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The synthesis and structural characterization of furanyl-1,2,3-triazole Gold(I) and its application in synthesis of enones from propargylic esters and alcohols

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ABSTRACT

Furanyl-1,2,3-triazole gold(I) was designed, synthesized and characterized by X-ray crystallography, and was found to exhibit high catalytic activity for the synthesis of enones in good to high yields through a propargylic ester rearrangement and subsequent hydration. Notably, excellent *E/Z* selectivity was observed in these transformations. This catalyst was also effective in catalyzing the rearrangement of propargylic alcohols and hydration of alkynes. Compared to triazole acetyl gold(III) and other gold complexes, the furanyl-1,2,3-triazole gold(I) is able to promote these transformations smoothly at a low temperature with the *E* isomer of enones as the only product.

1. Introduction

In past several decades, gold catalysis has attracted great attention in organic synthesis for its potential in delivering highly desirable derivatives from relatively accessible unsaturated compounds [1]. However, gold catalysis remains a highly challenging field and has received limited development, because of poor stability and easy decomposition at high temperatures, which usually yields gold nanoparticles or gold mirrors [2]. To address this limitation, scientists have developed ligands of strong coordination ability aiming to improve the stability of the gold catalyst [3]. In particular, Shi et al. found that triazole is able to enhance the stability [4] and thereby improve the catalytic efficiency of gold(I) complexes [5], which have found important applications in a variety of organic transformations [6]. Recently, we have developed a series of triazole coordinated gold catalysts which have exhibited improved stability and activity (Scheme 1) [7]. For example, we have synthesized the pyridyltriazole gold(III) complex (TA-Py-Au) which exhibits high catalytic activity to produce α-haloenones. We have also used the high efficiency of triazole to promote hydrogen borrowing reactions [8]. However, development of innovative ligands is highly desirable for the next generation gold catalysts. In this work, we designed and synthesized a novel triazole gold(I) complex, which revealed high catalytic activity for the synthesis of enones in good to high yields through a propargylic ester rearrangement and subsequent hydration.

2. Results and discussion

The novel Au complex (FTA-Au) was prepared as follows. First, 2-formylofuran was mixed with MeOH and KOH and stirred vigorously for 1 h in an ice bath to achieve 2-(2-nitrovinyl)furan **L1**. Next, furanyl-1,2,3-triazole **L2** was synthesized from **L1** and NaN_3 in DMSO using anhydrous aluminum chloride as catalyst (Scheme 2). Finally, the Au complex was successfully prepared in high yield by mixing $AuPPh_3Cl$, $AgSbF_6$ and corresponding triazole ligand **L2** in a 1:1.1:1.04 M ratio in DCM at RT for 4 h. The exact structure of the

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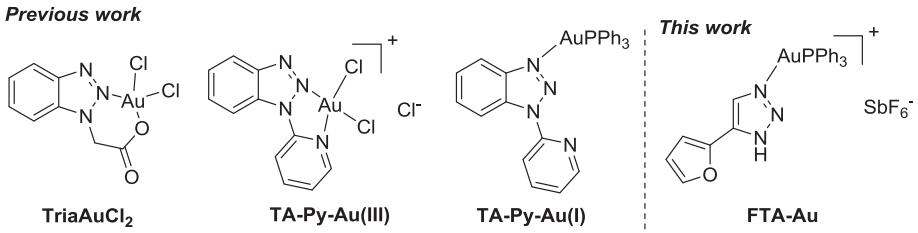
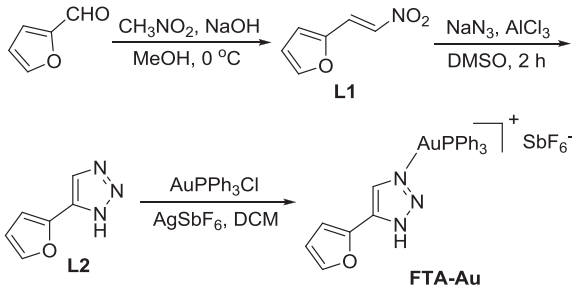


Scheme 1. Several gold complexes.



Scheme 2. Synthesis and X-ray of FTA-Au.

resulting gold complex FTA-Au was confirmed by a single-crystal X-ray diffraction analysis (CCDC number 1909674).

As illustrated in Fig. 1, complex FTA-Au adopted the general linear structure, with the triphenylphosphine chelating ligand occupying one coordination position, the furanyl-1,2,3-triazole ring acting as another ligand. In addition, the Au-P and Au-N1 distances were 2.2443(6) Å and 2.0715(19) Å, respectively. Notably, the Au—P bond length was longer than Au—N1 so the combination of gold and nitrogen may be stronger.

The catalytic activity of the FTA-gold(I) complex was found in the propargylic ester rearrangement to achieve allenes and enones [9,10]. The common propargyl ester **1a** was selected as the starting material in the model reaction with 2 mol% FTA-Au loaded. Initially, the allene product **2a** was obtained in 36% yield. Meanwhile, the starting material and enone (**3a**) were also found in 21% and 29% yield, respectively. A series of reaction conditions were attempted in order to improve the selectivity of allenes in this reaction. However, these attempts remained unsuccessful revealing the low activity nature of the FTA-Au in producing allenes. Since 29% of enone was seen in the aforementioned allene synthesis, we next focused on improving enone selectivity of this propargylic ester rearrangement. After screening several reaction conditions (Table 1), a mild condition was found to produce enone in high yield using 1,4-dioxane as the solvent (Table 1, entry 7). It should be noted that no reaction was found when $AuCl_3$ was employed as the catalyst. The following conditions revealed that the best result was obtained under 40 °C, while high temperature produced lower yields, which might be caused by the decomposition of gold catalysts.

With optimal reaction conditions in hand, the substrate scope of this Au catalyzed propargylic ester rearrangement was assessed and the substituent effect on the aryl moiety was investigated (Table 2). Several useful functional groups were found to be well tolerated in this reaction, including nitro, methyl, fluoro, methoxyl and chloro substituents. When a sterically hindered ortho substituent was used, a slightly lower yield was obtained. Furthermore, the diaryl substituents were also employed and found to be efficient to afford the desired product by this methodology. Overall, the highest yield was achieved when a methoxyl substituent was used in this transformation.

Since FTA-Au exhibited excellent catalytic efficiency and high stability, we next explored whether this FTA-Au could also be effective in promoting the Meyer—Schuster arrangement of propargylic alcohols. So we conducted the rearrangement of propargylic alcohols using FTA-Au as a catalyst and gladly found the enone product can be efficiently generated in good yield. Further

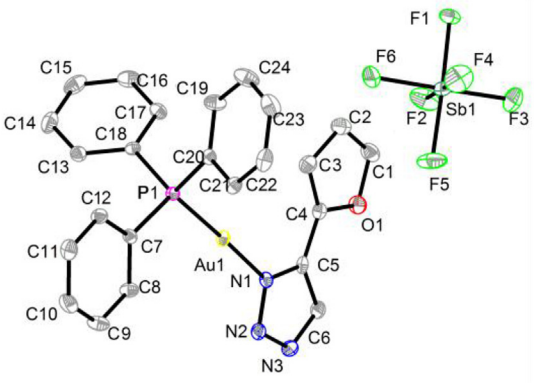
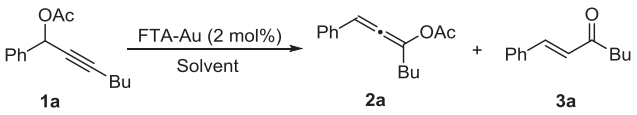


Fig. 1. X-ray crystal structure of FTA-Au with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au-P = 2.2443(6), Au-N1 = 2.0715(19), C4-C5 = 1.448(3), P-Ir-N1 = 177.18(5), N1-C5-C4 = 123.7(2).

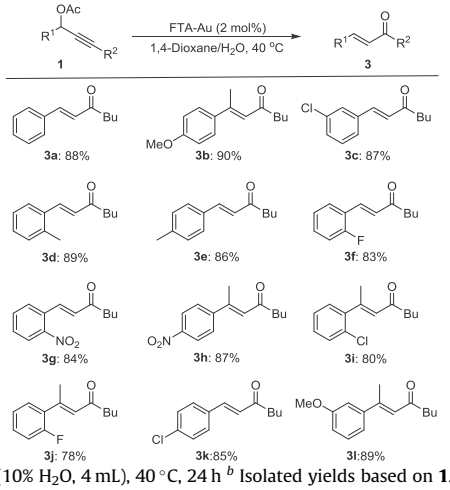
Table 1
Optimization of reaction conditions[a].



Entry	Solvent	T (°C)	Convn.	2a[%][b]	3a[%][b]
1	CH_2Cl_2	rt	79	36	29
2	1,4-dioxane	rt	85	8	61
3	acetone	rt	43	7	16
4	$CHCl_3$	rt	36	5	12
5	MeOH	rt	65	<5	54
6	EtOH	rt	58	<5	51
7	1,4-dioxane/H_2O	rt	93	<5	86
8	MeOH/H_2O	rt	84	<5	72
9	1,4-dioxane/H_2O	rt	37	5	16[c]
10	1,4-dioxane/H_2O	rt	<5	<5	<5[d]
11	1,4-dioxane/H_2O	40	>95	<5	88
12	1,4-dioxane/H_2O	50	>95	<5	88
13	1,4-dioxane/H_2O	60	>95	<5	87
15	1,4-dioxane/H_2O	70	>95	<5	79

[a] Conditions: **1a** (1.0 mmol), FTA-Au (2 mol%), solvent (4 mL), 24 h.
[b] Isolated yields.
[c] $AuCl_3$ was used.
[d] No [Au].

Table 2
Substrate experiments of propargylic ester[a,b].



[a] Conditions: **1** (1.0 mmol), FTA-Au (2 mol%), 1,4-dioxane (10% H_2O, 4 mL), 40 °C, 24 h [b] Isolated yields based on **1**.

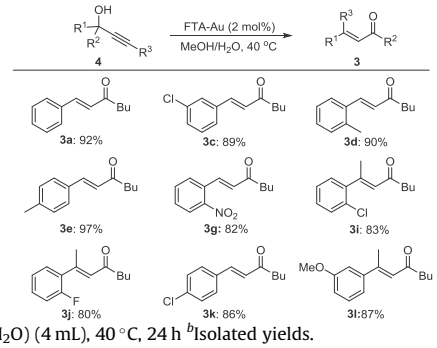
experiments revealed that the reaction could tolerate a large variety of substituted substrates, while also achieving good to excellent yields with the use of FTA-Au catalyst (Table 3).

At last, we attempted the hydration of alkynes to understand whether our novel gold(I) complex could promote this challenging reaction. To date, an example of this type of reaction was reported which was promoted by the complex formed *in situ* between alanine triazole ligand (ATA) and gold(III) salt [7a]. However, the exact structure was not very clear. To our delight, it was found that the FTA-Au also showed good catalytic activity for this transformation. For example, the simple phenylacetylene was used in this reaction to produce acetophenone in 86% yield in the presence of FTA-Au. In general, a wide range of substrates can be converted into the desired products in moderate to good yields through this reaction (Table 4).

3. Conclusions

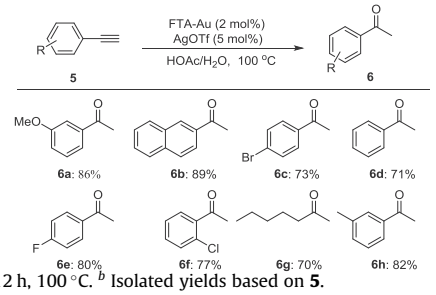
In conclusion, we synthesized the triazole gold(I) complex FTA-Au with furanyl-1,2,3-triazole and obtained a single crystal structural analysis of it. We described FTA-Au catalyzed rearrangement reactions of propargylic esters and propargylic alcohols to afford

Table 3
Substrate experiments of propargylic alcohols[a,b].



[a]Conditions: **4** (1.0 mmol), FTA-Au (2 mol%), MeOH (10% H_2O) (4 mL), 40 °C, 24 h [b]Isolated yields.

Table 4
FTA-Au-catalyzed hydration of alkynes. [a,b].



[a] Conditions: **5** (1.0 mmol), HOAc/H_2O (10:1 = *v:v*, 4 mL), 12 h, 100 °C. [b] Isolated yields based on **5**.

enones with moderate to good yields. These transformations further revealed the fact that the catalytic activity and stability of FTA-Au can be improved with the help of triazole. We anticipate that this new complex may find industrial applications through further developments in the near future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120944.

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