

Communication

**Re(I)-Catalyzed Hydropropargylation of Silyl Enol Ethers  
Utilizing Dynamic Interconversion of Vinylidene–  
Alkenylmetal Intermediates via 1,5-Hydride Transfer**

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# Re(I)-Catalyzed Hydropropargylation of Silyl Enol Ethers Utilizing Dynamic Interconversion of Vinylidene–Alkenylmetal Intermediates via 1,5-Hydride Transfer

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*Supporting Information Placeholder*

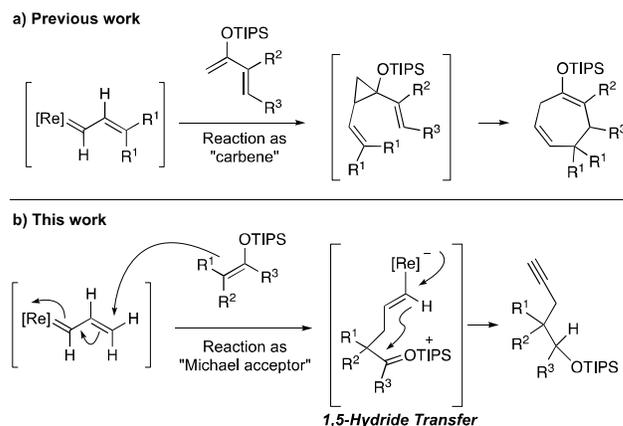
**ABSTRACT:** Re(I)-catalyzed hydropropargylation reaction of silyl enol ethers was realized utilizing dynamic interconversion of vinylidene–alkenylmetal intermediates, where alkenylmetals underwent 1,5-hydride transfer of the  $\alpha$ -hydrogen to generate vinylidene intermediates. Furthermore, this process was found to be in an equilibrium.

Vinylidene complexes have attracted a lot of attention as a useful reactive species in transition metal-catalyzed reactions.<sup>1</sup> In these reactions, vinylidene complexes are usually generated from terminal alkynes and their central carbons show high electrophilicity, which has been utilized for various synthetically useful catalytic transformations such as anti-Markovnikov additions,<sup>2</sup> cycloisomerization reactions,<sup>3</sup> etc.<sup>4</sup> In most of these reactions, addition of nucleophilic reagents to the central vinylidene carbon generates alkenylmetallic species, which further undergo transformations such as protonation with regeneration of the catalytic species. On the contrary, its reverse reaction, that is, generation of vinylidene complexes from alkenylmetallic species is rather limited even in the stoichiometric reactions,<sup>5–7</sup> and elimination of  $\alpha$ -hydrogen of alkenylmetallic species as hydride for the generation of vinylidene intermediates has not been utilized for catalytic reactions, except for the  $\alpha$ -hydrogen elimination proposed for generation of vinylidene complexes from terminal alkynes.<sup>8</sup> In this paper, we report Re(I)-catalyzed stereoselective hydropropargylation of silyl enol ethers by utilizing dynamic interconversion of vinylidene–alkenylmetal intermediates through reversible 1,5-hydride transfer of  $\alpha$ -hydrogen of alkenylrheniums.

We previously reported Re(I)-catalyzed generation of  $\alpha,\beta$ -unsaturated carbene complex intermediates from easily available propargyl ethers and their reactions with siloxydienes to give cycloheptadiene derivatives in high

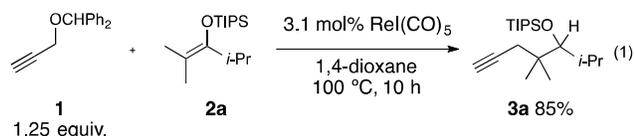
yields (Scheme 1a).<sup>9–11</sup> In this reaction,  $\alpha,\beta$ -unsaturated carbene complex intermediates reacted with siloxydienes at the carbene moiety to give cyclopropane intermediates, which further underwent divinylcyclopropane rearrangement to give the products. We then thought of the possibility of utilizing the  $\alpha,\beta$ -unsaturated carbene complex intermediates as a Michael acceptor.<sup>12,13</sup> For this purpose, we expected that use of silyl enol ethers with a substituent on the  $\beta$ -carbon would disfavor the reaction at the carbene moiety due to the steric repulsion and 1,4-addition of the silyl enol ethers would give addition intermediate, which we initially expected to give allylation products by hydrolysis.<sup>12</sup> In this paper, we describe exploitation of this approach, which has resulted in a discovery of entirely unexpected interconversion of vinylidene–alkenylmetal intermediates to realize a novel hydropropargylation reaction of silyl enol ethers.

## Scheme 1. Previous work/This work



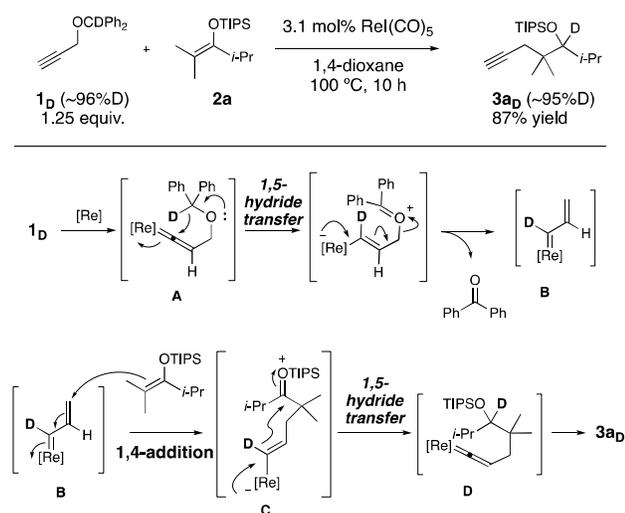
$\beta,\beta$ -Dimethyl-substituted silyl enol ether **2a** was chosen as a nucleophile and the reaction with primary propargyl ether **1** was examined.<sup>14</sup> The reaction was carried out by heating a 1.25 : 1 mixture of **1** and **2a** using 3.1 mol% amount of ReI(CO)<sub>5</sub> in dioxane at 100 °C for 10 hours. The reaction was found to proceed cleanly, and

surprisingly, instead of the expected allylation product, hydropropargylation product **3a** was obtained in 85% yield. (eq. 1)



Based on the structure of the product, the reaction was thought to proceed as follows (Scheme 2); in a similar manner to the previously reported reaction,<sup>9</sup> the  $\alpha,\beta$ -unsaturated carbene complex intermediate **B** was generated via 1,5-hydride transfer to the vinylidene intermediate **A** followed by elimination of benzophenone with electron-donation from the metal. Then silyl enol ether **2** added in a 1,4-addition manner to give alkenylrhenium(I) intermediate **C** having a silyloxonium moiety. At this point, instead of protonation of the alkenylrhenium(I) intermediate **C**, a novel 1,5-hydride transfer of the  $\alpha$ -hydrogen of the alkenylrhenium moiety to the silyloxonium moiety proceeded to give a vinylidene complex **D** containing a silyl ether moiety. It should be noted that hydride transfer from  $sp^2$ -carbon to generate  $sp$ -carbon center is a quite rare process.<sup>15,16</sup> The generated vinylidene complex released the terminal alkyne product **3** as a reverse reaction of vinylidene complex formation with regeneration of the Re(I) catalyst.<sup>17</sup> The overall transformation is a hydropropargylation of a silyl enol ether, a rare type of alkene functionalization reaction.<sup>18,19</sup> In this reaction, the vinylidene complex works as a hydride acceptor first to generate  $\alpha,\beta$ -unsaturated carbene complex intermediate **B**, and then, after addition of the silyl enol ether, the produced alkenylrhenium(I) **C** worked as a hydride donor to generate another vinylidene complex **D**. To support this mechanism, a deuterium-containing propargyl ether **1<sub>D</sub>** containing a deuterium atom at the

**Scheme 2. Deuterium experiment and proposed reaction mechanism**

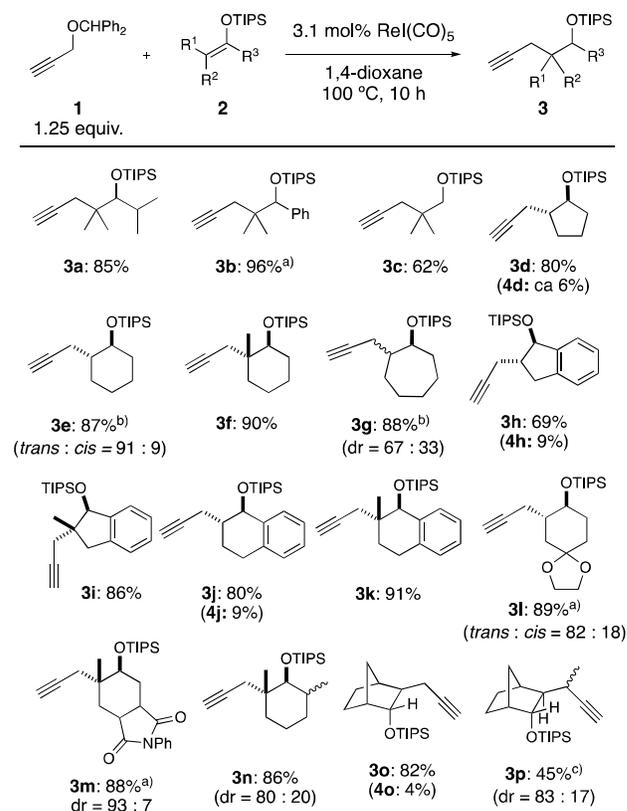


diphenylmethyl ether moiety (96%D) was subjected to this reaction, and the hydro-propargylation product **3a<sub>D</sub>**

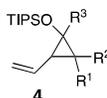
containing the deuterium atom at  $\alpha$ -position of the silyl ether (95%D) was obtained in good yield. In a similar manner, terminally deuterated propargyl ether **1<sub>D'</sub>** (>98%D) gave terminally deuterated product **3a<sub>D'</sub>** with 93% deuterium incorporation (for details, see SI).<sup>20</sup> These results supported the proposed mechanism (Scheme 2). Thus hydride transfers associated with dynamic vinylidene-alkenylmetal interconversion enabled this unique transformation.

We then examined the generality of the present reaction. The reaction of aromatic silyl enol ethers **3b** proceeded smoothly to give the corresponding hydropropargylation product in high yield. The reaction of silyl enol ether **3c** derived from isobutyraldehyde also proceeded without problem. As the second hydride transfer step would occur intramolecularly, the reaction of cyclic silyl enol ethers was examined next expecting high stereoselectivity. The reaction of 1-siloxycyclopentene gave the expected *trans*-2-propargyl-1-cyclopentanol derivative **3d** in good yield as a single stereoisomer accompanied by a small amount of a cyclopropanation

**Table 1. Generality of the silyl enol ether**

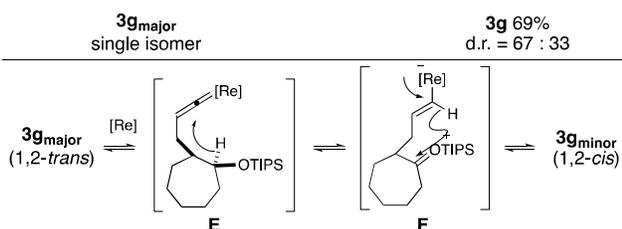
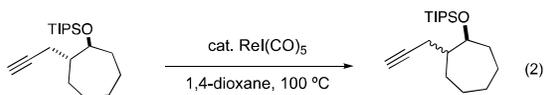


a) 5.0 mol% of  $\text{ReI}(\text{CO})_5$  and 2.0 equiv. of **1** were used. b) A trace amount of **4** was included. c) BOM ether of 3-butyne-2-ol was employed. The yield was determined by  $^1\text{H}$  NMR by internal standard method.



product **12d**. In the case of 1-siloxycyclohexene derivative, *trans*-2-propargyl-1-cyclohexanol derivative **3e** was obtained in good yield, but in this case a small amount of *cis*-isomer was also obtained. 2-Methyl-1-siloxycyclohexene derivative gave the desired product **3f** again as a single isomer. It is likely that 2-methyl group inhibited the 1,5-hydride transfer from the opposite face. Siloxy-indene or dihydronaphthalene derivatives also gave the desired *trans*-2-propargyl-1-cycloalkanol derivatives **3h-k** as a single isomer. Several functional groups such as cyclic acetal and imide were compatible under the reaction conditions to give the desired hydropropargylation products **3l,m** in good yield. Thus, the reaction showed wide generality concerning the silyl enol ether. On the contrary, the reaction of secondary or tertiary propargyl ethers was rather sluggish, and in one instance, hydropropargylation product **3p** was obtained in about 45% yield by the reaction of BOM ether of 3-butyn-2-ol with a silyl enol ether derived from 2-norbornanone.

During the examination of the generality of the reaction, another dynamic nature of the reaction was discovered in the product-forming step. As shown in Table 1, the cycloheptene derivative gave two isomeric products **3g** in 67 : 33 ratio, and the major *trans* product was isolated as a diastereomerically pure compound. Interestingly, on treatment of this *trans* product **3g<sub>major</sub>** with a catalytic amount of  $\text{Re}(\text{CO})_5$  at 100 °C in dioxane, isomerization reaction was found to proceed to give again a 67 : 33 mixture of two diastereomeric products. (eq 2) This result suggests the presence of the reversible pathway for the hydride transfer of the alkenylrhenium intermediates, that is, the vinylidene complex **E** is generated from the product and the hydrogen at the carbon connected to the siloxy group undergoes 1,5-hydride transfer to the vinylidene carbon to give alkenylrhenium species **F**.<sup>21</sup> Thus, this reaction is comprised of dynamic interconversion of vinylidene-alkenylmetal intermediates all through the reaction sequence.



This hydropropargylation reaction was further applied to the intramolecular reaction to realize a facile construction of polycyclic compounds with high diastereoselectivity (Table 2). A siloxy-cyclohexene derivative containing a propargyl ether moiety **5a** gave the *cis*-bicyclo[4.4.0]decane derivative **6a** in 80% yield as a

mixture of two isomers in a ratio of 88 : 12 (entry 1). The structure of the major isomer was determined by NMR analysis. Tertiary propargyl ether **5b** was also employable to give the *cis*-decalin **6b** as a single isomer (entry 2). The reaction of regioisomeric 1-siloxycyclohexene substrate **5c** also proceeded without problem to give a bicyclo[3.3.1]octane derivative **6c** in 82% yield as a single isomer (entry 3). It is also noted that acyclic silyl enol ether **5d** gave the monocyclic compound **6d** with high diastereoselectivity (entry 4). The structure of **6b**, **6c** and **6d**(major) was determined by single crystal X-ray analysis. Thus this protocol affords a useful method for the stereoselective synthesis of polycyclic compounds.

**Table 2. Generality of the intramolecular reaction**

Entry	Substrate	Product	yield
5 mol% $\text{Re}(\text{CO})_5$ 1,4-dioxane 100 °C, 5 h			
1			80% (dr = 88 : 12) <sup>a</sup>
2			70% single isomer
3			82% single isomer
4			62% (dr = 84 : 16) <sup>a</sup>

a) Determined by <sup>1</sup>H NMR.

In summary, we have developed the hydropropargylation reaction of silyl enol ethers utilizing the dynamic interconversion of vinylidene-alkenylmetal intermediates via reversible 1,5-hydride transfer process. The siloxycycloalkene gave the *trans*-2-propargyl-1-siloxycycloalkane derivatives with high stereoselectivity. The reaction was further applied to intramolecular reactions to give useful polycyclic compounds stereoselectively.

## ASSOCIATED CONTENT

**Supporting Information.** Preparative methods, spectral, and analytical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Note

The authors declare no competing financial interest.

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(20) Cross-over experiment was also carried out using a 1 : 1 mixture of **1<sub>D</sub>** and **1<sub>D'</sub>**, and no obvious formation of doubly deuterated product was observed by mass analysis (for details, see SI).

(21) No isomerization occurred when **3g-Me**, in which terminal alkyne of **3g<sub>major</sub>** was methylated, was subjected to the reaction conditions (for details, see SI).

## TOC Graphic

