrast, aerobic oxidation was preferred in the reaction of benzylic alcohols, giving the corresponding ketones selectively (entry 10).

Next, the source of the hydrogen at the terminal carbon was studied by sequential combinations of D-labeled solvents (Table 3). Compound **2a**-D was obtained when DMF-d_7 was employed, instead neither **2a**-D was obtained nor kinetic isotope effect (KIE) was observed in the case of DMF-d_6. These results strongly suggested that the formyl hydrogen of DMF played selectively as a hydrogen source in the reaction.

A possible mechanism for the reaction is shown in Scheme 1. As proposed in previous studies [3–6], the reaction is initiated by the formation of key intermediate **A**, which possesses an electron-deficient site generated by adsorption of O_2 onto the surface of the Au. **A** acts as a Lewis acid, activating both alkoxide and alkene by adsorption onto the surface (**B**), and giving **C** by either the insertion of an alkene into O–Au bond or the external attack of oxygen to the alkene adsorbed on Au. From this C–Au intermediate, neither β-elimination (Wacker-type process), O_2 insertion (oxygenation), nor protonation proceeds; only DMF acts as a hydrogen source to afford **2** accompanied by the regeneration of free Au clusters. In total, formal Lewis acidic reaction (addition reaction) takes place as a main pathway, but the aerobic oxidation also proceeds behind using DMF as a sacrificial reductant. This fact informs us that the choice of appropriate hydrogen source (sacrificial reductant) might be important.

Table 2 Intramolecular heterocyclization of γ-hydroxyalkenes catalyzed by **Au:PVP**.

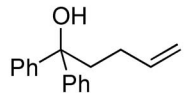
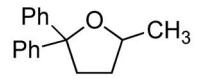
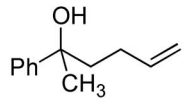
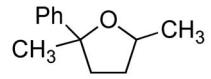
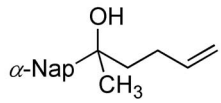
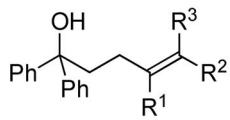
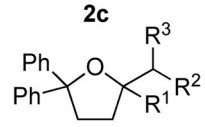
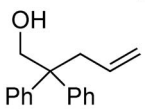
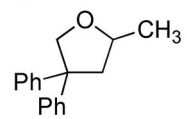
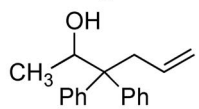
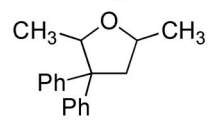
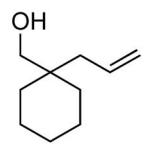
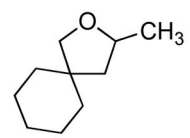
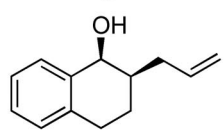
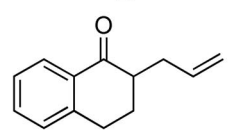
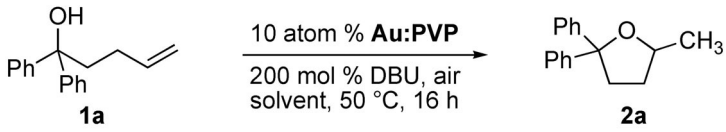
Entry	Alkene	Product	Yield, %
1	 **1a**	 **2a**	87
2	 **1b**	 **2b**	0
3	 **1c**	 **2c**	62 (1.1:1)
			
4	**1d** $R^1 = CH_3$, $R^2 = H$, $R^3 = H$	**2d**	38
5	**1e** $R^1 = H$, $R^2 = CH_3$, $R^3 = H$	**2e**	8
6	**1f** $R^1 = H$, $R^2 = CH_3$, $R^3 = CH_3$	**2f**	0
7	 **1g**	 **2g**	93
8	 **1h**	 **2h**	93 (3.6:1)
9	 **1i**	 **2i**	33
10	 **1j**	 **2j**	77

Table 3 Labeling experiment in the reaction of **1a**.



1a **2a**

Entry	Solvent	Yield, %	%D	KIE
1	H_2O/DMF	87	0	–
2	D_2O/DMF	80	0	1.49
3	H_2O/DMF-d_7[a]	63	71	7.5
4	D_2O/DMF-d_7[a]	42	67	10.6
5	D_2O/DMF-d_6[b]	84	4	1.06

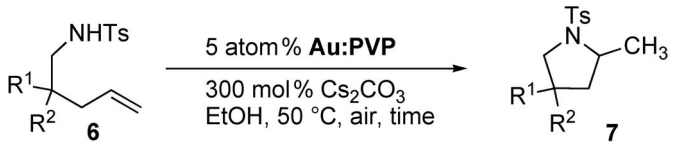
[a]$(CD_3)_2NCDO$ [b]$(CD_3)_2NCHO$

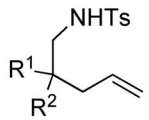
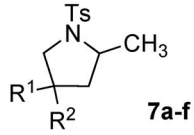
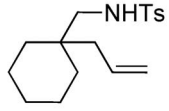
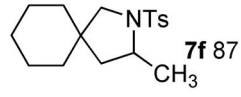
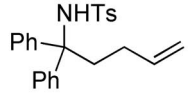
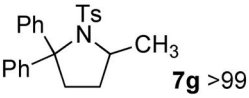
Intramolecular heterocyclization of γ-toluenesulfonylaminoalkenes [11]

The addition of the amino group to the C–C multiple bond offers an efficient atom-economical route to N-containing molecules and is one of the most extensively studied transformations [12]. In particular, intramolecular reaction provides a useful method for the construction of heterocycles. Various types of activating reagents have been reported for the reaction with unactivated alkenes, including transition metals [13] and acids [14]. However, many of the reported catalysts have a limited scope of substrates, sensitivity toward moisture and oxygen, and sluggish rates for reactions involving unactivated substrates. In the previous section, we demonstrated that **Au:PVP** promoted the intramolecular heterocyclization of γ-hydroxyalkenes. According to an analogous reactivity, it is expected that the similar reaction of γ-toluenesulfonylaminoalkenes could proceed using the **Au:PVP** catalyst under milder, basic, and aerobic conditions.

Pyrrolidine derivative **7a** was obtained in quantitative yield when toluenesulfonamide (**6a**) was treated with 5 atom % of **Au:PVP** and 300 mol % of Cs_2CO_3 at 50 °C for 1 h in EtOH as solvent under aerobic conditions (Table 4, entry 1). Cyclization did not occur under carefully degassed conditions (entry 2), or with the use of **Au:PVP**(9.5) catalyst (entry 3) [3–6]. These results indicate that molecular oxygen also plays an essential role in the reaction. The geminal effect at the β-position was then investigated. The cyclization proceeded smoothly in the reaction with methyl-phenyl- (**6b**), phenyl- (**6c**), and dimethyl- (**6d**) substitutes, to afford the corresponding pyrrolidine derivatives **7b**, **7c**, and **7d** in excellent yields, respectively (entries 4–6). Cycloaddition even took place using **6e** without the geminal effect, resulting in a moderate yield (entry 7). These results are in contrast to those for the reaction with alcohols, which displayed an unusual substituent effect on the β-position (Table 2). The bicyclic product **7f** was also obtained in good yield (entry 8). The diphenyl substitute at the α-position **6g** also underwent quantitative cyclization after 1 h (entry 9).

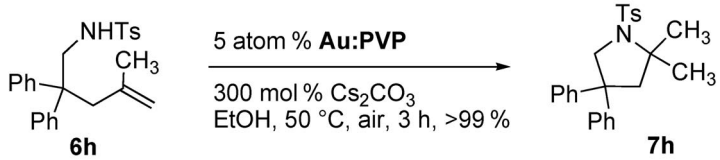
Table 4 Au:PVP-catalyzed intramolecular heterocyclization of γ-toluenesulfonylaminoalkenes.



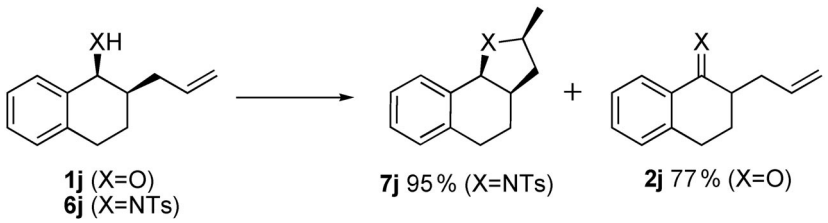
Entry	Alkene	Time, h	Yield, %[a]
	 **6a-f**		 **7a-f**
1	**6a** R^1, R^2 = Ph	1	**7a** >99
2	**6a**		**7a** 0[b]
3	**6a**		**7a** 0[c]
4	**6b** R^1 = Ph, R^2 = CH_3	4	**7b** 93 (1.9:1)[d]
5	**6c** R^1 = Ph, R^2	4	**7c** 89 (1.2:1)[d]
6	**6d** R^1, R^2 = CH_3	16	**7d** 81
7	**6e** R^1, R^2	16	**7e** 41
8	 **6f**	1	 **7f** 87
9	 **6g**	1	 **7g** >99

[a]Isolated yield, [b]under Ar, [c]9.5 nm Au:PVP, [d] ^{1}H NMR ratio.

To elucidate the source of hydrogen at the methyl group of the product, **6a** was treated with 300 mol % Cs_2CO_3 at 50 °C in EtOD or EtOH-d_6. Cyclization proceeded quantitatively in EtOD after 6 h; however, **7a-**D was not obtained. **7a-**D was obtained in 96 % yield (69.5 % D) after 20 h when EtOH-d_6 was employed, which reveals that the hydrogen is introduced from the ethyl group of EtOH. From these results, the reaction mechanism is likely to be similar to that of γ-hydroxyalkenes. The major difference is the hydrogen source is changed from DMF to EtOH.



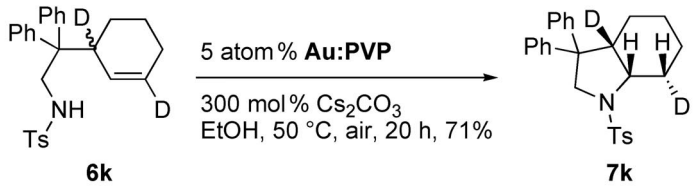
(1)



(2)

1j : 10 atom% **Au:PVP**, 200 mol% DBU, H_2O/DMF, 50 °C, air, 24 h.
6j : 5 atom% **Au:PVP**, 300 mol% Cs_2CO_3, H_2O/EtOH, 50 °C, air, 4 h.

Higher reactivity of toluenesulfonamides allows the determination of the reaction pathway at the C–O bond formation, the insertion of an alkene into O–Au bond, or the external nucleophilic attack of oxygen to the alkene adsorbed on Au. As shown in eq. 3, *anti*-adduct **7k** was obtained stereoselectively from **6k**, indicating the external nucleophilic attack is involved in the mechanism [13a].



(3)

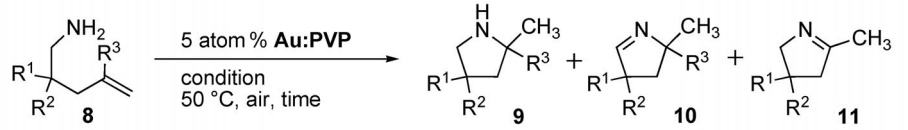
Intramolecular heterocyclization from primary amines [15]

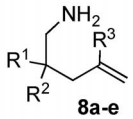
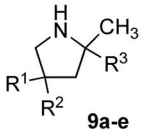
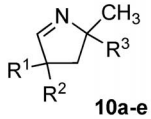
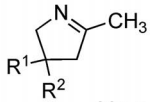
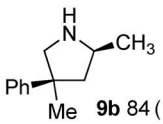
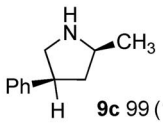
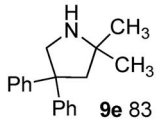
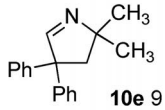
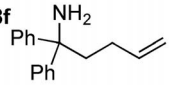
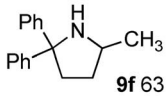
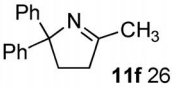
Among the reported catalysts for the cyclization from primary amines, such as organolanthanides [12], group IV metals [16], alkali metals [17], and transition metals [18], there are still few moisture- and air-stable catalyst systems [19]. In addition, the reactivity of the catalysts is highly dependent on the substituent located on nitrogen, and no versatile catalyst for various types of amine derivatives is known. We anticipated that **Au:PVP** would function as a moisture-/air-stable catalyst for the reaction from primary amines, but disappointingly, the cyclized product was obtained in only 3 % yield under similar conditions to that used for the toluenesulfonamide reaction. After screening, we finally found that formic acid derivatives are the appropriate hydrogen source (sacrificial reductant) in the reaction of primary amines. It was also found that the reaction was dependent on the acidity of the solvent.

Results of the reaction of primary amines are summarized in Table 5. In the reaction with **8a**, **8b**, and **8c**, conditions C, B, and A gave the best results, respectively, affording the corresponding pyrrolidines **9a**, **9b**, and **9c** in high yields (entries 1–9). The *cis*-diastereomer was obtained as a major product. On the other hand, no reaction occurred with the non-substituted amine **8d** (entry 10). The δ-methyl-substituted alkene **8e** underwent cyclization in good yield with the **3e** imine as a minor product (entries 11–13). **9f** was also obtained in moderate yield from **8f** at 27 °C with the **11f** imine as a minor product (entries 14–16).

Next, **8a** was treated with 1000 mol % of HCO_2NH_4 or DCO_2NH_4 in D_2O and/or EtOH-d_6 (condition A), and the results are listed in Table 6. For the heterocyclization of γ-hydroxyalkenes and γ-aminoalkenes, the hydrogen at the terminal methyl group of the products was introduced from the formyl group of DMF and the ethyl group of EtOH, both of which were used as a solvent, respectively. In contrast, EtOH was not a major hydrogen source in the case of the primary amines, as shown in entries 1–3. **9a**-D was obtained effectively when DCO_2NH_4 was employed, which revealed that hydrogen was introduced from the formyl group of HCO_2NH_4 (entry 4).

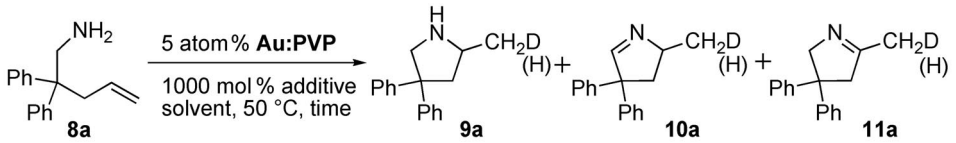
Table 5 Cyclization of primary amines catalyzed by **Au:PVP**.



Entry	Alkene	Condition[a]	Time/h	Yield/%		
	 **8a-e**			 **9a-e**	 **10a-e**	 **11a-e**
1	**8a** R^1, R^2 = Ph R^3 = H	A	4	**9a** 83	**10a** 4	**11a** 7
2		B	4	80	3	3
3		C	4	94	2	4
4	**8b** R^1 = Ph, R^2 = CH_3 R^3 = H	A	2	 **9b** 84 (1.2:1)[b]	-	-
5		B	3	>99 (1.2:1)[b]	-	-
6		C	2	72 (1.2:1)[b]	-	-
7	**8c** R^1 = Ph, R^2 = H R^3 = H	A	2	 **9c** 99 (1.5:1)[b]	-	-
8		B	10	88 (1.2:1)[b]	-	-
9		C	4	11 (1.1:1)[b,d]	-	-
10	**8d** R^1, R^2, R^3 = H	A	-	no reaction		
11	**8e** R^1, R^2 = Ph R^3 = CH_3	A	4	 **9e** 83	 **10e** 9	-
12		B	13	77	4	-
13		C	4	55[d]	-	-
14	**8f** 	A	24[c]	 **9f** 63	-	 **11f** 26
15		B	13[c]	56	-	38
16		C	24[c,d]	29	-	26

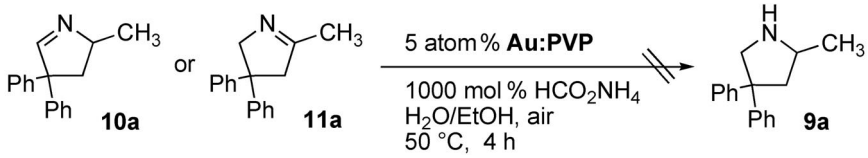
[a]Condition A: 1000 mol % HCO_2NH_4, H_2O/EtOH, 50 °C, 4 h, Condition B: 400 mol % HCO_2H, pH 6.86 buffer solution/EtOH, 50 °C, 4 h, Condition C: 1000 mol % HCO_2H, 400 mol % NH_3 aq., pH 4.01 buffer solution/EtOH, 50 °C, 4 h. [b]Diastereomer ratio was determined as the corresponding toluenesulfonamide. [c]27 °C. [d]8 was recovered (Entry 9: 42 %, Entry 13: 35 %, Entry 16: 29 %).

Table 6 Labeling experiment in the reaction of **8a**.



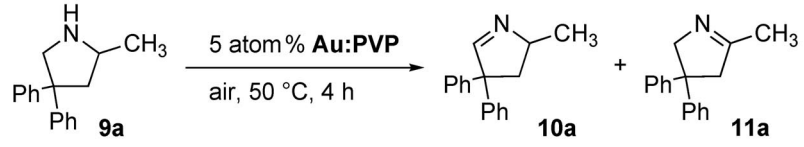
Entry	Solvent	Additive	Time/h	Yield/% (%D)		
				9a	**10a**	**11a**
1	D_2O/EtOD	HCO_2NH_4	17	81 (0)	9 (0)	7 (0)
2	H_2O/EtOH-d_6	HCO_2NH_4	17	67 (9)	9 (5)	5 (2)
3	D_2O/EtOH-d_6	HCO_2NH_4	17	81 (11)	8 (4)	8 (1)
4	H_2O/EtOH	DCO_2NH_4	4	82 (89)	-	trace (82)

It should be noted that the D/H ratios in the imines **10a/11a** were slightly smaller than that in **9a** in every case, which indicates that a minor pathway without hydrogenation by a formate could occur. It is also noteworthy that D was selectively introduced at the terminal methyl position and no other positions, such as the methine position, as determined from ^{2}H NMR. This indicates that the formate does not act as a reductant of the imines. **10a** or **11a** were treated under condition A to afford a quantitative recovery of the imines (eq. 4).



(4)

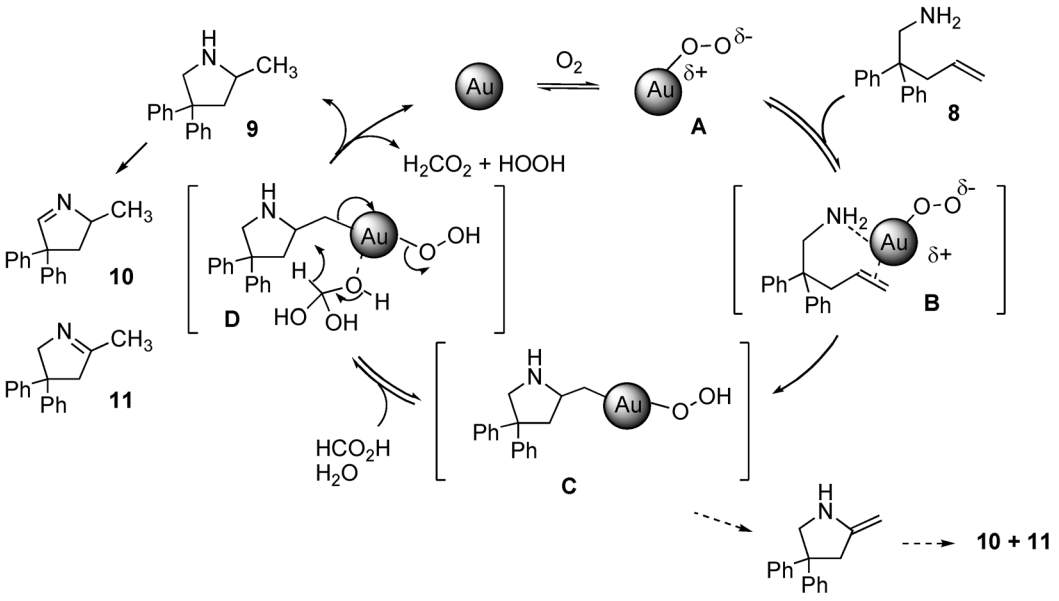
Due to the character of **Au:PVP** as an aerobic oxidation catalyst [3–6], the imines **10a** and **11a** could be formed by the secondary oxidation of **9a** [21]. Since the aerobic oxidation is performed under basic conditions, it is expected that the pathway for the secondary oxidation of **9a** might be more efficient in a higher pH reaction mixture caused by the consumption of formic acid as a hydrogen source. Therefore, **9a** was treated with 5 atom % **Au:PVP** in various pH (pH = 9.18, 6.86, 4.01 buffer)/EtOH solutions at 50 °C. Although the oxidation to **10a** or **11a** did not proceed sufficiently in every case, the reaction rate was slightly higher under basic conditions (eq. 5). The imines **10a** or **11a** were not detected by ^{1}H NMR from the pH = 6.86 and 4.01 buffer/EtOH solutions after 4 h, which indicates that secondary oxidation is promoted under basic conditions.



1000 mol% HCO_2NH_4 H_2O/EtOH,	6%	7%
pH=9.18 Buffer/EtOH	5%	3%
pH=6.86 Buffer/EtOH	-	-
pH=4.01 Buffer/EtOH	-	-

(5)

The reaction mechanism is describable as similar to the previous two reactions as shown in Scheme 2. The reaction is initiated by the adsorption of O_2 onto the surface of the Au NCs as a key intermediate (**A**) that possesses an electron-deficient site. The most important difference from the previous examples is that the reaction should be carried out under neutral to slightly acidic conditions. In the reaction with alcohols or toluenesulfonamides, basic conditions are necessary to assist the adsorption of less nucleophilic substrates. In contrast, substrates with primary amino group can adsorb onto the Au surface, even under neutral/slightly acidic conditions (**B**) [22]. Although the reason why the cyclization does not proceed under basic conditions is not yet clear, the formal Lewis acidic character of Au clusters might be more efficient under neutral/acidic conditions. After C–N bond formation to generate a Au–C intermediate (**C**), selective hydrogenation from HCO_2H might occur. The formyl group hydrogen is abstracted, affording amine **9**. The formation of imines **10** and **11** might occur through both the secondary oxidation of amine **9** as a major pathway and through isomerization after β-hydrogen elimination from the Au–C intermediate **C** as a minor pathway. The latter is supported by the smaller D/H ratio in **10/11** than that in **9**. The former oxidation pathway can be reduced using the buffer as a co-solvent, because the pH of the reaction mixture gradually increases by the consumption of formic acid as a hydrogen source.



Scheme 2. Possible mechanism of **Au:PVP**-catalyzed heterocyclization of γ-aminoalkenes.

CONCLUSION

As described above, **Au:PVP** can be used as a formal Lewis acid catalyst for the heterocyclization of γ-hydroxyalkenes and γ-aminoalkenes although aerobic oxidation activity is an essential role. Combination with the appropriate sacrificial reductant is important for the efficient catalytic reaction. Characteristic features of **Au:PVP** catalyst involve a versatile and easy-to-handle Lewis acid catalyst due to its moisture-/air-stability and operation under mild reaction conditions.

EXPERIMENTAL

General

Melting points were determined on a Yanaco MP-J3 and were uncorrected. Infrared (IR) spectra were recorded on a JASCO FT IR-4100 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JMN LAMBDA 400 spectrometer at 23 °C at 400 and 100 MHz, respectively. $CDCl_3$ was used as a solvent, and the residual solvent peaks were used as an internal standard (^{1}H NMR: 7.26 ppm; ^{13}C NMR: 77.00 ppm). Elemental analyses were measured on a Yanaco CHN corder MT-6. Mass spectra were measured on a JEOL JMS-777V spectrometer using electron impact mode (EI). Silica gel chromatography was performed on Kanto 60N, Wako Wakosil C-300, or Yamazen Hi-Flash column using a Yamazen YFLC purification system. TLC analysis was performed using Merck Silica gel 60 F_{254}, and preparative TLC was conducted using Wako Wakogel B-5F. GPC was performed with Japan Analytical Industry LC-908 using chloroform as a solvent. **Au:PVP** (0.5 mM) was prepared according to the literature we reported previously [6a,7]. All reagents and solvents were commercially purchased and further purified according to the standard methods, if necessary.

General procedure for the heterocyclization of γ-hydroxyalkenes

A test tube (φ = 30 mm) was placed with **1** (0.05 mmol), DBU (15 µl, 0.10 mmol), and DMF (5 ml). The aqueous solution of **Au:PVP** (0.5 mM, 10 ml = 10 atom %) was added, and the reaction mixture was stirred vigorously (1300 rpm) at 50 °C for 16–24 h. The reaction mixture was extracted with MTBE (3 × 10 ml) and then the combined organic layers were washed with water (100 ml) and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the product was carried out by preparative thin-layer chromatography (PTLC) or gel permeation chromatography (GPC).

General procedure for the heterocyclization of γ-toluenesulfonylaminoalkenes

Into a test tube (φ = 30 mm) was placed **1** (0.1 mmol), Cs_2CO_3 (97.7 mg, 0.30 mmol), and dried **Au:PVP** (38.1 mg = 5 atom %). EtOH (30 ml) was added, and the reaction mixture was stirred vigorously (1300 rpm) at 50 °C for the time specified. The reaction mixture was extracted with ethyl acetate (3 × 20 ml), and then the combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the product was carried out by PTLC.

General procedure for the reaction with primary amine

A test tube (φ = 30 mm) was placed with **1** (0.1 mmol) and dried **Au:PVP** (38.1 mg = 5 atom %). Water (20 ml), EtOH (10 ml), and HCO_2NH_4 (63.1 mg, 0.1 mol) were added. The reaction mixture was stirred vigorously (1300 rpm) at 50 °C for the time specified. The reaction mixture was quenched by saturated $NaHCO_3$ solution (10 ml) and extracted with ethyl acetate (3 × 20 ml), and then the combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the product was carried out by PTLC.

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REFERENCES

1. M. Haruta, T. Kobayashi, H. Sano, N. Yamada. *Chem. Lett*. 405 (1987).
2. (a) M. Haruta. *Chem. Rec*. **3**, 75 (2003); (b) A. S. K. Hashmi, G. J. Hutchings. *Angew. Chem., Int. Ed.* **45**, 7896 (2006); (c) T. Matsumoto, N. Ueno, S. Kobayashi. *Chem. Asian J*. **3**, 196 (2008); (d) C. D. Pina, E. Falletta, L. Prati, M. Rossi. *Chem. Soc. Rev*. **37**, 2077 (2008); (e) A. Corma, H. Garcia. *Chem. Soc. Rev*. **37**, 2096 (2008).
3. (a) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda. *J. Am. Chem. Soc.* **127**, 9374 (2005); (b) H. Tsunoyama, H. Sakurai, T. Tsukuda. *Chem. Phys. Lett.* **429**, 528 (2006); (c) H. Tsunoyama, T. Tsukuda, H. Sakurai. *Chem. Lett.* **36**, 212 (2007); (d) H. Tsunoyama, N. Ichikuni, H. Sakurai, T. Tsukuda. *J. Am. Chem. Soc.* **131**, 7086 (2009).
4. H. Sakurai I. Kamiya, H. Kitahara, H. Tsunoyama, T. Tatsuya. *Synlett* 245 (2009).
5. H. Sakurai, H. Tsunoyama, T. Tsukuda. *Trans. Mater. Res. Soc. Jpn.* **31**, 521 (2006).
6. (a) H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda. *Langmuir* **20**, 11293 (2004); (b) H. Sakurai, H. Tsunoyama, T. Tsukuda. *J. Organomet. Chem.* **692**, 368 (2007).
7. I. Kamiya, H. Tsunoyama, T. Tsukuda, H. Sakurai. *Chem. Lett.* **36**, 646 (2007).
8. (a) J. Muzart. *Tetrahedron* **62**, 5955 (2006); (b) R. C. Larock, W. W. Leong. In *Comprehensive Organic Synthesis*, Vol. 4, B. M. Trost, I. Fleming (Eds.), Pergamon Press, New York (1991); (c) T. Hosokawa, S. Murahashi. *Acc. Chem. Res.* **23**, 49 (1990).
9. (a) T. L. B. Boivin. *Tetrahedron* **43**, 3309 (1987); (b) J. Hartung, M. Greb. *J. Organomet. Chem.* **661**, 67 (2002).
10. (a) C.-G. Yang, C. He. *J. Am. Chem. Soc.* **127**, 6966 (2005); (b) X. Zhang, A. Corma. *J. Dalton Trans.* 397 (2008); (c) T. Hirai, A. Hamasaki, A. Nakamura, M. Tokunaga. *Org. Lett.* **11**, 5510 (2009).
11. H. Kitahara, I. Kamiya, H. Sakurai. *Chem. Lett.* **38**, 908 (2009).
12. (a) T. E. Müller, M. Beller. *Chem. Rev.* **98**, 675 (1998); (b) S. Hong, T. J. Marks. *Acc. Chem. Res.* **37**, 673 (2004); (c) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada. *Chem. Rev.* **108**, 3795 (2008).
13. (a) J. Zhang, C.-G. Yang, C. He. *J. Am. Chem. Soc.* **128**, 1798 (2006); (b) X.-Y. Liu, C.-H. Li, C.-M. Che. *Org. Lett.* **8**, 2707 (2006); (c) J. L. McBee, A. T. Bell, T. D. Tilley. *J. Am. Chem. Soc.* **130**, 16562 (2008); (d) D. Karshtedt, A. T. Bell, T. D. Tilley. *J. Am. Chem. Soc.* **127**, 12640 (2005); (e) K. Komeyama, T. Morimoto, K. Takaki. *Angew. Chem., Int. Ed*. **45**, 2938 (2006).
14. (a) D. C. Rosenfeld, S. Shekhar, A. Takemiya, M. Utsunomiya, J. F. Hartwig. *Org. Lett.* **8**, 4179 (2006); (b) B. Schlummer, J. F. Hartwig. *Org. Lett.* **4**, 1471 (2002).
15. H. Kitahara, H. Sakurai. *Chem. Lett.* **39**, 46 (2010).
16. (a) J. A. Bexrud, J. D. Beard, D. C. Leitch, L. L. Schafer. *Org. Lett.* **7**, 1959 (2005); (b) J. Y. Kim, T. Livinghouse. *Org. Lett.* **7**, 4391 (2005); (c) S. Majumder, A. L. Odom. *Organometallics* **27**, 1174 (2008).
17. (a) J. Seayad, A. Tillack, C. G. Hartung, M. Beller. *Adv. Synth. Catal.* **344**, 795 (2002); (b) C. Quinet, P. Jourdain, C. Hermans, A. Ates, I. Lucas, I. E. Marko. *Tetrahedron* **64**, 1077 (2008).
18. (a) J. Seayad, A. Tillack, C. G. Hartung, M. Beller. *Adv. Synth. Catal.* **344**, 795 (2002); (b) C. Quinet, P. Jourdain, C. Hermans, A. Ates, I. Lucas, I. E. Marko. *Tetrahedron* **64**, 1077 (2008).
19. (a) Z. Liu, J. F. Hartwig. *J. Am. Chem. Soc.* **130**, 1570 (2008); (b) H. Ohmiya, T. Moriya, M. Sawamura. *Org. Lett.* **11**, 2145 (2009); (c) K. D. Hesp, M. Stradiotto. *Org. Lett.* **11**, 1449 (2009); (d) C. F. Bender, R. A. Widenhoefer. *Chem. Commun*. 4143 (2009); (e) C. F. Bender, R. A. Widenhoefer. *Chem. Commun*. 2741 (2008); (f) E. B. Bauer, G. T. S. Andavan, T. K. Hollis, R. J. Rubio, J. Cho, G. R. Kuchenbeiser, T. R. Helgert, C. S. Letko, F. S. Tham. *Org. Lett.* **10**, 1175 (2008); (g) A. Minatti, K. Muniz. *Chem. Soc. Rev.* **36**, 1142 (2007).

