

## Synthesis and Structural Characterization of Stable Organogold(I) Compounds. Evidence for the Mechanism of Gold-Catalyzed Cyclizations

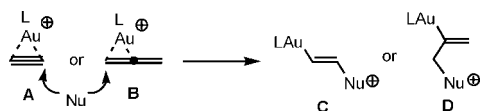
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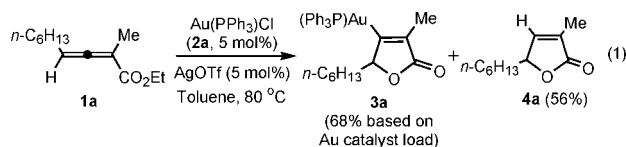
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The development of efficient and selective Au-catalyzed transformations has enriched the field of organic synthesis. The importance of these transformations is reflected in the various reviews, highlights, and perspectives on gold catalysis that have appeared in the literature.<sup>1</sup> The vast majority of homogeneous Au-catalyzed reactions have exploited the propensity of Au to activate unsaturated carbon-carbon bonds as electrophiles. It is generally assumed that a nucleophile (Nu) attacks a Au-activated carbon-carbon multiple bond ( $\pi$ -complex **A** or **B**) to give an alkenyl Au intermediate ( $\sigma$ -complex **C** or **D**), notwithstanding the fact that complexes **C** or **D** are hitherto unknown (Scheme 1).<sup>2</sup>

### Scheme 1



During our recent investigations on the reactivity of allenoates,<sup>3</sup> we found that Au(I) catalyzed the cyclization of allenoate **1a** to give the  $\gamma$ -lactone product **4a** (eq 1).<sup>4</sup> To our surprise, in addition



to this cyclization product, we obtained compound **3a**, a very stable Au complex of type **D**, in good yield based on the amount of catalyst used. This discovery could provide the experimental evidence required to support the postulated mechanism of Au-catalyzed reactions. Herein, we wish to publish the reactions of cationic Au(I) reagents with allenoates under mild conditions, which not only provide a synthetic entry to novel and stable  $\gamma$ -lactone gold(I) complexes but also furnish experimental evidence for the mechanism of Au-catalyzed cyclizations.<sup>5</sup>

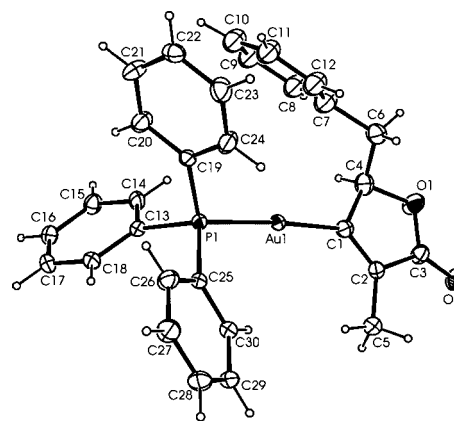
To explore the formation of this interesting gold complex **3**, we investigated the stoichiometric reaction of Au(I) with allenoates. Using the Au(PPh<sub>3</sub>)Cl/AgOTf system as the equivalent of Au(PPh<sub>3</sub>)OTf, we found that the *in situ* generated cationic Au(I) reagent reacted with ethyl  $\alpha$ -methyl- $\gamma$ -(*n*-hexyl)-allenoate **1a** in dichloromethane at room temperature to give the desired gold complex **3a** in 85% yield (Table 1, entry 1).<sup>6</sup>

Next, we studied the reactions of the cationic Au(I) reagent with various allenoates. These results are summarized in Table 1. The reaction took place readily with alkyl groups substituted on the allenoates, and the corresponding products **3b–3f** were obtained in good yields (Table 1, entries 2–6). However, no reaction took place with the phenyl-substituted allenoate (Table 1, entry 7), perhaps due to the electronic deficiency of the double bond in the

**Table 1.** Reactions of Au(PR<sub>3</sub>)OTf (*in situ*) with Allenoate **1a**<sup>a</sup>

entry	R <sup>1</sup> /R <sup>2</sup> /R <sup>3</sup> /R <sup>4</sup>	<b>3</b> , yield <sup>b</sup>
1	<i>n</i> -C <sub>6</sub> H <sub>13</sub> /H/Me/C <sub>6</sub> H <sub>5</sub>	<b>3a</b> , 85
2	<i>i</i> Pr/H/Me/C <sub>6</sub> H <sub>5</sub>	<b>3b</b> , 82
3	Me/H/Me/C <sub>6</sub> H <sub>5</sub>	<b>3c</b> , 75
4	Bn/H/Me/C <sub>6</sub> H <sub>5</sub>	<b>3d</b> , 81
5	Me/H/H/C <sub>6</sub> H <sub>5</sub>	<b>3e</b> , 46
6	Me/Me/Me/C <sub>6</sub> H <sub>5</sub>	<b>3f</b> , 68
7	Ph/H/Me/C <sub>6</sub> H <sub>5</sub>	no reaction
8	<i>n</i> -C <sub>6</sub> H <sub>13</sub> /H/Me/ <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3g</b> , 71
9	<i>n</i> -C <sub>6</sub> H <sub>13</sub> /H/Me/ <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3h</b> , 68
10	<i>n</i> -C <sub>6</sub> H <sub>13</sub> /H/Me/ <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3i</b> , 70
11	<i>n</i> -C <sub>6</sub> H <sub>13</sub> /H/Me/ <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>3j</b> , 62
12	<i>n</i> -C <sub>6</sub> H <sub>13</sub> /H/Me/cyclohexyl	<b>3k</b> , 54

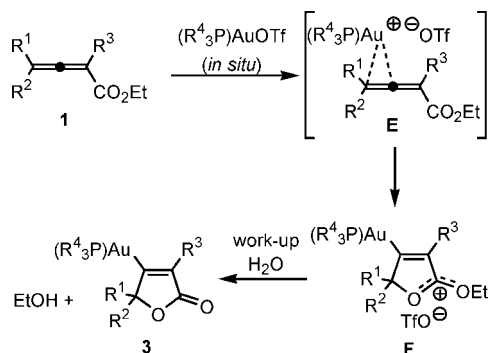
<sup>a</sup> General conditions: allenoate **1** 0.24 mmol, Au(PR<sub>3</sub>)Cl **2** 0.2 mmol, AgOTf 0.2 mmol, CH<sub>2</sub>Cl<sub>2</sub> 2.0 mL. <sup>b</sup> Isolated yields.



**Figure 1.** ORTEP-3 (Farrugia) diagram (50% ellipsoids) illustrating one independent molecule of the gold complex **3d**. H atoms are shown as small spheres of arbitrary radii. Selected bond lengths (Å) and angles (deg): Au1–C1 = 2.036(5), Au1–P1 = 2.2955(12), C1–C2 = 1.326(7), C1–C4 = 1.531(8), C1–Au1–P1 = 175.61(15), C2–C1–Au1 = 129.5(4), C4–C1–Au1 = 123.2(4), C2–C1–C4 = 107.3(5).

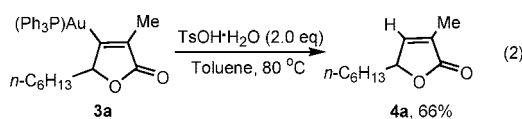
allenoate.<sup>4a</sup> The scope of phosphine ligands was also investigated, and these results are also outlined in Table 1. Both aromatic (Table 1, entries 8–11) and aliphatic (Table 1, entry 12) phosphines proved to be adequate ligands for the obtention of the stable gold(I) products **3g–3k**.

The structure of **3** was determined by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopic data and X-ray crystallography of complex **3d** (Figure 1).<sup>7</sup>

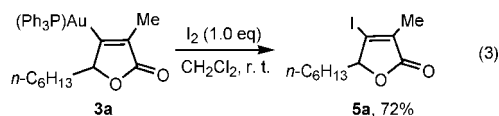
**Scheme 2.** Plausible Mechanism for the Formation of Gold Complex **3**

*In situ*  $^{31}\text{P}$  and  $^1\text{H}$  NMR studies were performed to understand the mechanism for the formation of complex **3**. The  $^{31}\text{P}$  NMR spectrum of the crude reaction mixture of **1g** showed two new peaks at  $\delta$  43.0 ppm (major) and 46.1 ppm<sup>8</sup> (minor) in  $\text{CDCl}_3$ . A large downfield chemical shift of the ethyl group was also observed in the  $^1\text{H}$  NMR spectrum of the mixture (shift from  $\delta$  1.32 to  $\delta$  1.60 ppm for  $\text{CH}_3$  and from  $\delta$  4.22 ppm to 4.94 ppm for  $\text{CH}_2$ ).<sup>9</sup> This downfield chemical shift could be ascribed to the formation of oxonium intermediate **F** (Scheme 2). The  $^1\text{H}$  NMR spectrum of the reaction mixture, taken 12 h later, showed additional proton signals corresponding to ethanol.<sup>10</sup> Based on these findings, we propose the reaction mechanism shown in Scheme 2. The double bond of the allenolate is activated by coordination to cationic gold to form intermediate **E**, which then undergoes an intramolecular cyclization<sup>5f</sup> to give intermediate **F** (observed signal at  $\delta$  43.0 in  $^{31}\text{P}$  NMR spectrum). Complex **3** was obtained after workup, and the ethyl group was hydrolyzed to ethanol.

To demonstrate that **3** is the actual intermediate in Au(I)-catalyzed cyclizations, we performed two controlled reactions (eqs 2 and 3). In one experiment,  $\gamma$ -lactone **4a** was obtained in 66% yield when gold complex **3a** was treated with TsOH in toluene at 80 °C (eq 2). In another experiment, **3a** was treated with iodine in



dichloromethane at room temperature to produce the  $\gamma$ -iodolactone **5a** in 72% isolated yield (eq 3).<sup>11</sup> The results of these two controlled



reactions imply that gold complex **3** is indeed the common intermediate in Au-catalyzed cyclizations.

In summary, we have found that cationic gold compounds can react with allenates to form a series of room temperature stable organogold(I) complexes and that these complexes are likely intermediates in the Au-catalyzed reaction of carbon–carbon

multiple bonds. Other studies related to this novel Au(I) complex, and its chiral version, are currently ongoing in our laboratory.

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**Supporting Information Available:** The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopic data of the new compounds shown in Tables 1 and eqs 1–3, and the detailed description of experimental procedures. Crystallographic data for compound **3d** are provided as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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