Triazole Acetyl Gold(III) Catalyzed Meyer-Schuster Rearrangement of Propargyl Alcohols

Yongchun Yang,^a Yanan Shen,^a Xiaoli Wang,^a Yao Zhang,^a Dawei Wang*^a and Xiaodong Shi*^b

^a The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu Province, China.

^b 4202 E Fowler Ave, Department of chemistry, University of South Florida, Tampa, Florida, USA.

Email: wangdw@jiangnan.edu.cn, xmshi@usf.edu, Tel./fax: +86 510 85917763

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ABSTRACT

A new type triazole acetyl gold(III) was prepared and found to be an effective catalyst in Meyer-Schuster rearrangement of propargyl alcohols. The reactions proceeded well under much milder conditions to afford enones bearing a wide range of functional groups, thereby opening a new avenue for gold(III) catalysis. In addition, TriaAuCl_2 catalyst was also effective on promotion of α -haloenones synthesis.

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1. Introduction

Gold catalysis has been widely applied in organic transformations, and methods for their efficient, selective functionalization to construct more complex molecules during the past several decades.^{1,2} Gold(I) catalysts are usually two coordinated with 180° linear geometry, while gold(III) catalysts have a planar coordination geometry, and hence the spatial environment around the gold center can be more easily fine-tuned through ligand design studies. However, gold(I) catalysis has achieved much more development and concern than gold(III) catalysis, which should be attributed to the heat stability of gold catalyst.³ The typical gold(III) catalyst is the PicAuCl_2 and their derivatives, which enriched and evidenced the development of gold(III) catalysis (Scheme 1A). After some pioneering works on PicAuCl_2 ,⁴ Hashmi reported PicAuCl_2 catalyzed phenol synthesis, which revealed that gold(III) precatalysts represents a typical step in catalyst-tuning by ligand design, while they found Au(I) showed low selectivity.⁵ Toste *et al* described a PicAuCl_2 catalyzed synthesis of azepines via intermolecular [4 + 3]-annulation reaction.⁶ In 2013, Waser *et al* developed the selective synthesis of 2- and 3-alkynylated furans based on a domino cyclization/alkynylation process with PicAuCl_2 as catalyst.⁷ Chan group showed that PicAuCl_2 catalyzed selective 1,3-acyloxy migration/5-exo-dig cyclization/1,5-acyl migration to afford cis-cyclopenten-2-yl δ -diketones.⁸

Scheme 1. PicAuCl_2 and TriaAuCl_2 .

Our research in developing new triazole ligands to balance the stability and reactivity of gold catalysts has led to the recent discovery of triazole gold(I) complexes (TA-Au),^{9,10} which was achieved several applications on hydroamination, Hashmi phenol synthesis and 3,3-rearrangements with TA-Au(I) as a catalyst. We have a concern about triazole ligands: could triazole adjust the stability and reactivity of gold catalysts gold(III)? Herein, we synthesized the TriaAu(III)Cl_2 complex, which showed excellent catalytic activity in Meyer-Schuster rearrangement of propargyl alcohols for enone synthesis under mild conditions, which avoid the preparation of corresponding acetate derivatives and have large substrates exploration (Scheme 1B).

Scheme 2. The synthesis of TriaAu(III)Cl_2 complex.

The designed (triazol-1-yl)acetic acid (**1a**) was synthesized from benzotriazole and methyl 2-bromoacetate via two steps with 86% yield,¹¹ following dealt with potassium tetrachloroaurate under base conditions and the obtained TriAu(III)Cl_2 complex (**1b**) was obtained in 81% yield.¹² Next, we explored the catalytic activity of this new catalyst TriAu(III)Cl_2 . Compared to the 3,3'-rearrangement of propargyl esters,¹³ Meyer-Schuster rearrangement of propargyl alcohols is quite difficult. Propargyl alcohol (**2a**) was selected as a model substrate for reaction screening. It is very disappointed that the hydration product was found only with low yield (Table 1, Entry 1). Based on our previous results on Au(I) ,¹⁴ we firstly examined the effect of solvents on the reactivity using TriAuCl_2 as the catalyst. As shown in Table 1, the reaction was strongly solvent-dependent. Excellent reactivity was achieved in MeOH . It should be noted that the Meyer-Schuster rearrangement of propargyl alcohols could not take place in the absence of gold catalyst.

Table 1. Screening of reaction conditions ^a

Entry	Solvent	T	Convsn.	3a [%] (<i>E/Z</i>) ^b
1	1,4-dioxane	rt	23	15
2	acetone	rt	<5	<5
3	toluene	rt	<5	<5
4	CH_2Cl_2	rt	<5	<5
5	H_2O	rt	<5	<5
6	MeOH	rt	26	20
7	MeOH	40	75	62
8	MeOH	60	>95	89 (>20:1)
9	MeOH	60	<5	<5 ^c

^a Conditions: **2a** (0.5 mmol), TriAu(III)Cl_2 (**1b**) (1 mol%), wet solvent (10% H_2O), 6 h. ^b Isolated yields based on **2a**. ^c No[Au] was used.

Having established the optimal conditions, the substrate scope of TriAuCl_2 catalyzed Meyer-Schuster rearrangement of propargyl alcohols was examined. The reactions were carried out in MeOH (10% H_2O) at 60 °C. Generally, all the propargyl alcohols were converted completely into the corresponding enones. High yields were achieved regardless of the electronic properties and steric hindrance of substituent groups (Table 2). The propargyl alcohols with MeO group (**3m**) gave the highest yield, while a slightly lower yield was obtained when the nitro substituent was in the substrate (**3l**).

Table 2. Substrate expansion of propargyl alcohols ^{a,b}

^a Conditions: **2** (0.5 mmol), TriAu(III)Cl_2 (**1b**) (1 mol%), MeOH (10% H_2O), 60 °C, 6 h. ^b Isolated yields based on **2**.

In addition, we attempted the experiment with alkyl-substituted propargyl alcohol as a substrate. As illustrated in Scheme 3, the alkyl-substituted enone was achieved in only *E* isomer 81% yield.

Scheme 3. Substrate experiment with alkyl-substituted propargyl alcohol.

Moreover, TriAu(III)Cl_2 was also an effective catalyst on α -haloenones synthesis,¹⁵ although a slight lower yield was achieved (Table 3). It was found that the electronic and steric natures of aromatic ring of propargyl esters had no obvious effect on the results. For example, the propargyl esters bearing electron-donating (like Me , MeO) or electron-withdrawing groups at *para*-, *meta*-, or *ortho*-positions were well tolerated, and afforded the corresponding products in moderate yields. Notably, this transformation didn't work for the terminal alkyne since the 1,2-rearrangement was usually preferred for terminal alkyne propargyl acetate.

Table 3. Substrate expansion of propargyl esters ^{a,b}

^a Conditions: **4** (0.5 mmol), NIS (0.75 mmol), TriAu(III)Cl_2 (**1b**) (1 mol%), CH_2Cl_2 (3 mL), 12 h, rt. ^b Isolated yields based on **4**.

Conclusions

In summary, we developed a new type TriaAu(III)Cl_2 complex, which showed good catalytic activity in Meyer-Schuster rearrangement of propargyl alcohols for enone synthesis under mild conditions, which avoid the preparation of corresponding acetate derivatives and have large substrates exploration. In addition, TriaAuCl_2 complex was also effective on promotion of α -haloenones synthesis. Further applications of TriaAu(III)Cl_2 catalyst to other reactions for the construction of carbon-heteroatom bonds are currently in progress in our laboratory.

Supporting Information

Supplementary data related to this paper is available free of charge via the Internet.

Acknowledgements

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Scheme 1. PicAuCl₂ and TriaAuCl₂. **Scheme 2.** The synthesis of TriaAu(III)Cl₂ complex. **Scheme 3.** Substrate experiment with alkyl-substituted propargyl alcohol.

Table 1. Screening of reaction conditions ^a

Entry	Solvent	T	Convsn.	3a [%] (<i>E/Z</i>) ^b
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5	H ₂ O	rt	<5	<5
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7	MeOH	40	75	62
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^a Conditions: **2a** (0.5 mmol), TriaAu(III)Cl₂(**1b**) (1 mol%), wet solvent (10% H₂O), 6 h. ^b Isolated yields based on **2a**.^c No[Au] was used.**Table 2.** Substrate expansion of propargyl alcohols ^{a,b}

 3a : 89% <i>E/Z</i> > 20:1	 3b : 87% <i>E/Z</i> > 20:1	 3c : 84% <i>E/Z</i> = 19:1	 3d : 90% <i>E/Z</i> > 20:1
 3e : 80% <i>E/Z</i> = 16:1	 3f : 91% <i>E/Z</i> > 20:1	 3g : 88% <i>E/Z</i> > 20:1	 3h : 78% <i>E/Z</i> > 20:1
 3i : 85% <i>E/Z</i> > 20:1	 3j : 87% <i>E/Z</i> = 19:1	 3k : 89% <i>E/Z</i> > 20:1	 3l : 76% <i>E/Z</i> = 13:1
 3m : 93% <i>E/Z</i> > 20:1	 3n : 82% <i>E/Z</i> > 20:1	 3o : 83% <i>E/Z</i> > 20:1	 3p : 86% <i>E/Z</i> > 20:1

^a Conditions: **2** (0.5 mmol), TriaAu(III)Cl₂(**1b**) (1 mol%), MeOH (10% H₂O), 60 °C, 6 h. ^b Isolated yields based on **2**.**Table 3.** Substrate expansion of propargyl esters ^{a,b}

^aConditions: **4** (0.5 mmol), NIS (0.75 mmol), TriaAu(III)Cl₂(**1b**) (1 mol%), CH₂Cl₂ (3 mL), 12 h, rt. ^bIsolated yields based on **4**.

Graphical Abstract

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^a The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu Province, China. ^b 4202 E Fowler Ave, Department of chemistry, University of South Florida, Tampa, Florida, USA.

A new type triazole acetyl gold(III) was prepared and found to be an effective catalyst in Meyer-Schuster rearrangement of propargyl alcohols. The reactions proceeded well under much milder conditions to afford enones bearing a wide range of functional groups, thereby opening a new avenue for gold(III) catalysis. In addition, TriaAuCl₂ catalyst was also effective on promotion of α -haloenones synthesis.