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Platinum(II)-Catalyzed Intermolecular [3 + 2] Cycloaddition of Propadienyl Silyl Ethers and Alkenyl Ethers

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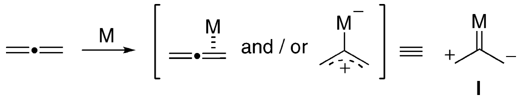
The use of allenes as a three-carbon unit for [3 + *n*] cycloaddition reactions is relatively unexplored compared with [2 + *n*]-type reactions using allenes as a 2π unit.[1] Representative examples of such transformation are the Lewis acid-promoted [3 + 2] cycloaddition reactions of allenylsilanes[2] and the phosphine-triggered reactions of 2,3-butadienoates[3k] with electron-deficient alkenes,[3a−h] imines,[3c,i] aziridines,[3j] etc. On the contrary, transition-metal-catalyzed [3 + *n*] cycloaddition reactions had not been reported until recent reports of intramolecular [3 + 2][4] and [3 + 4][5] cycloaddition reactions, and to date there is still no report of an intermolecular reaction using the 1,2-propadiene moiety of allene derivatives as a three-carbon unit.[6]

We previously reported that 1,2,4-trienes undergo $PtCl_2$-catalyzed cyclization to give cyclopentadiene derivatives.[7] In this reaction, $PtCl_2$ electrophilically activates the 1,2-propadiene moiety, which is expected to behave like a metal-containing 1,3-dipole **I**, as shown in eq 1. Then we thought of the possibility of carrying out intermolecular [3 + 2] cycloaddition reactions of 1,2-propadienes and appropriate dipolarophiles by using a Pt(II) catalyst. This paper describes the successful realization of such a concept, that is, the Pt(II)-catalyzed intermolecular [3 + 2] cycloaddition reaction of silyl 1,2-propadienyl ether and alkenyl ethers to give functionalized cyclopentene derivatives.

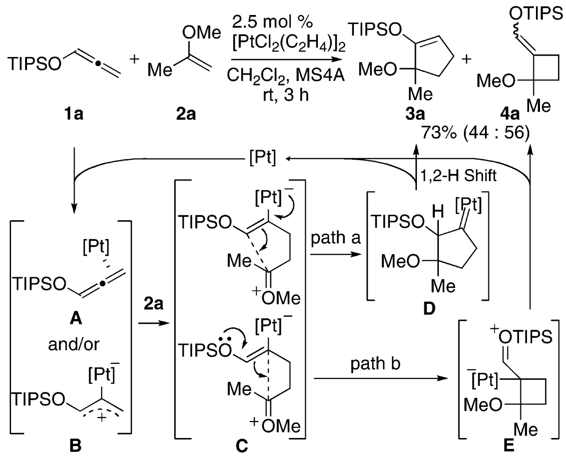


(1)

We chose the combination of silyl 1,2-propadienyl ether and alkenyl ether with the expectation that selective electrophilic activation of the silyl 1,2-propadienyl ether would be possible in the presence of alkenyl ether because of its higher inherent reactivity and that the alkenyl ether would attack the activated Pt(II)-containing 1,3-dipole in a [3 + 2] cycloaddition manner. In fact, when a mixture of triisopropylsilyl (TIPS) 1,2-propadienyl ether **1a** and 2-methoxypropene **2a** was treated with 2.5 mol % $[PtCl_2(CH_2{=}CH_2)]_2$ in CH_2Cl_2 at room temperature, the reaction proceeded smoothly to give the desired cyclopentene derivative **3a** along with methylenecyclobutane derivative **4a** in a combined yield of 73% in a 44:56 ratio.

The reaction was thought to proceed as follows (Scheme 1). TIPS propadienyl ether **1a** was activated by Pt(II) electrophilically to give the corresponding π complex **A** or π-allyl cationic intermediate **B** first.[8] Next, 2-methoxypropene attacked this intermediate at the nonsubstituted terminus to give Pt(II)-containing zwitterionic intermediate **C**. Ring closure with electron flow from the anionic platinum to the oxonium carbon at the position β to the metal (path a) would give the cyclopentylidene Pt(II) complex intermediate **D**, which finally underwent 1,2-hydrogen shift to give cyclopentene derivative **3a** with regeneration of the platinum catalyst. Methylenecyclobutane derivative **4a** was thought to be produced by the attack of the silyl enol ether at the oxonium carbon to give the cyclobutylplatinum(II) intermedate **E** (path b), which eliminated the platinum catalyst to give **4a**.[9]

Scheme 1. Proposed Reaction Mechanisms



To improve the chemoselectivity toward cyclopentene derivative **3a**, several reaction conditions were examined (Table 1). It was found that the phosphine ligand [equimolar amount per Pt(II)] had some effect on the ratio of the two products, and the rather bulky tri(*o*-tolyl)phosphine gave the products in a 57:43 ratio (entry 3).[10] It is likely that increasing the bulkiness around the platinum moiety disfavored cyclobutane formation as a result of steric repulsion. The addition of 2 equiv of phosphine ligand for platinum suppressed the reaction, suggesting that the catalytically active species was the platinum(II) monophosphine complex. In regard to the reaction solvent, ethyl acetate was the solvent of choice, giving the products in 95% yield with a ratio of 72:28 (entry 6).

To further improve the chemoselectivity toward the cyclopentene derivative, we thought of lowering the nucleophilicity of the silyl enol ether moiety by using the less electron-donating *tert*-butyldiphenylsilyl (TBDPS) group instead of the TIPS group. In fact, the corresponding cyclopentene derivative was obtained in a 92:8 ratio in the reaction of TBDPS 1,2-propadienyl ether **1b** (entry 7), and the selectivity was further improved to 98:2 without decreasing the yield by carrying out the reaction at 0 °C (entry 8).

As summarized in Table 2, this reaction showed wide generality concerning alkenyl ethers. 1,1-Disubstituted and 1,1,2-trisubstituted alkenyl ethers, 1-methoxycycloalkenes, dihydrofuran, and dihydropyran could be employed for this reaction, giving the corresponding cyclopentene derivatives in good yield with high selectivity. Methylenetetrahydrofuran generated in situ from pent-4-yn-1-ol **2m** reacted with **1b** to give the spirocyclic compound. Furthermore, indole **2n** could be employed for this reaction, providing a synthetically useful tricyclic indole derivative, albeit in moderate yield.

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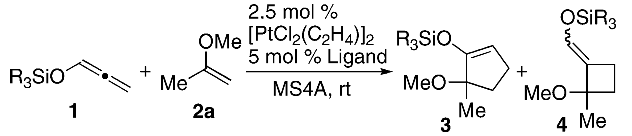
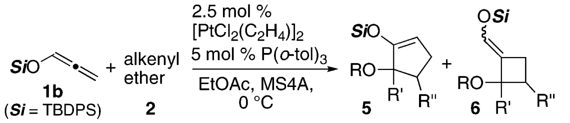
Table 1. Optimization of Reaction Conditions[a]

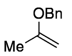
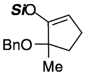
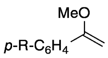
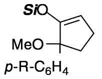
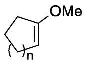
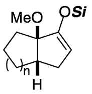
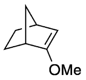
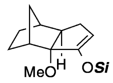
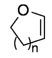
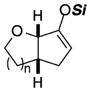
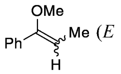
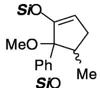
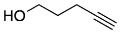
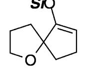
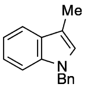
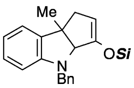


entry	R_3Si	ligand	solvent	time (h)	yield (**3** + **4**) (%)	ratio (**3**:**4**)
1	TIPS (**1a**)	–	CH_2Cl_2	3	73	44:56
2		PPh_3		0.5	79	38:62
3		P(*o*-tolyl)$_3$		1	80	57:43
4			toluene	1	78	37:63
5			THF	1	78	59:41
6			EtOAc	0.5	95	72:28
7	TBDPS (**1b**)			1	93[b]	92:8
8				1	97[b,c]	98:2

[a] Yields and product ratios were determined by ^1H NMR analyses. [b] Isolated yield. [c] At 0 °C.

Table 2. Generality of the Pt(II)-Catalyzed Intermolecular [3 + 2] Cycloaddition Reaction



entry	alkenyl ether		product	yield (**5**+**6**) (%)	ratio (**5** : **6**)
1		**2b**		quant	96 : 4
2		R = Br (**2c**)		89[a] (84)[b]	97 : 3
3		NO_2 (**2d**)		85	92 : 8
4		n = 1 (**2e**)		98	93 : 7
5		2 (**2f**)		94	97 : 3
6		3 (**2g**)		89	93 : 7
7		4 (**2h**)		86[a]	89 : 11
8[c]		4 (**2h**)		94	92 : 8
9[c]		**2i**		97	93 : 7
10		n = 1 (**2j**)		97	86 : 14
11[c]		2 (**2k**)		95	90 : 10
12[d]	 (*E* : *Z* = 2 : 1) (**2l**)			90[e]	97 : 3
13		**2m**		66	–[f]
14[g]		**2n**		35 (50[a])	–[f]

[a] NMR yield. [b] The product was isolated as a ketone after hydrolysis of the silyl enol ether moiety. [c] At −40 °C. [d] At room temperature. [e] The product **5** was obtained as an inseparable mixture of diastereomers (1.2:1). [f] A mixture of unidentified products was obtained, and the formation of [2 + 2] adduct could not be confirmed. [g] Using 5 mol % catalyst, 10 mol % phophine, and 5 Å molecular sieves.

In conclusion, we have developed a Pt(II)-catalyzed [3 + 2] cycloaddition reaction of silyl propadienyl ethers and alkenyl ethers as the first example of the utilization of allenes as a three-carbon unit in a transition-metal-catalyzed intermolecular cycloaddition reaction. This reaction gave synthetically useful functionalized cyclopentanone derivatives with wide generality, and this process would be complementary to the well-precedented phosphine-catalyzed [3 + 2] cycloaddition of electron-deficient allenes with electrophilic 2π components.

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Supporting Information Available: Preparative methods and spectral and analytical data for compounds **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Use of tris(*p*-tolyl)-or tris(*p*-methoxyphenyl)phosphine gave results similar to those for PPh_3. Thus, the electronic effect on the selectivity was not large.

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