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# Triazole acetyl gold(III) catalyzed Meyer–Schuster rearrangement of propargyl alcohols

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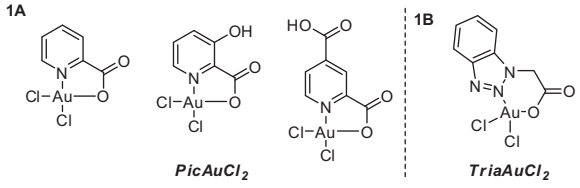
ABSTRACT

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 a-haloenones synthesis.



## 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 represent 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




**Scheme 1.** PicAuCl$_2$ and TriaAuCl$_2$.

1,3-acyloxy migration/5-*exo*-dig cyclization/1,5-acyl migration to afford *cis*-cyclopenten-2-yl δ-diketones.[8]

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 substrate exploration (Scheme 1B).

The designed (triazol-1-yl)acetic acid (**1a**) was synthesized from benzotriazole and methyl 2-bromoacetate via two steps with

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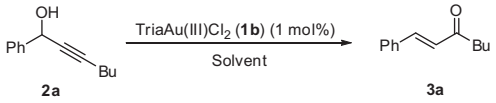
86% yield,[11] following dealt with potassium tetrachloroaurate under base conditions and the obtained TriaAu(III)$Cl_2$ complex (**1b**) was obtained in 81% yield.[12] Next, we explored the catalytic activity of this new catalyst TriaAu(III)$Cl_2$. Compared to the 3,3′-rearrangement of propargyl esters,[13] Meyer–Schuster rearrangement of propargyl alcohols is quite difficult. Propargyl alcohol (**2a**) was selected as a model substrate for reaction screening. It is very disappointing that the hydration product was found only with low yields (Table 1, entry 1). Based on our previous results on Au(I),[14] we firstly examined the effect of solvents on the reactivity using TriaAu$Cl_2$ 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 (Scheme 2).

Having established the optimal conditions, the substrate scope of TriaAu$Cl_2$ 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 the MeO group (**3m**) gave the highest yield, while a slightly lower yield was obtained when the nitro substituent was in the substrate (**3l**).

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.

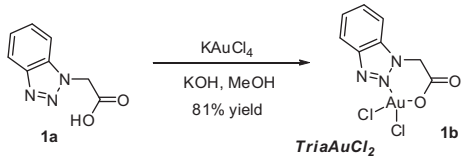
Moreover, TriaAu(III)$Cl_2$ was also an effective catalyst on a-haloenones synthesis,[15] although a slightly lower yield was achieved (Table 3). It was found that the electronic and steric natures of aromatic ring of propargyl esters had no obvious effect on the results. For example, the propargyl esters bearing electron-donating (like Me, MeO) or electron-withdrawing groups

**Table 1**
Screening of reaction conditions[a]



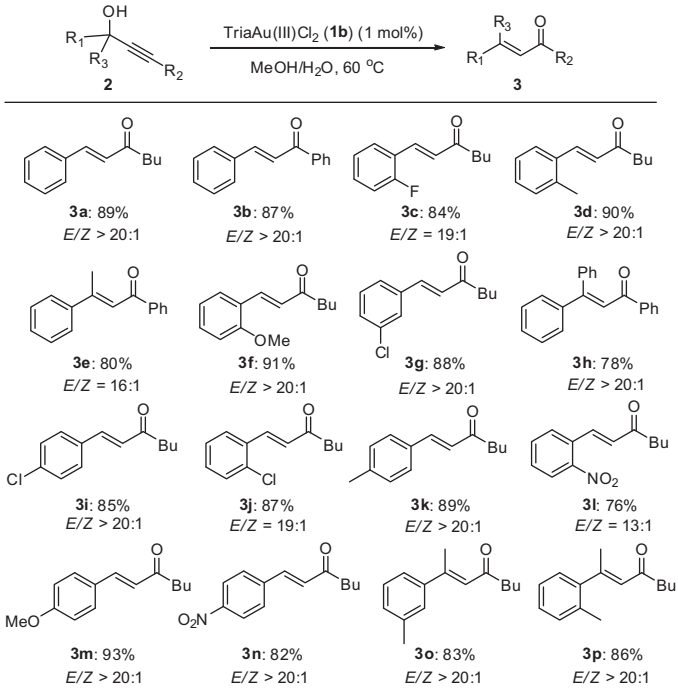

| Entry | Solvent | *T* | Convn. | **3a** [%] (*E*/*Z*)[b] |
|---|---|---|---|---|
| 1 | 1,4-Dioxane | rt | 23 | 15 |
| 2 | Acetone | rt | <5 | <5 |
| 3 | Toluene | rt | <5 | <5 |
| 4 | $CH_2Cl_2$ | rt | <5 | <5 |
| 5 | $H_2O$ | rt | <5 | <5 |
| 6 | MeOH | rt | 26 | 20 |
| 7 | MeOH | 40 | 75 | 62 |
| 8 | MeOH | 60 | >95 | 89 (>20:1) |
| 9 | MeOH | 60 | <5 | <5[c] |

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

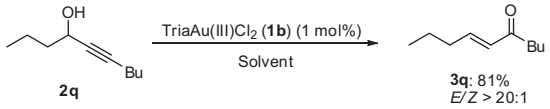



**Scheme 2.** The synthesis of TriaAu(III)$Cl_2$ complex.

**Table 2**
Substrate expansion of propargyl alcohols[a,b]

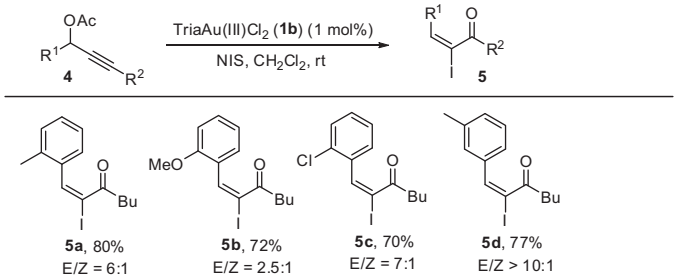



[a] Conditions: **2** (0.5 mmol), TriaAu(III)$Cl_2$ (**1b**) (1 mol %), MeOH (10% $H_2O$), 60 °C, 6 h.
[b] Isolated yields based on **2**.




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

**Table 3**
Substrate expansion of propargyl esters[a,b]




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

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-rearramgement was usually preferred for terminal alkyne propargyl acetate.

## 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 substrate exploration. In addition, TriaAu$Cl_2$ complex was also effective on promotion of a-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.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.04.043.

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