Cycloaddition Reactions

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Rhenium(I)-Catalyzed Generation of α,β-Unsaturated Carbene Complex Intermediates from Propargyl Ethers for the Preparation of Cycloheptadiene Derivatives

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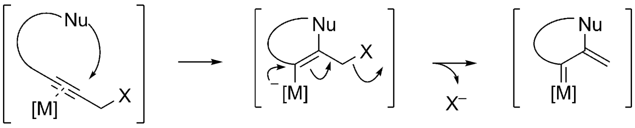
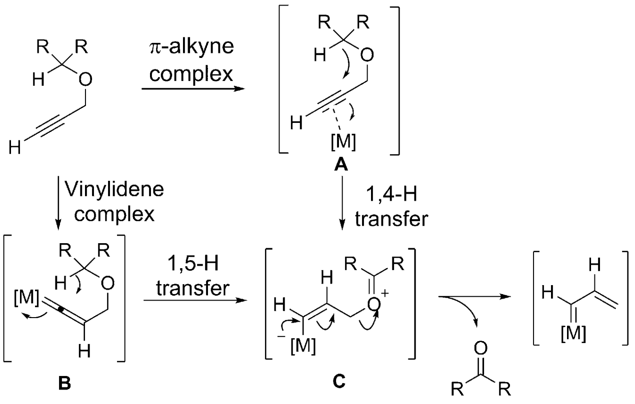
Abstract: *The rhenium(I)-catalyzed generation of α,β-unsaturated carbene complex intermediates from easily available propargyl ethers was achieved for the concise construction of cycloheptadiene derivatives through the formal [4+3] cycloaddition reaction with siloxydienes.*

Catalytic generation of α,β-unsaturated carbene complex intermediates through electrophilic activation of alkynes has attracted much attention as a useful method for the reaction of novel three-carbon reactive species.[1–4] In these reactions, the nucleophilic addition of appropriate internal nucleophiles onto alkynes having a leaving group at the propargylic position, followed by electron donation from the metal to release the leaving group, generates α-Nu-substituted α,β-unsaturated carbene complex intermediates (Scheme 1).



Scheme 1. Generation of α,β-unsaturated carbene complex intermediates.

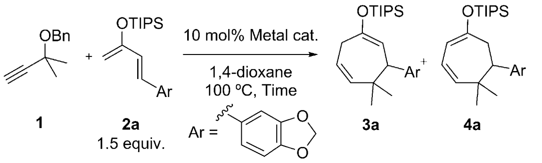


Scheme 2. Generation of α,β-unsaturated carbene complex intermediates from propargyl ethers.

We then thought of the possibility of using easily available propargyl ethers as substrate for catalytic generation of α,β-unsaturated carbene complex intermediates with the expectation that hydride transfer from the ether moiety would be promoted by electron donation from the lone pair of the oxygen atom (Scheme 2).[5–8] For generation of α,β-unsaturated carbene complex intermediates, the reaction necessitates 1,4-hydride transfer onto the π-alkyne complex **A**, which is rather rare in such systems,[6,9] and we also thought of examining the possibility of 1,5-hydride transfer through vinylidene intermediate **B**, which has several precedents as a stoichiometric reaction for preparation of metathesis catalysts.[10–13] These hydride transfers would generate the same intermediate **C** containing an oxonium moiety, which would work as an efficient leaving group for carbene generation. Herein, we report our successful realization of this concept for catalytic generation of simple α,β-unsaturated carbene complexes from propargyl ethers and their utilization as a three-carbon unit for the concise preparation of cycloheptadiene derivatives.

The reaction was examined with various metal catalysts using the benzyl ether of 1,1-dimethyl-2-propyn-1-ol **1a** and 1.5 molar amounts of 4-aryl-2-siloxy-1,3-butadiene **2a** as a carbene trapping reagent expecting the formation of cycloheptadiene **3a** as [4+3]-cycloadduct (Table 1).[4i,j] It was found that $ReX(CO)_5$ and $PtCl_2$ were the active catalyst for this reaction, and the desired product **3a** was obtained by carrying out of the reaction in 1,4-dioxane at 100 °C along with a small amount of its olefinic isomerization product

Table 1: Examination of various reaction conditions.



Entry	Metal cat.	Time [h]	**3a**+**4a** [%][a]	**3a**:**4a**[b]
1	$PtCl_2$	12	33	93:7
2	$ReCl(CO)_5$	12	62	>95:5
3	$ReBr(CO)_5$	4	84	95:5
4	$ReI(CO)_5$	2	96	>95:5
5[c]	$ReI(CO)_5$	4	97	>95:5
6[c,d]	$ReI(CO)_5$	4	75	61:39
7[c,d,e]	$ReI(CO)_5$	4	90	>95:5

Reaction conditions : **1a** (0.10 mmol), **2a** (0.15 mmol), and Metal cat. (0.01 mmol) in 1,4-dioxane (2.0 mL) at 100 °C. [a] Yield of isolated product. [b] Determined by ^1H NMR spectroscopy. [c] 0.10 M of **1a** and 2.5 mol% of $ReI(CO)_5$ were used. [d] 1.0 equiv of **2a** was used. [e] Activated 4 Å M.S. were used.

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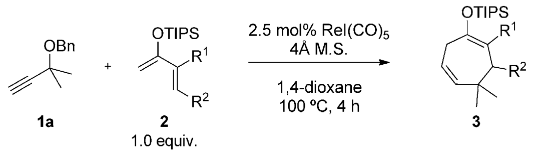
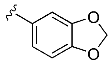
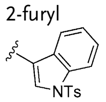
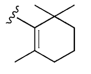
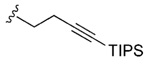
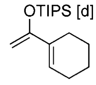
4a.[14] Formation of bezaldehyde was noted in these reactions. Among several $ReX(CO)_5$, $ReI(CO)_5$ gave the best result (entries 1–4), and even 2.5 mol% of $ReI(CO)_5$ afforded the cycloheptadiene **3a** in 97% yield (entry 5). Even an equimolar amount of propargyl ether **1a** and siloxydiene **2a** gave the desired product **3a** in good yield by carrying out the reaction in the presence of activated 4 Å M.S.(entries 6 and 7).[15]

Generality of the reaction with various 2-siloxydienes **2** was examined using propargyl benzyl ether **1a** under the optimized conditions (Table 2). Various 4-aryl substituted 2-siloxy-1,3-dienes such as electron-donating and electron-withdrawing phenyl, furyl, and indolyl groups underwent the reaction smoothly to give the products in high yield (entries 1–7). 4-Alkenyl and 4-alkyl-2-siloxy-1,3-dienes also gave the corresponding cycloheptadienes **3** in good yield (entries 8–11). Even 3-alkyl- and 3,4-dialkyl-substituted 2-siloxy-1,3-dienes were also employable without problem (entries 12 and 13). All these reactions proceeded by heating just an equimolar mixture of **1a** and **2** to give synthetically useful cycloheptadiene derivatives **3** in good yield.

Table 2: Examination of various siloxydienes.

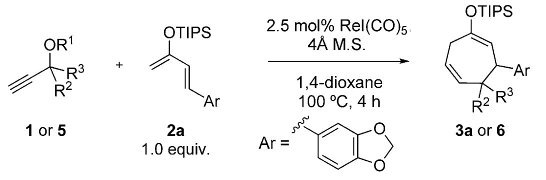


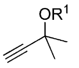
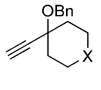
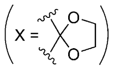
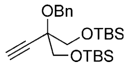
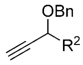
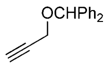
Entry	R^1	R^2			Yield [%]
1	H		**2a**	**3a**	90
2	H	Ph	**2b**	**3b**	86
3	H	p-$MeOC_6H_4$	**2c**	**3c**	88
4	H	p-BrC_6H_4	**2d**	**3d**	86
5	H	2,5-$(MeO)_2C_6H_3$	**2e**	**3e**	92
6	H	2-furyl	**2f**	**3f**	63
7	H		**2g**	**3g**	88
8	H		**2h**	**3h**	82
9	H	nPr	**2i**	**3i**	77
10	H	iPr	**2j**	**3j**	85
11	H		**2k**	**3k**	93
12[a]	C_2H_4OBOM[b]	H	**2l**	**3l**	72
13[c]			**2m**	**3m**	91

[a] The reaction was carried out for 12 h. [b] BOM = benzyloxymethyl. [c] The reaction was carried out for 8 h. [d] That is, $R^1,R^2 = (CH_2)_4$.

The result of the examination of the generality of the propargyl ethers is shown in Table 3. Various ethers such as alkyl and THP ethers were also employable to give the product **3a** in good yield (entries 1 and 2). A propargyl ether containing cyclohexane moiety gave a spirocyclic product in good yield (entry 3). Functional groups such as carbamate, acetal, and silyl ether were compatible under the reaction conditions, and desired products were obtained without problem (entries 4–6). Secondary propargyl ether gave the corresponding product with reasonable diastereoselectivity (entries 7 and 8). More importantly, a simple propargyl ether itself gave the corresponding product in reasonable yield (entry 9). In this case, formation of methylene cyclohexane derivative **7g** in 17% yield was also noted.[16]

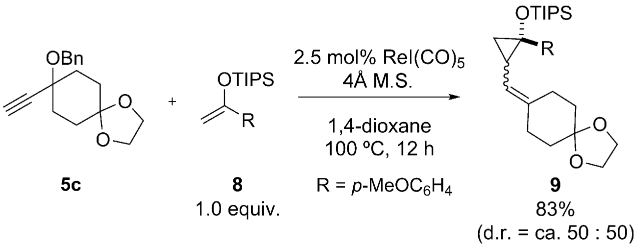
Table 3: Examination of various propargyl ethers.



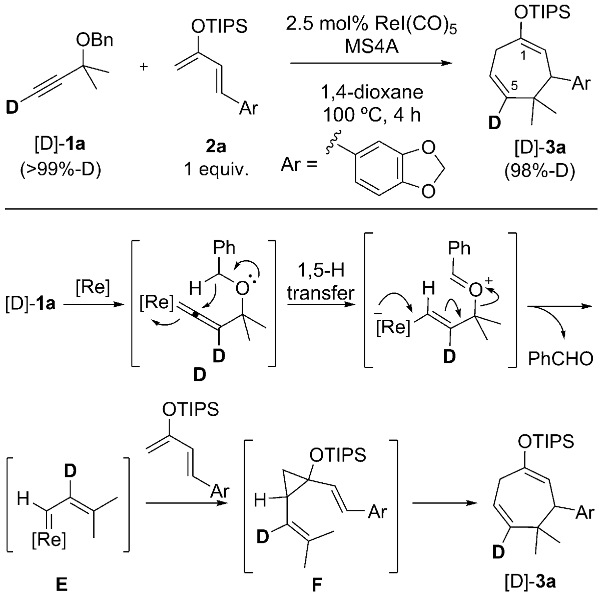
Entry	Propargyl ethers				Yield [%]
1[a]		$R^1 = C_{14}H_{29}$	**1b**	**3a**	90
2[b]		R^1 = THP	**1c**	**3a**	59
3		X = CH_2	**5a**	**6a**	80
4[b]		X = NBoc	**5b**	**6b**	65
5[c]			**5c**	**6c**	87
6[b]			**5d**	**6d**	69
7[c]		R^2 = iPr	**5e**	**6e**	75 (cis/trans 79:21)[e]
8[d]		R^2 = Me	**5f**	**6f**	69 (cis/trans 77:23)[e]
9[d,f]			**5g**	**6g**	58[g]

[a] For 6 h. [b] For 12 h. [c] For 8 h. [d] 5 mol% Re catalyst was used. [e] The ratio was determined by ^{1}H NMR spectroscopy. [f] 1.5 equiv of **2a** was used. [g] Obtained as a mixture with **7g**. The yield was determined by ^{1}H NMR spectroscopy.

To obtain information on the mechanism of the reaction, several control experiments were carried out. First, the reaction of **5c** with silyl enol ether **8** was examined under the standard reaction conditions, and cyclopropane **9** was obtained in good yield, confirming generation of the α,β-unsaturated carbene complex intermediate (Scheme 3). Next, a deuterium labeling experiment was carried out (Scheme 4). When propargyl ether [D]-**1a** with the hydrogen atom of the terminal alkyne deuterated was employed as substrate, the deuterium was introduced onto C-5 position of the product [D]-**3a**. This result clearly showed that the reaction proceeded through the vinylidene intermediate in which terminal deuterium transferred to the internal position. Based on



Scheme 3. Cyclopropanation of silyl enol ether.



Scheme 4. Deuterium labeling experiments.

these results, the total mechanism of the reaction was shown in Scheme 4. Thus, one or two of the carbonyl ligands of $ReX(CO)_5$ are liberated by heating and vinylidene intermediate **D** is generated by the reaction with propargyl ether.[17] Then 1,5-hydride transfer of the benzylic hydrogen onto the vinylidene carbon followed by elimination of benzaldehyde generates α,β-unsaturated carbene complex intermediate **E**.[18] This intermediate reacts with siloxydiene to give divinylcyclopropane **F**, which undergoes Cope rearrangement to give the product.[19]

In conclusion, a very concise and practical method for generation of simple α,β-unsaturated carbene complex intermediates is realized by the reaction of easily available propargyl ethers with a catalytic amount of $ReI(CO)_5$. Further intermolecular addition reaction with siloxydienes efficiently gives synthetically useful silyloxycycloheptadienes in high yields.

Experimental Section

General procedure: 4 Å M.S. (150 mg) were placed in a test tube and was activated by heating at 230 °C for 8 h under reduced pressure (ca. 0.30 mmHg). The test tube was cooled to room temperature under reduced pressure. $ReI(CO)_5$ (1.7 mg, 3.8 μmol, 2.5 mol %), propargyl ether (0.15 mmol, 1.0 equiv), and siloxydiene (0.15 mmol, 1.0 equiv) were dissolved in 1,4-dioxane (1.5 mL) under argon atmosphere and the resulting mixture was transferred to the test tube. The test tube was closed and the mixture was stirred at 100 °C for 4 h. The reaction was quenched by addition of TMEDA (0.2 mL). After filtration to remove the 4 Å M.S., the filtrate was concentrated under reduced pressure in vacuo. The crude product was purified by preparative TLC to give the [4+3] addition product.

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Keywords: cycloaddition reactions · propargyl ether · rhenium · unsaturated carbene complex · vinylidene

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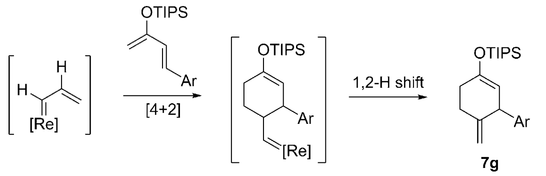

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Communications

Cycloaddition Reactions

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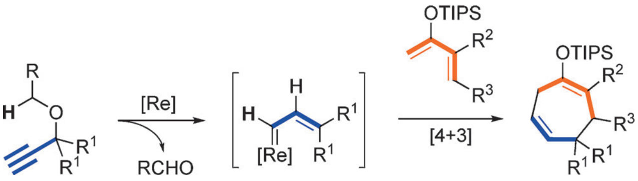
Rhenium(I)-Catalyzed Generation of α,β-Unsaturated Carbene Complex Intermediates from Propargyl Ethers for the Preparation of Cycloheptadiene Derivatives



The rhenium(I)-catalyzed generation of α,β-unsaturated carbene complex intermediates from easily available propargyl ethers was achieved for the concise construction of cycloheptadiene derivatives through the formal [4+3] cycloaddition reaction with siloxydienes.