

Efficient Control for the Cationic Platinum(II)-Catalyzed Concise Synthesis of Two Types of Fused Carbocycles with Angular Oxygen Functionality

Hiroyuki Kusama, Eiichi Watanabe, Kento Ishida, and Nobuharu Iwasawa*^[a]

Fused carbocyclic structures containing a seven-membered ring with an angular hydroxy group are frequently found in natural products (Figure 1),^[1] and exploitation of

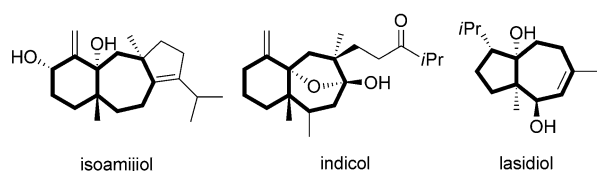


Figure 1. Various terpenoids containing a fused seven-membered ring with an angular oxygen functionality.

an efficient synthetic methodology for the construction of such carbocycles is of great importance in the field of organic synthesis.^[2] Utilization of carbonyl ylides is one of the most useful methods for the preparation of this class of compounds, however, this method suffers from several problems such as the use of diazo compounds as the precursor of the ylides and the difficulty in preparing required substrates for the construction of fused carbocycles.^[3,4]

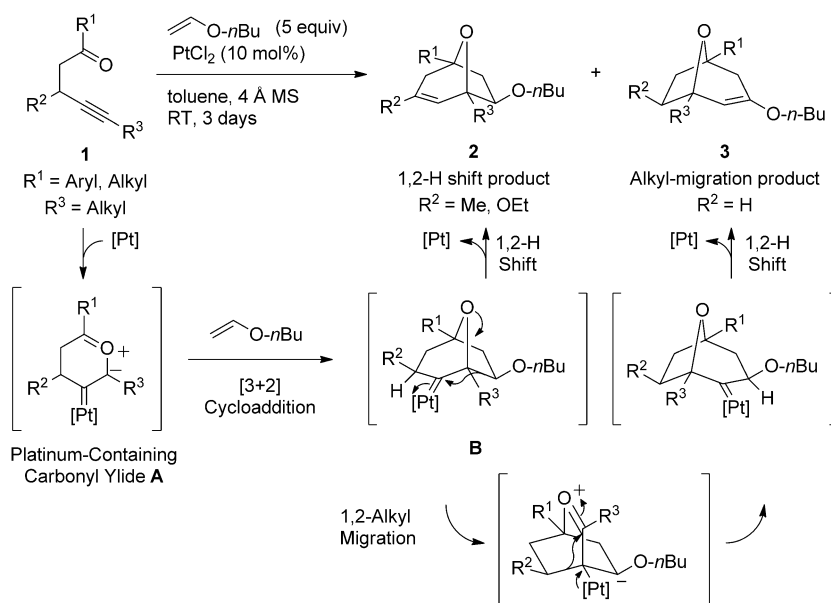
We have already reported that platinum-containing carbonyl ylides **A** could be generated from simple acyclic γ,δ -ynones **1** and PtCl_2 by attack of the carbonyl oxygen in an *endo* manner onto the electrophilically activated alkyne moiety,^[5–7] and subsequently they undergo an intermolecular [3+2] cycloaddition reaction with vinyl ethers to give cycloadducts as carbene complex intermediates **B**. These intermediates then further undergo typical reactions of carbene complexes such as 1,2-H shift or 1,2-alkyl migration to afford two kinds of oxygen-bridged cycloheptene deriva-

tives, 1,2-H shift products **2** or alkyl migration products **3**, selectively depending on the presence or absence of the substituent at the propargylic position (Scheme 1).^[5c] By using this reaction, carbonyl ylides could be generated easily without using diazo compounds, and synthetically useful cyclic compounds with several oxygen functionalities were readily obtained starting from ynones and vinyl ethers in the presence of a catalytic amount of PtCl_2 . However, the two reaction pathways were dependent on the substrates and intentional control of the two pathways was not realized in spite of their high potential as a synthetic protocol. In this study, we report a facile method for the construction of two kinds of synthetically useful fused seven-membered ring skeletons bearing an oxygen functionality at the angular position by using 2-(alka-2-ynyl)cycloalkanones as easily available substrates, where both kinds of products are obtained selectively by the appropriate combination of the vinyl ether and the cationic platinum(II) catalyst.

We first examined the reaction of 2-(buta-2-ynyl)cyclohexanone **4**, which was easily prepared by alkylation of 2-ethoxycarbonylcyclohexanone followed by decarboxylation, with benzyl vinyl ether in the presence of a catalytic amount of PtCl_2 in toluene at room temperature (Table 1, entry 1).^[8] Although this substrate had no propargylic substituent, the fused carbocycle **5** (corresponding to the 1,2-H shift product **2**, Scheme 1) was obtained albeit in low yield (<12%) after three days. To improve the yield of the product, several other platinum complexes were examined. Although the use of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ ^[9] in dichloromethane gave no desired product (Table 1, entry 2), by using the cationic complex generated in situ from *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and AgSbF_6 ^[10] dramatically accelerated the reaction rate and improved the yield of product **5** to 55% with moderate diastereoselectivity (Table 1, entry 3; *trans/cis* = 25:75).^[11] Interestingly, *trans*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ - AgSbF_6 gave no cycloaddition product; this is probably owing to the steric repulsion between the alkyne moiety and the two phosphine ligands (Table 1, entry 4). The yield was further improved by using *cis*- $[\text{PtCl}_2(\text{P}(m\text{-tol})_3)_2]$ or *cis*- $[\text{PtCl}_2(\text{P}(n\text{Bu})_3)_2]$ as a platinum catalyst, although the diastereoselectivity remained almost the same

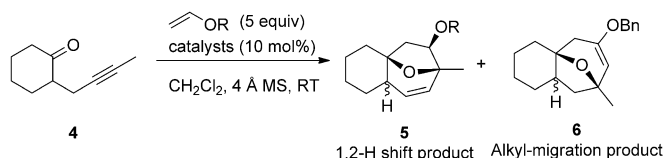
[a] Dr. H. Kusama, E. Watanabe, Dr. K. Ishida, Prof. Dr. N. Iwasawa
Department of Chemistry
Tokyo Institute of Technology
2-12-1, O-okayama, Meguro-ku, Tokyo 1528551 (Japan)
Fax: (+81) 3-5734-2931
E-mail: niwasawa@chem.titech.ac.jp

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Scheme 1. Preparation of 8-oxabicyclo[3.2.1]octane derivatives.

Table 1. Survey of platinum catalysts.



Entry	Catalysts	R	Time [h]	5 [%]	trans/cis	6 [%]	trans/cis
1 ^[a]	PtCl ₂	Bn	73	< 12	n.d. ^[b]	—	—
2	cis-[PtCl ₂ (PPh ₃) ₂]	Bn	10	0	—	—	—
3	cis-[PtCl ₂ (PPh ₃) ₂], AgSbF ₆	Bn	3	55	25:75	—	—
4	trans-[PtCl ₂ (PPh ₃) ₂], AgSbF ₆	Bn	15	0	—	—	—
5	cis-[PtCl ₂ (P(<i>m</i> -tol) ₃) ₂], AgSbF ₆	Bn	3	79	22:78	—	—
6	cis-[PtCl ₂ (P(<i>n</i> Bu) ₃) ₂], AgSbF ₆	Bn	6	66	33:67	—	—
7	cis-[PtCl ₂ (P(<i>m</i> -tol) ₃) ₂], AgSbF ₆	TIPS	3	84	53:47	—	—
8	cis-[PtCl ₂ (P(<i>n</i> Bu) ₃) ₂], AgSbF ₆	TIPS	3	83	88:12	—	—
9	cis-[PtCl ₂ (PMe ₃) ₂], AgSbF ₆	Bn	3	13 ^[d]	n.d. ^[b]	70 ^[d]	81:19
10 ^[c]	cis-[PtCl ₂ (PMe ₂ Ph) ₂], AgSbF ₆	Bn	3	14 ^[d]	n.d. ^[b]	73 ^[e]	90:10
11	cis-[PtCl ₂ (PMe ₂ Ph) ₂], AgSbF ₆	TIPS	4	78 ^[d]	78:22 ^[d]	trace ^[d]	n.d. ^[b]

[a] Toluene was used as solvent. [b] n.d. = not determined. [c] 2 equivalents of vinyl ether were used. [d] Determined by ¹H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. [e] Isolated as a ketone by hydrolysis of 6.

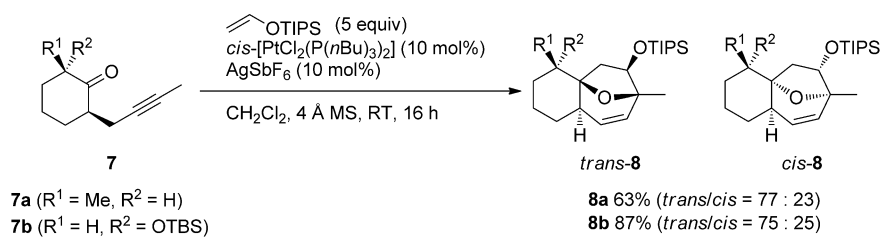
(Table 1, entries 5 and 6).^[10d] More importantly, it was found that triisopropylsilyl (TIPS) vinyl ether could be employed instead of benzyl vinyl ether to give the 1,2-H shift product **5** (R = TIPS) in good yield, and high *trans* diastereoselectivity was achieved by using the *cis*-[PtCl₂(P(*n*Bu)₃)₂]-AgSbF₆ catalyst (83 %, *trans/cis* = 88:12).

Surprisingly, when *cis*-[PtCl₂(PMe₃)₂] or *cis*-[PtCl₂(PMe₂Ph)₂] was employed in combination with AgSbF₆, the other type of cycloaddition product, alkyl migration product **6**, was obtained as a major product (Table 1, entries 9 and 10). High diastereoselectivity of the product (*trans/cis* = 90:10) was also achieved in this reaction.^[11] It was also noted that the reaction with the combination of the hin-

dered vinyl ether (TIPS vinyl ether) and the small phosphine ligand (PMe₂Ph) mainly provided the 1,2-H shift product (**5**/**6** = 95:5); this suggested that the reaction pathway was mainly determined by the vinyl ether rather than the phosphine ligand (Table 1, entry 11). Thus, selective preparation of two types of synthetically useful, oxygenated bicyclo[5.4.0]undecane derivatives was realized starting from the same, easily available alkynyl cyclohexanone **4** by judicious selection of the vinyl ether and the catalyst. It should be noted that few examples on the use of mono-cationic platinum(II) complexes in alkyne-activation chemistry have been reported, and this study is a very rare example in which the reaction pathway is controlled efficiently by the combination of the vinyl ether and the phosphine ligand on the cationic platinum complex.

As both types of cycloaddition products were found to be obtained selectively by the appropriate choice of the reaction parameters, we next examined the reaction of various 2-(buta-2-ynyl)cycloalkanones with TIPS vinyl ether using *cis*-[PtCl₂(P(*n*Bu)₃)₂] with AgSbF₆ as the platinum catalyst to obtain the 1,2-H shift product selectively (Scheme 2 and Table 2).

The reaction of cyclohexanone derivatives **7a** with a methyl substituent at the 6-position gave the corresponding product **8a** in reasonable yield. A cyclohexanone derivative **7b** with a siloxy group also gave a highly oxygenated product **8b** in high yield as a mixture of diastereoisomers (Scheme 2). The reaction of 2-methyl derivative **7c** gave the *trans* product^[11] as a single diastereoisomer, which has the same stereochemistry of the methyl and the oxygen functional group to that of some terpenoids such as isoamijiol and indicol (Table 2, entry 1).^[1] The reaction of cyclohexanone derivatives containing an acetal moiety **7d** also provided cycloaddition product **8d** (Table 2, entry 2). We further examined the reaction of cyclohexanone derivatives with an oxygen functionality at the terminal propargylic position, as



Scheme 2. The reaction of cyclohexanone derivatives with a substituent at the 6-position. TBS = *tert*-butyldimethylsilyl.

Table 2. Reaction of various cyclohexanones using *cis*-[PtCl₂(P(*n*Bu)₃)₂] as a platinum complex.

Entry	R ¹	R ²	X	Yield [%]	<i>trans/cis</i>
1	Me	Me	-CH ₂ -	73 (8c)	> 95:5
2 ^[a]	H	Me	C(OCH ₂ CH ₂ O)	73 (8d)	70:30
3	H	CH ₂ OTBS	-CH ₂ -	92 (8e)	88:12
4 ^[b]	H	CH ₂ OTr	-CH ₂ -	70 (8f)	> 95:5
5	H	vinyl	-CH ₂ -	7g	89:11
6	H	<i>n</i> Bu	-CH ₂ -	7h	90:10
7	H	(CH ₂) ₂ Ph	-CH ₂ -	7i	89:11
8	H	(CH ₂) ₂ OBn	-CH ₂ -	7j	88:12

[a] 20 h. [b] 0 °C. Trace amounts of isomers were also obtained.

this would be a useful element for cleaving the oxygen bridge to give 1-hydroxybicyclo[5.4.0]undecane derivatives.^[12] As a result, highly oxygenated cycloheptene derivatives **8e** and **8f** were obtained without any difficulty (Table 2, entries 3 and 4). Further examination revealed that various substituents (R^2 = vinyl, *n*Bu, (CH₂)₂Ph, (CH₂)₂OBn) could be employed as the alkyne substituent and 1,2-H shift products were obtained in high yield with mostly 90:10 diastereoselectivity (Table 2, entries 5–8).

We next examined the generality of the reaction for the preparation of alkyl migration products by the reaction of various cyclohexanone derivatives **7** and benzyl vinyl ether using a catalytic amount of *cis*-[PtCl₂(PMe₂Ph)₂]-AgSbF₆.^[13]

As shown in Table 3, the reaction preferentially gave the alkyl migration products **9** in good yield with reasonable diastereoselectivity. Cyclohexanone derivatives containing a methyl or a siloxy substituent

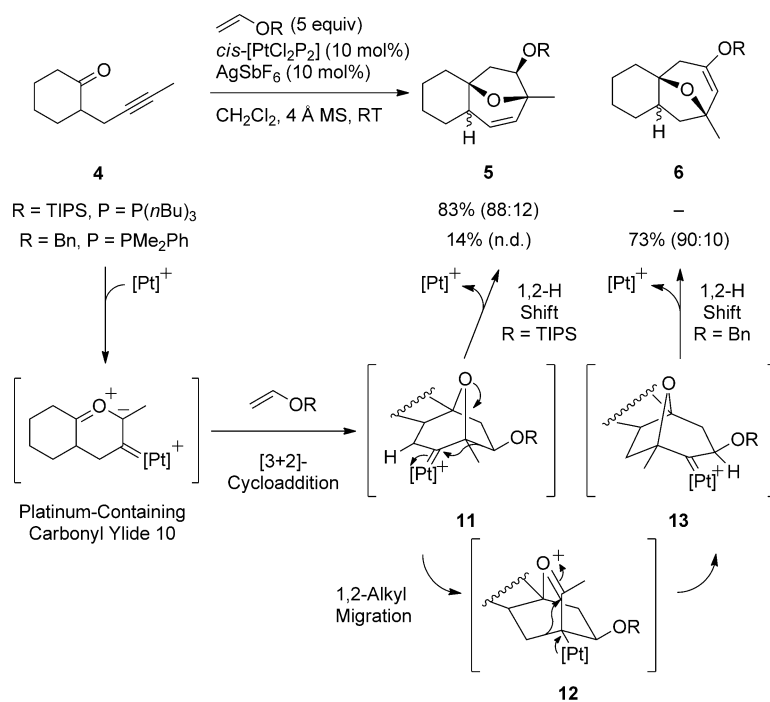
Table 3. Reaction of various cyclohexanones using *cis*-[PtCl₂(PMe₂Ph)₂] as a platinum complex.

Reaction scheme showing the conversion of cyclohexanone derivative **7** to bicyclic enone **9**. Reagents: OBn (2 equiv), *cis*-[PtCl₂(PMe₂Ph)₂] (10 mol%), AgSbF₆ (10 mol%), CH₂Cl₂, 4 Å MS, RT, 2.5 ~ 20 h, followed by 1N HCl in THF, RT. The product **9** is a bicyclic enone with a trans/cis ratio.

Entry	R ¹	R ²	Yield [%]	<i>trans/cis</i>
1 ^[a]	Me	Me	7a 83 (9a)	88:12
2 ^[a]	OTBS	Me	7b 60 (9b)	89:11
3	H	<i>n</i> Bu	7h 82 (9h)	93:7
4	H	(CH ₂) ₂ Ph	7i 76 (9i)	91:9
5	H	(CH ₂) ₂ OBn	7j 72 (9j)	85:15
6	H	CH ₂ OTBS	7e 49 (9e)	75:25
7	H	CH ₂ OTr	7f 63 (9f)	85:15

[a] The stereochemistry between the R¹ and buta-2-ynyl substituent was the same as shown in Scheme 2.

provided the desired products **9e**, **9f** in a somewhat lower yield because of the decomposition of the substrates (Table 3, entries 6 and 7).



Scheme 3. The control of two reaction pathways depending on the catalyst and the vinyl ether.

Discrimination of the two reaction pathways, that is, 1,2-H shift or 1,2-alkyl migration from the carbene complex intermediate **12**, could be explained as follows (Scheme 3):^[5c] From the experimental results, the carbene complex intermediate **11** derived from vinyl ether containing a large substituent ($R = \text{TIPS}$) and a large phosphine ligand ($P = P(n\text{Bu})_3$, cone angle = 136°) undergoes 1,2-H shift preferentially to provide **5** directly,^[14] while that with a small substituent ($R = \text{Bn}$) and a small ligand ($P = \text{PMe}_2\text{Ph}$, cone angle = 122°) gives alkyl-migration product **6** selectively.^[14] It is likely that due to the steric repulsion of the platinum complex and the TIPS group, formation of the intermediate **12** and/or **13** with a large substituent ($R = \text{TIPS}$) and a large ligand ($P = P(n\text{Bu})_3$) is not favorable, and **11** preferentially undergoes a 1,2-H shift to afford **5**. On the contrary, intermediate **11** with a small substituent ($R = \text{Bn}$) and a small ligand ($P = \text{PMe}_2\text{Ph}$) undergoes 1,2-alkyl migration to generate intermediate **12**.^[15] Further alkyl migration to the oxonium moiety of **12** produces another nonstabilized carbene intermediate **13**, which undergoes 1,2-H shift to give the alkyl migration product **6**.^[16]

In conclusion, an efficient method for the preparation of bicyclo[5.4.0]undecanes with an angular oxygen functionality was developed starting from easily available cyclic ketones and vinyl ethers based on the [3+2] cycloaddition reaction of the platinum-containing carbonyl ylide. Two types of synthetically useful products were selectively obtained depending on the substituent of the vinyl ether and the phosphine ligand of the cationic platinum(II). This is a unique example of controlling two catalytic reaction pathways simply by choosing appropriate reaction parameters.

Experimental Section

General Procedure

A dichloromethane solution (1.0 mL) of cyclic γ,δ -ynone (15.0 mg, 0.100 mmol) was added to *cis*-[PtCl₂(P(*n*Bu)₃)₂] (6.7 mg, 0.010 mmol) and AgSbF₆ (3.4 mg, 0.010 mmol) and the mixture was stirred at room temperature. After one minute, a dichloromethane solution (1.0 mL) of TIPS vinyl ether (100.2 mg, 0.5 mmol) was added to the mixture and stirred at room temperature until the starting material disappeared or for approximately 10 h. The reaction was quenched with triethylamine (0.1 mL) and the mixture was filtered through a short pad of Celite with ethyl acetate (30 mL) as an eluent and then the solvent was removed under reduced pressure to give crude product, which was purified by silica-gel column chromatography (3% ethyl acetate in hexane) to give alkene **5-trans** and **5-cis** (29.1 mg, 83%, *trans/cis* = 88:12) as a diastereomeric mixture.

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Keywords: alkynes • carbonyl ylide • cycloaddition • platinum • ring expansion

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- [14] We examined the reactions with various phosphine ligands. The trend in product selectivity is correlated mainly with the steric factor (cone angle) of phosphine ligands rather than with their electronic factor (the Tolman electronic parameter). Suitable phosphines for preparation of the alkyl-migration product: PMe₃ (cone angle = 118°, $\nu(\text{CO}) = 2064.1 \text{ cm}^{-1}$) and PMe₂Ph (cone angle = 122°, $\nu(\text{CO}) = 2065.6 \text{ cm}^{-1}$). Phosphines which preferentially gave the alkyl-migration product: P(*n*Bu)₃ (cone angle = 136°, $\nu(\text{CO}) = 2060.3 \text{ cm}^{-1}$), P(*m*-tol)₃ (cone angle = 165°, $\nu(\text{CO}) = 2067.2 \text{ cm}^{-1}$), PPh₃ (cone angle = 145°, $\nu(\text{CO}) = 2068.9 \text{ cm}^{-1}$). For IR data [$\nu(\text{CO})$] of [Ni(CO)₃L] with various phosphines, see: C. A. Tolman, *J. Am. Chem. Soc.* **1970**, 92, 2953–2956.
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