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Iridium- and Rhodium-Catalyzed C-H Activation for the
Synthesis of Enol Ethers, Enynes, and Vinylboronic Esters

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2001

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**Iridium- and Rhodium-Catalyzed C–H Activation
for the Synthesis of Enol Ethers, Enynes, and
Vinylboronic Esters**

A Thesis

Submitted to Graduate School of Engineering, Hokkaido
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by

Toshimichi Ohmura

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General Introduction

The activation of C–H bonds is of the same fundamental importance as the formation of C–C bonds for the synthesis of organic molecules. As compared with the substitution or coupling reactions depending on leaving groups such as halides, the catalytic C–H activating processes is simple, clean, and economy. Therefore, the development of transition metal catalysts for the activation of C–H bonds is one of the major challenges of modern chemistry.¹

A great deal of attention has been denoted for development of the synthetic reactions *via* catalytic activation of C–H bonds since the last century. In 1993 a decisive breakthrough was achieved by Murai and coworkers, who reported the addition of *ortho* C–H bond of acetophenones to vinylsilane by ruthenium catalyst.² Now a diverse range of activation of C–H bonds has been achieved by using a wide variety of transition

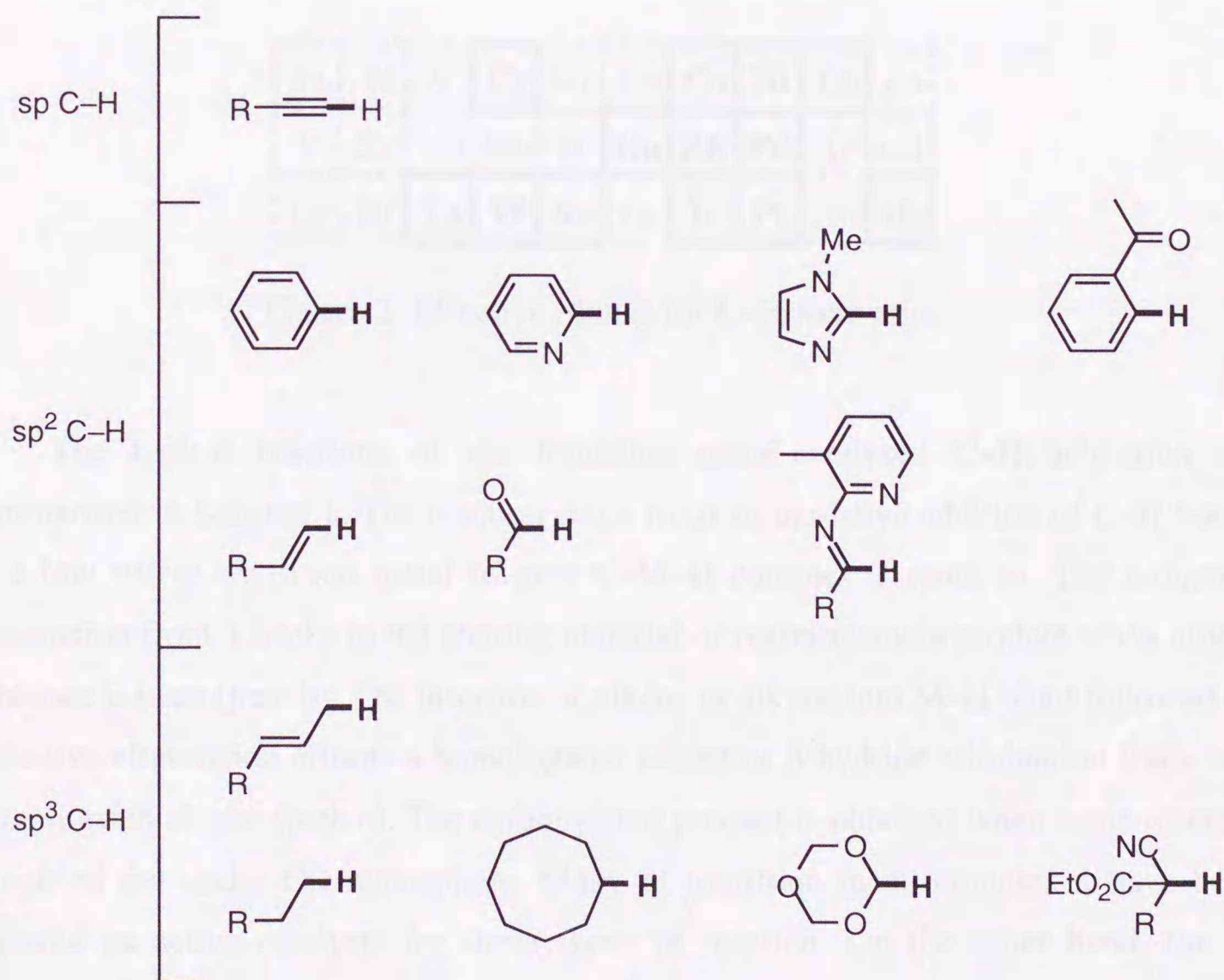


Figure 1. Examples of Substrates for Catalytic C–H activation

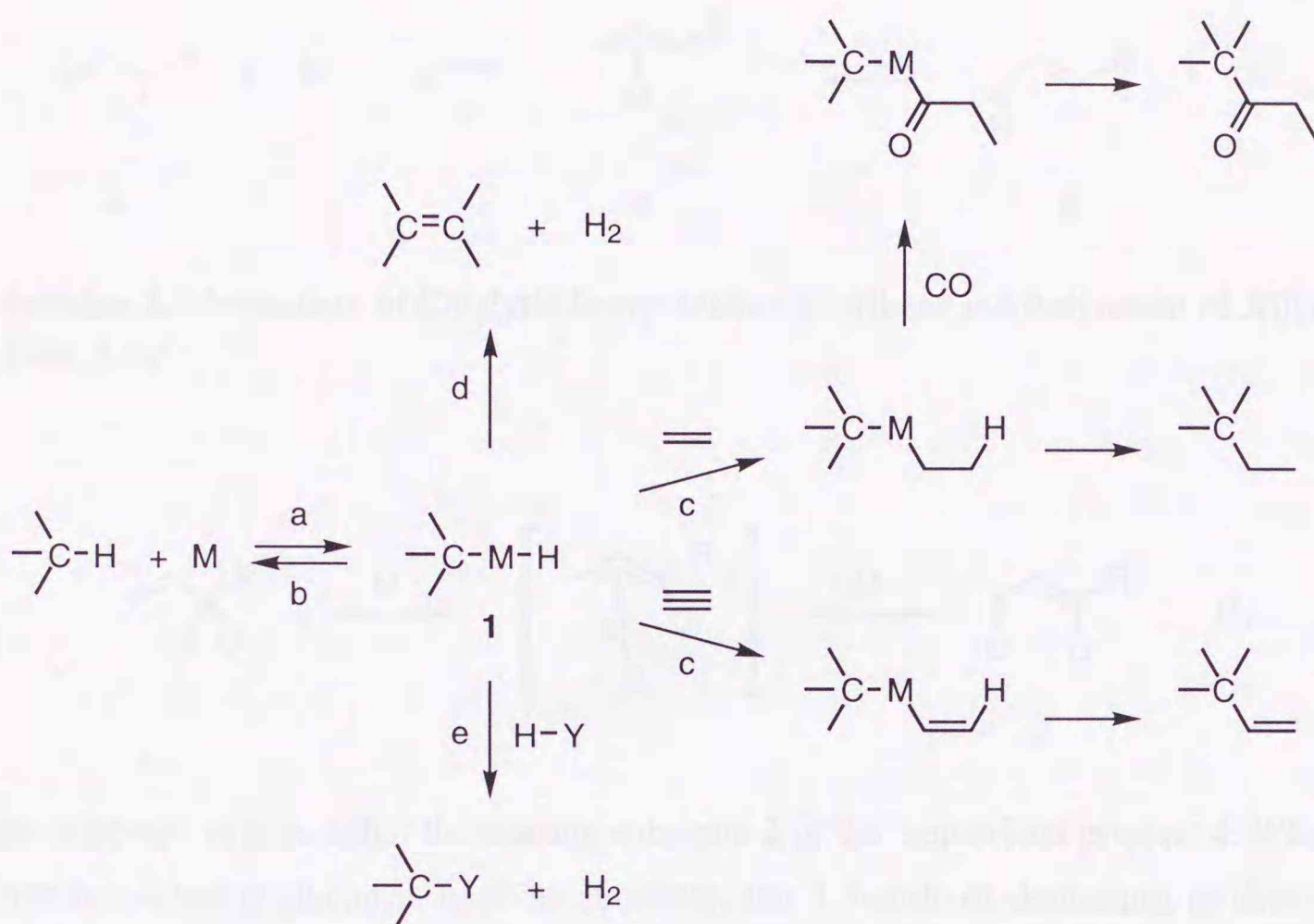
metal catalysts (Figure 1). Acetylenic sp C–H bonds, aromatic and vinylic sp^2 C–H bonds, and allylic and even simple alkyl sp^3 C–H bonds have been activated and catalytically used for organic transformations.

In addition to the diversification of the substrate applying to C–H activation, the enlargement of the variation of transition metal complexes implying catalyst activity has been also remarkable. The metals effective for catalytic C–H activation are shown in Figure 2. Ruthenium and palladium catalysts are currently used most frequently, closely followed by rhodium complexes. Ruthenium has proved to be particularly efficient for the C–H activation of arenes.³ Palladium is useful for the activation of both aromatic and acetylenic C–H bonds.⁴ Rhodium has found to be a valuable catalyst for the activation of aldehyde or aldimine C–H bonds.⁵ Iridium has shown high activity for the dehydrogenation of cycloalkanes.⁶ Mercury displays catalyst activity on photochemical excitation in the gas phase.⁷ Very recently, rhenium-catalyzed borylation of alkane C–H bond under photochemical conditions has reported.⁸

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Figure 2. Effective Metals for C–H Activation

The typical reactions of the transition metal-catalyzed C–H activation are summarized in Scheme 1. The reaction starts from an oxidative addition of C–H bonds to a low valent transition metal to give C–M–H complex **1** (path a). The reductive elimination from **1** backs to the starting material or rearrangement product when allylic substrate is used (path b). The insertion of alkene or alkyne into M–H bond followed by reductive elimination affords a homologated alkane or β -hydride elimination leads to a homologated alkene (path c). The carbonylated product is obtained when same reaction is carried out under CO atmosphere. Many of transition metal complexes have been reported as active catalysts for these types of reaction. On the other hand, the β -elimination from **1** provides a dehydrogenated product and hydrogen (path d). For example, the iridium-catalyzed dehydrogenation of cyclooctane gives cyclooctene in the

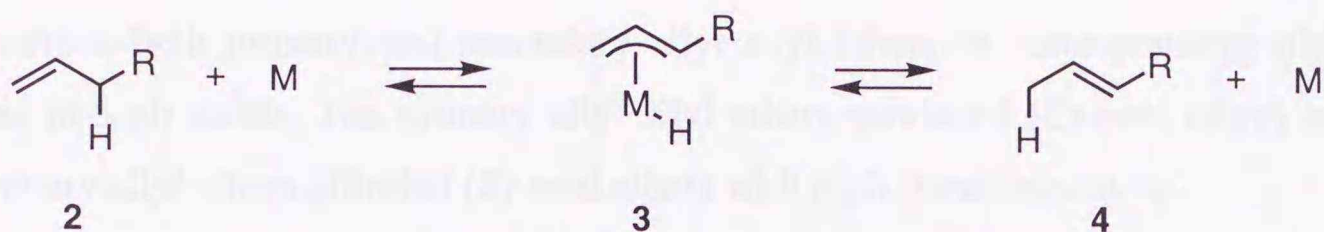


Scheme 1. (a) oxidative addition, (b) reductive elimination, (c) insertion, (d) β -elimination, (e) dehydrogenative coupling

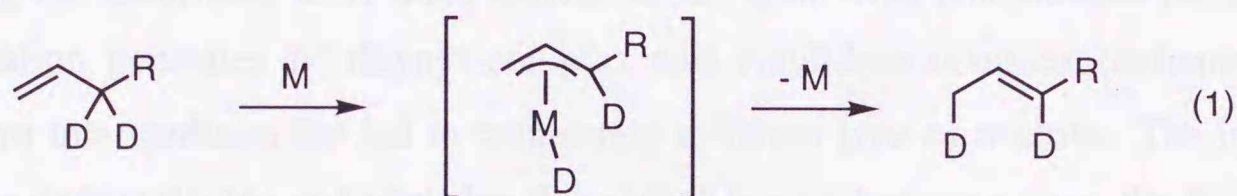
presence of *tert*-butylethylene as the hydrogen acceptor.⁶ The dehydrogenative coupling provides a convenient method for directly functionalizing alkanes and alkenes (path e). Dehydrogenative silylations of aromatic C-H bonds with hydrosilane by platinum and rhodium catalysts have been reported.⁹

In this thesis, I wish to describe the catalytic activation of allylic and acetylenic C-H bonds by iridium or rhodium complexes for the synthesis of enol ethers, enynes, and vinylboronic esters.

The oxidative addition of allylic C-H bonds to transition-metal complexes is faster than that of aromatic and alkylic C-H bonds. However, the difficulty in controlling the regiochemistry has not yet been solved. The isomerization of alkenes, which is a clean and convenient procedure and available for industrial scale synthesis, is a typical reaction for the catalytic activation of allylic C-H bonds.¹⁰ Mechanism of the alkene isomerization is shown in Scheme 2. The oxidative addition of allylic C-H bond to a low valent metals (**2**) gives π -allyl(hydride) complex **3**. The reductive elimination is

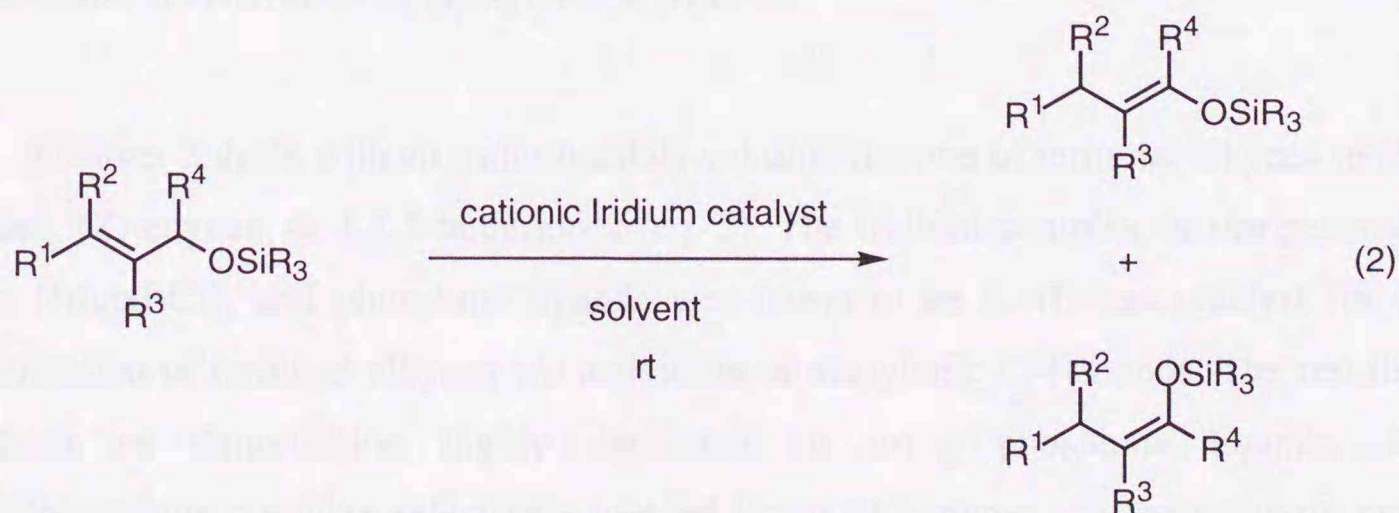


Scheme 2. Mechanism of Catalytic Isomerization of Alkene *via* Activation of Allylic C-H Bond



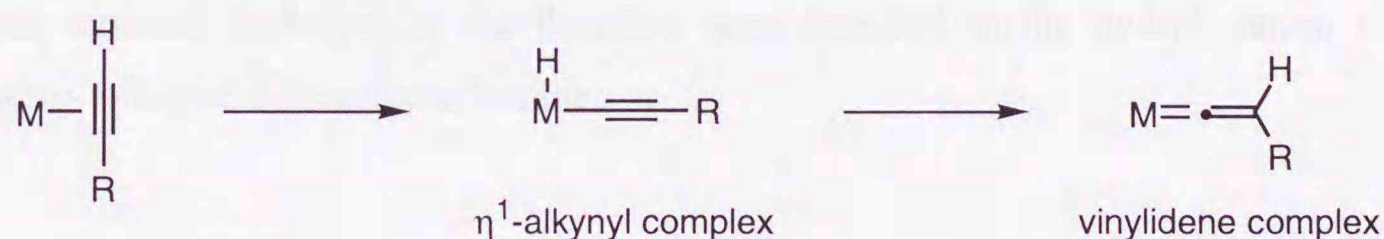
then followed to give either the starting substrate **2** or the isomerized product **4**. When a deuterium-labeled alkene is used as substrate, the 1,3-shift of deuterium is observed after isomerization (eq 1). A number of transition metal complexes catalyze the isomerization of alkenes *via* activation of allylic C-H bonds.¹⁰ However, most of catalysts have been applied to limited substrates and suffered from low stereoselectivity of the product.

Chapter 1 deals with a stereoselective isomerization of allyl silyl ethers to (*E*)- or (*Z*)-silyl enol ethers using cationic iridium complexes (eq. 2). The iridium complexes, *in situ* prepared by treating $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ with catecholborane or $[\text{Ir}(\text{cod})_2]\text{PF}_6-2\text{PPr}_3$ with hydrogen, were found to be an excellent catalysts for the isomerization of allyl ethers *via* the activation of allylic C-H bonds. The catalysts



isomerized both primary and secondary allyl silyl ethers to corresponding silyl enol ethers in high yields. The primary allyl silyl ethers produced (*E*)-enol ethers and the secondary allyl ethers afforded (*Z*)-enol ethers with high stereoselectivity.

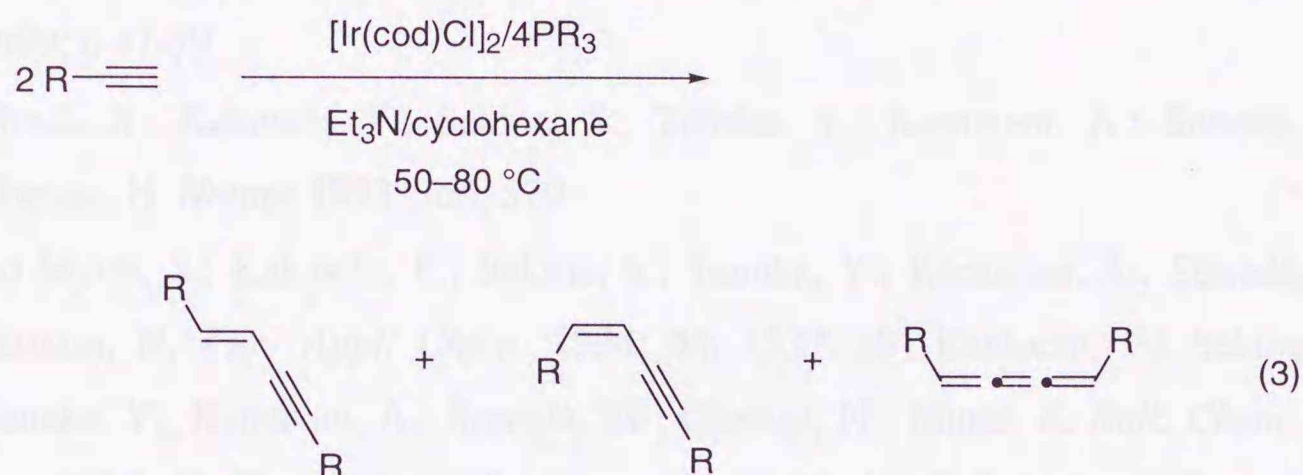
The activation of acetylenic C–H bonds *via* oxidative addition has also been studied extensively than that of aromatic and alkylic C–H bonds, because of the high acidity of acetylenic proton and the strong coordination ability of alkyne for oxidative addition of acetylenic C–H bond to the metal center. But the catalytic reactions involving the acetylenic C–H bond activation are somewhat complicated because the isomerization generates η^1 -alkynyl complex and vinylidene complex (Scheme 3).^{11,12} These two intermediates are led to completely different type of reaction. The insertion of carbon-carbon double and triple bonds to M–H bond takes place from the η^1 -alkynyl complex. Many of examples have been reported for the catalytic addition reactions of acetylenic C–H bonds *via* this η^1 -alkynyl complex. On the other hand, typical reactions of the vinylidene complex are follows: (1) attack of nucleophile on the vinylidene α -carbon, (2) migratory insertion into metal–carbon σ bond, similarly to the insertion of CO, and (3) [2+2] cycloaddition between M=C bond and unsaturated carbon–carbon double or triple bond. The catalytic reaction involving vinylidene intermediate is very attractive, but it has not yet been developed enough.^{11c}



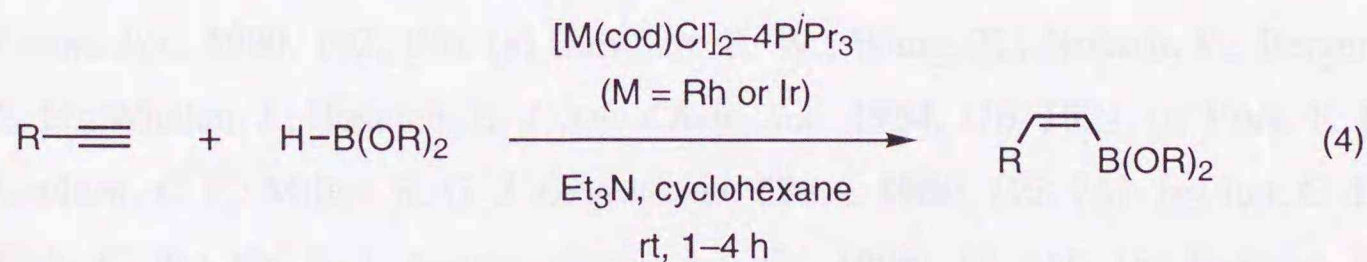
Scheme 3. Activation of Acetylenic C–H Bond

Chapter 2 deals with an iridium-catalyzed dimerization of terminal alkynes to (*E*)-enynes, (*Z*)-enynes, or 1,2,3-butatrienes (eq. 3). The iridium complex *in situ* generated from $[\text{Ir}(\text{cod})\text{Cl}]_2$ and phosphine ligands was found to be a efficient catalyst for the dimerization of terminal alkynes *via* activation of acetylenic C–H bonds. The resulting products of dimerization highly depended on using phosphine ligands. The triarylphosphine complex selectively yielded linear (*E*)-enynes *via* the catalytic cycle

involving a η^1 -alkynyl intermediate, while the tripropylphosphine complex provided linear (Z)-enynes or 1,2,3-butatrienes through a cycle participating in vinylidene complex.



Chapter 3 deals with a rhodium- or iridium-catalyzed *trans*-hydroboration of terminal alkynes, giving (Z)-1-alkenylboronic esters (eq. 4). The complex *in situ* prepared from $[\text{M}(\text{cod})\text{Cl}]_2$ ($\text{M} = \text{Rh}$ or Ir) and P^iPr_3 found to be a efficient catalyst for *trans*-hydroboration of terminal alkynes with dialkoxyboranes *via* activation of acetylenic C–H bonds. The reaction gave synthetically useful (Z)-1-alkenylboronic esters in high yields with excellent stereoselectivity. The mechanism proceeding through a vinylidene complex was proposed because the selective migration of the alkyne terminal hydrogen to the β -carbon was observed in the hydroboration of 1-deuterio-1-octyne with catecholborane.



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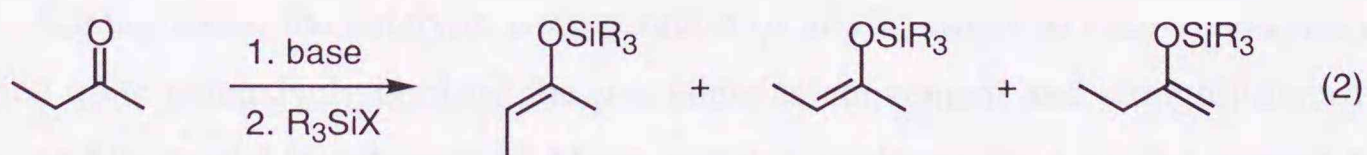
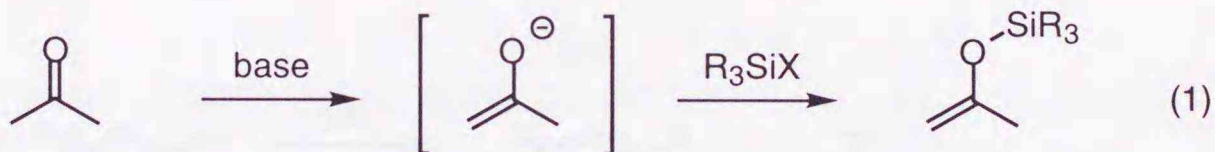
Chapter 1

A Stereoselective Isomerization of Allyl Silyl Ethers to (*E*)- or (*Z*)-Silyl Enol Ethers Using Cationic Iridium Complexes

Abstract: The stereoselective isomerization of allyl silyl ethers to (*E*)- or (*Z*)-silyl enol ethers was carried out in the presence of a cationic iridium(I) catalyst. The complex, prepared *in situ* by treating $[\text{Ir}(\text{cod})_2]\text{PF}_6 \cdot 2\text{PPr}_3$ with hydrogen, was found to be an excellent catalyst for the isomerization of primary and secondary allyl ethers in high yields. The primary allyl silyl ethers produced (*E*)-enol ethers and the secondary allyl ethers afforded (*Z*)-enol ethers with high stereoselectivity, often exceeding 99%.

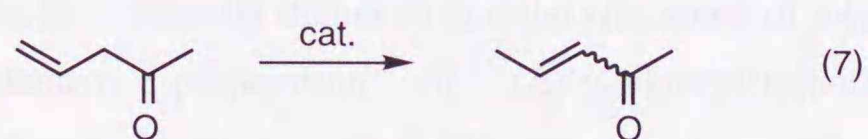
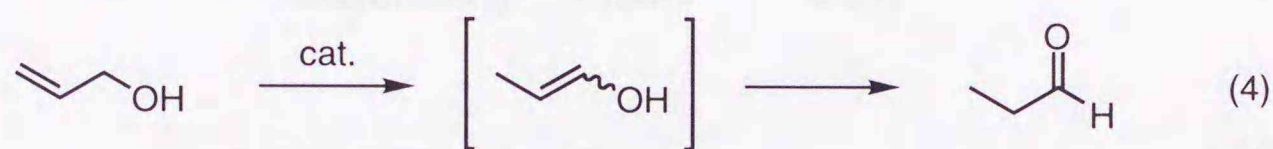
1. Introduction

Considerable attention has recently been focused on the synthesis of silyl enol ethers due to their usefulness in various synthetic transformations.¹ One of the early and still one of the most frequently used route to (*E*)- or (*Z*)-silyl enol ethers is the trapping of ketone or aldehyde enolates generated under conditions of either kinetic- or equilibrium-controlled conditions (eq. 1).^{2,3,4} However, the method is often suffered from low regio- and stereoselectivity in the synthesis of silyl enol ethers from unsymmetrical acyclic ketones. The selectivity highly depends on the reaction conditions such as base, substrate, solvent, reaction temperature, and experimental procedure (eq. 2). Another efficient and alternative synthetic method of silyl enol ethers is a transition metal catalyzed 1,4-addition of hydrosilanes to α,β -unsaturated ketones (eq. 3).⁵ The reaction converts conjugate enones to corresponding silyl enol ethers with high regioselectivity, but the reaction results in a mixture of (*E*)- and (*Z*)-isomers in the synthesis of acyclic enol ethers.

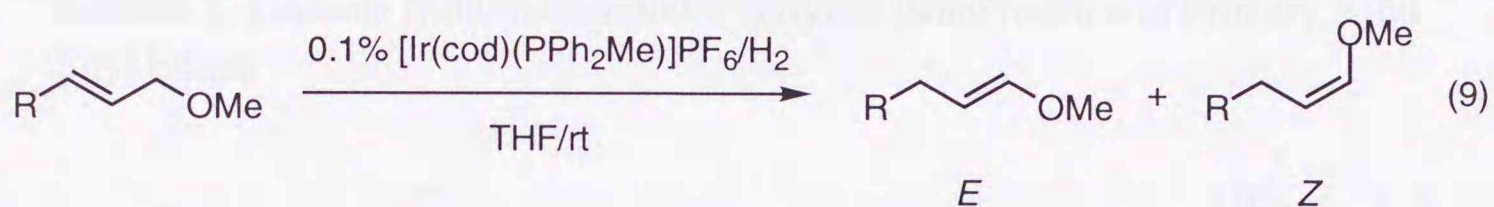
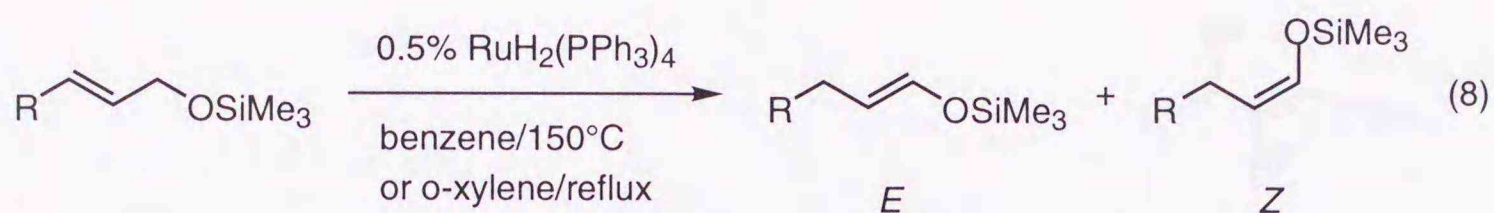


The transition metal-catalyzed positional isomerization of double bonds is an excellent method which has been used in a variety of organic transformations.⁶

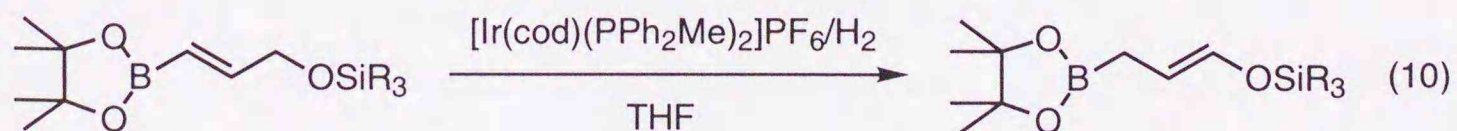
Generally, the double bonds migrate to yield a thermodynamically more stable olefine. For examples, transition metal catalysts convert allylic alcohols to saturated ketones and aldehydes via enols (eq. 4),⁷ allylic ethers to enol ethers (eq. 5),^{8,9} allylic amines to enamines (eq. 6),¹⁰ and nonconjugated and unsaturated carbonyl compounds to conjugated ones (eq. 7).¹¹ These reactions allow a short-step synthesis of desired compounds with high yields from readily available starting materials.

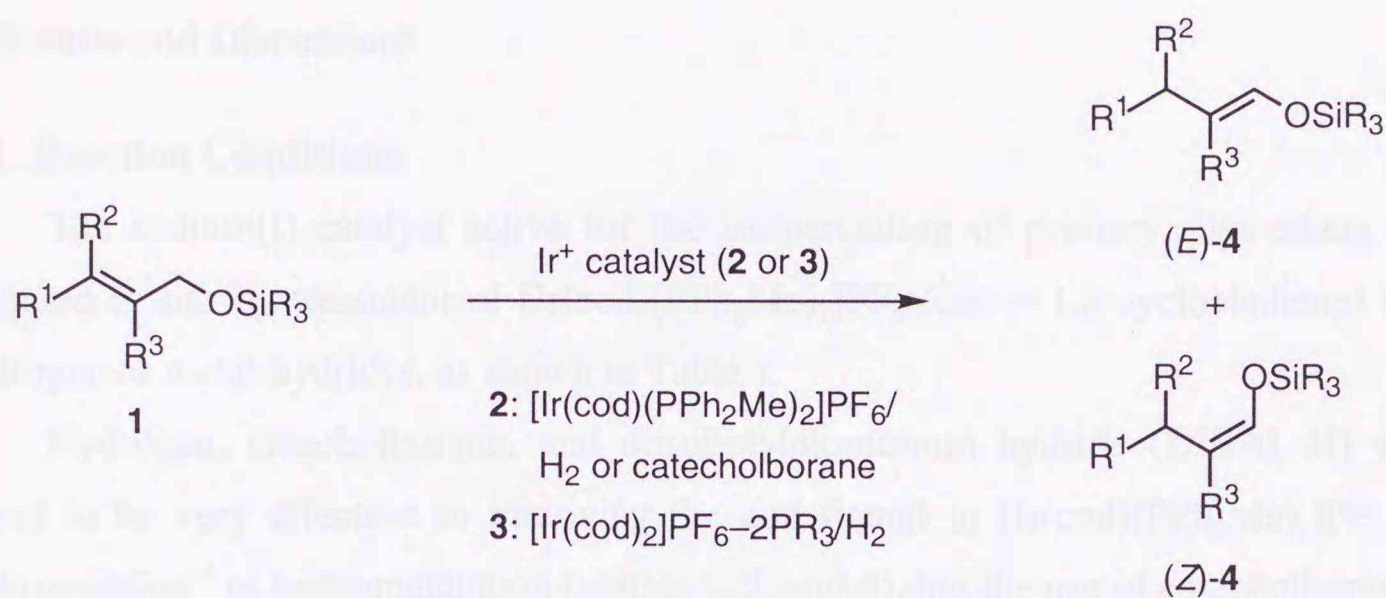


Among them, the catalytic isomerization of allylic ethers to enol ethers has been studied quite extensively because the procedure is convenient and straightforward and uses readily available substrate.^{8,9} Many metal complexes have been reported to be effective catalysts for the isomerization of allylic ethers, but the stereoselectivity of such transformations has not received much attention. The enol ethers thus obtained are either (*Z*)- or (*E*)-isomers or, in most cases, a mixture of the two. For example, the ruthenium complex gives an equilibrium mixture with the (*Z*)-enol ethers predominating (*Z* > 55–68%, eq. 8).^{9d} In contrast, the cationic iridium(I) complex stereospecifically produces (*E*)-enol ethers (*E* > 97%, eq. 9).⁸

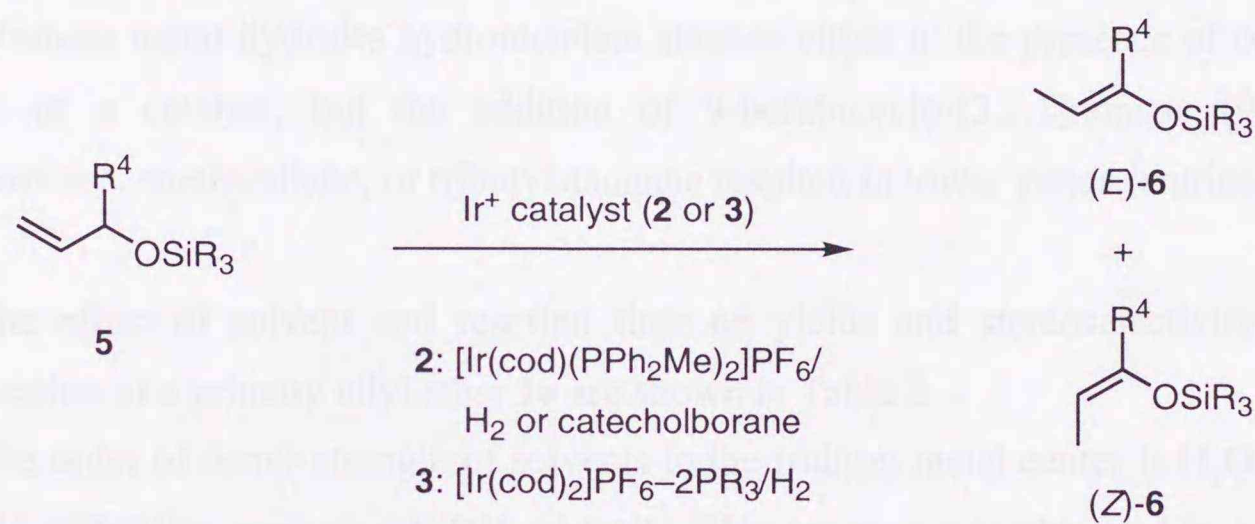


We have recently demonstrated the efficiency of a cationic iridium catalyst for the stereoselective preparation of (*E*)- γ -alkoxyallylboronates from (3-alkoxy-1-alkenyl)boronates (eq. 10).¹² However, the difficulty in reproducing high stereoselectivities on various substrates prompted us to reinvestigate the reaction in detail using allyl silyl ethers. The iridium(I) complex was prepared in situ by treating [Ir(cod)₂]₂PF₆–2PPr₃ with hydrogen and was found to be an excellent catalyst for achieving high yields and high stereoselectivity in the isomerization of various allyl silyl ethers under mild conditions (Schemes 1 and 2).^{13,14}





Scheme 1. Cationic Iridium Complex Catalyzed Isomerization of Primary Allyl Silyl Ethers



Scheme 2. Cationic Iridium Complex Catalyzed Isomerization of Secondary Allyl Silyl Ethers

2. Results and Discussions

2-1. Reaction Conditions

The iridium(I) catalyst active for the isomerization of primary allyl ethers was prepared in situ by treatment of $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (cod = 1,5-cyclooctadiene) with hydrogen or metal hydrides, as shown in Table 1.

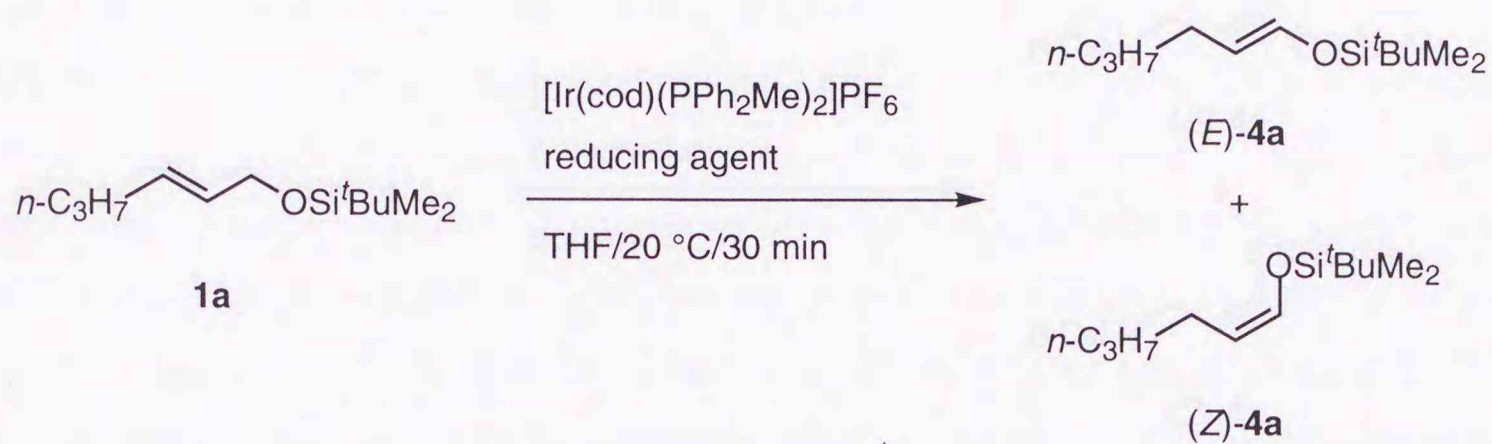
Hydrogen, catecholborane, and diisobutylaluminium hydride (DIBAL-H) were found to be very effective in removing the cod ligand in $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ via hydrogenation¹⁵ or hydrometalation (entries 1, 2, and 4), but the use of catecholborane is recommended because of the operational simplicity in its use to achieve reproducible results. The isomerization was readily initiated by the addition of catecholborane (1 equiv to the iridium complex) to a mixture of $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ and an allyl silyl ether. Various metal hydrides hydrometalate alkenes either in the presence of or in the absence of a catalyst, but the addition of 9-borabicyclo-[3.3.1]nonane (9-BBN), trichlorosilane, triethylsilane, or tributylstannane resulted in lower yields (entries 3, 5, 6, and 7).

The effect of solvent and reaction time on yields and stereoselectivity in the isomerization of a primary allyl ether **1a** are shown in Table 2.

The order of donor strength of solvents to the iridium metal center is $\text{H}_2\text{O} \cong \text{THF} < {}^t\text{BuOH} < {}^i\text{PrOH} < \text{acetone} < \text{EtOH} < \text{MeCN}$.¹⁶ No reaction was observed in a solvent that strongly coordinates to the metal such as DMF and MeCN (entries 1 and 2). In contrast, the reaction was very fast in methylene chloride, but an equilibrium mixture of both stereoisomers resulted in a nondonor solvent (entry 7). Promising results were obtained in acetone and THF (entries 3–5). Although the reaction in both solvents achieved complete conversion within 30 min with high (*E*)-stereoselectivities (entries 3 and 5), the product of the reaction in THF tended to isomerize slowly to an (*E*)- and (*Z*)-**4a** mixture because of its lower donor ability compared to that of acetone (entry 6). Thus, acetone was recognized as the best solvent, to achieve both quantitative conversion and high (*E*)-selectivity, since the undesirable *cis*–*trans* isomerization was very much slower than the positional isomerization of the double bond.

The NMR study of the reaction mixture of **1a** and **2** (3 mol %) in $\text{CD}_2\text{Cl}_2/\text{acetone-}d_6$ (50/1)) at 0 °C revealed that the reaction involves two isomerization processes; the positional isomerization of the double bond to give (*E*)-**4a** was followed by its

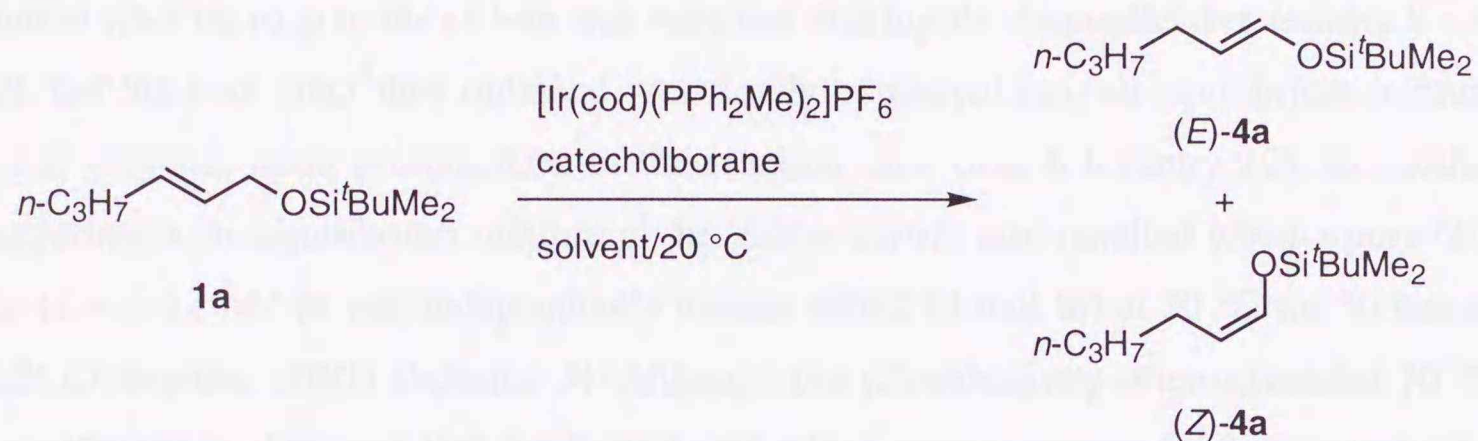
Table 1. Preparation of Catalysts^a



entry	reducing agent	yield/% ^b	E/Z ^c
1 ^d	H ₂	92	92/8
2	catecholborane	93	81/19
3	9-BBN	0	-
4	DIBAL-H	84	91/9
5	HSiCl ₃	0	-
6	HSiEt ₃	22	100/0
7	HSnBu ₃	25	100/0

^a A mixture of $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (0.015 mmol) and **1a** (0.5 mmol) in THF was treated with reducing agent (0.015 mmol) and then stirred at 20 °C unless otherwise noted. ^b Isolate yields by chromatography over silica gel. ^c Determined by ¹H NMR. ^d A THF solution (3 ml) of $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (0.015 mmol) was treated with hydrogen. Then **1a** (0.5 mmol) was added and then stirred at 20 °C under argon atmosphere.

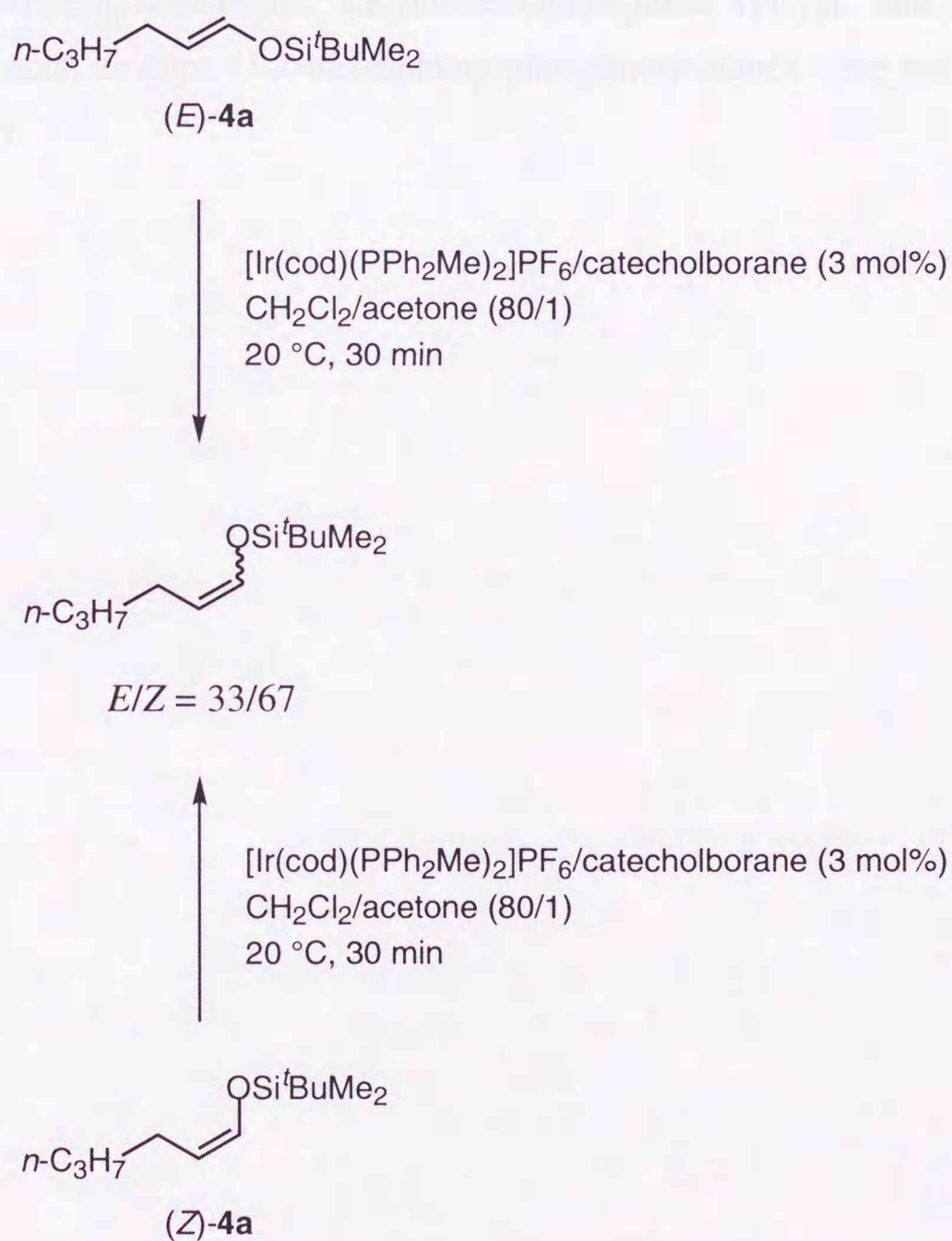
Table 2. Effects of Solvent and Reaction Time on the Isomerization of **1a**^a



entry	solvent	time/min	conversion/% ^{b,c}	<i>E/Z</i> ^c
1	DMF	30	0	-
2	CH ₃ CN	30	0	-
3	acetone	30	99	<i>E</i> >99
4	acetone	900	99	96/4
5	THF	30	99	97/3
6	THF	1440	99	51/49
7	CH ₂ Cl ₂	30	99	32/68
8 ^d	CD ₂ Cl ₂ /acetone- <i>d</i> ₆ (50/1)	5	61	98/2
9 ^d	CD ₂ Cl ₂ /acetone- <i>d</i> ₆ (50/1)	20	95	95/5
10 ^d	CD ₂ Cl ₂ /acetone- <i>d</i> ₆ (50/1)	60	>99	85/15
11 ^d	CD ₂ Cl ₂ /acetone- <i>d</i> ₆ (50/1)	180	>99	57/43
12 ^d	CD ₂ Cl ₂ /acetone- <i>d</i> ₆ (50/1)	360	>99	38/62

^a To a mixture of $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (0.015 mmol), solvent (3 ml), and **1a** (0.5 mmol) was added catecholborane (0.015 mmol) and then stirred at $20\text{ }^\circ\text{C}$. ^b The ratio of product/substrate. ^c Determined by ^1H NMR. ^d The reactions were carried out at $0\text{ }^\circ\text{C}$ in a NMR tube.

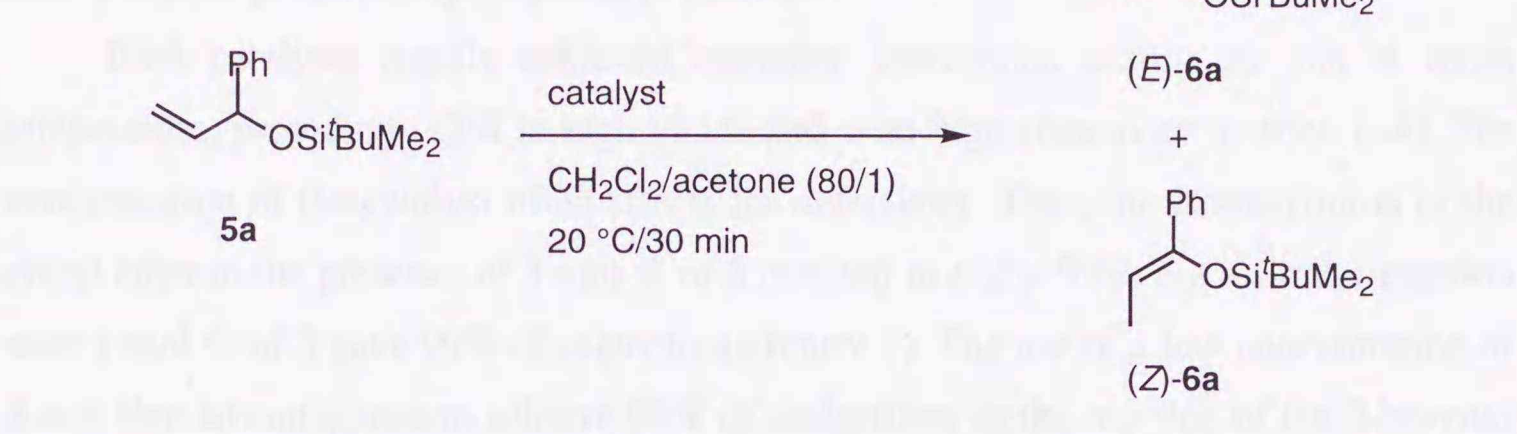
stereochemical isomerization leading to a mixture of (*E*)- and (*Z*)-**4a** (entries 8–12). The initial reaction to give the (*E*)-**4a** was very fast and highly stereoselective (entries 8 and 9), but the enol ether thus obtained was slowly converted into an equilibrium mixture (*E*/*Z* = 38/62) upon prolongation of the reaction time over 6 h (entry 12). In another experiment, an equilibrium mixture of **4a** (*E*/*Z* = 33/67) also resulted when a pure (*E*)- or (*Z*)-enol ether **4a** was independently treated with **2** (3 mol %) at 20 °C for 30 min in CH₂Cl₂/acetone (80/1) (Scheme 3). Although the (*Z*)-selectivity often exceeded 70 %, all attempts at obtaining 100 % (*Z*)-silyl enol ethers were unsuccessful for primary allyl silyl ethers.



Scheme 3. Isomerization Between (*E*)-**4a** and (*Z*)-**4a**

The effect of catalysts on the isomerization of **5a** is shown in Table 3.

The catalyst developed by Felkin efficiently catalyzes the isomerization of various primary allyl ethers, but unfortunately it was not effective for secondary allyl ethers (entry 1). The treatment of $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ with catecholborane generated a more active catalyst solution than that with hydrogen, but arylphosphine derivatives did not give good results due to their large steric hindrance (entries 2 and 3). Finally, Ir-trialkylphosphine complexes (**3**) obtained by hydrogenation of a mixture of $[\text{Ir}(\text{cod})_2]\text{PF}_6$ and PR_3 ($\text{R} = \text{Et}, \text{Pr}, \text{Bu}$) (2 equiv) were found to be excellent catalysts for the isomerization of secondary allyl ethers with the (Z)-**6** predominating (Z, 88–92 %) (entries 5–7). The reaction was very slow in pure acetone, but fast in a mixed solvent of $\text{CH}_2\text{Cl}_2/\text{acetone}$. Trimethylphosphine, tricyclohexylphosphine (PCy_3), and bidentate phosphine ligands such as dppe (1,2-bis(diphenylphosphino)ethane) were not effective (entries 4, 8, and 9).



^a To a solution of [Ir(cod)(PPh₂Me)₂]PF₆ (0.015 mmol) (entry 1) or a mixture of [Ir(cod)₂]PF₆ (0.015 mmol) and PR₃ (0.03 mmol) (entries 4–9) in CH₂Cl₂ (3 ml)/acetone (0.037 ml, 0.5 mmol) treated with H₂ was added **5a** (0.5 mmol), and the resulting solution was then stirred at 20 °C. ^b Isolated yields. ^c Determined by ¹H NMR. ^d To a solution of [Ir(cod)(PPh₂Me)₂]PF₆ or [Ir(cod)(PPh₃)₂]PF₆ (0.015 mmol) and **5a** (0.5 mmol) in CH₂Cl₂ (3 ml)/acetone (0.037 ml, 0.5 mmol) was added catecholborane (0.015 mmol) and then stirred at 20 °C.

2-2. Scope and Limitations

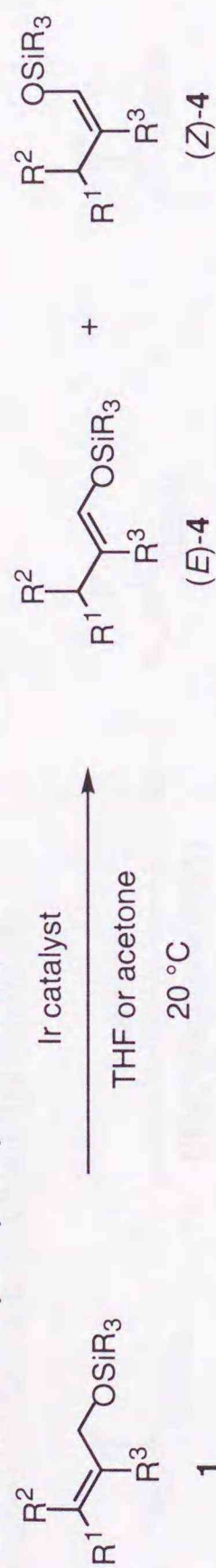
The two catalysts (**2** and **3** ($R = Pr$)) are compared for the isomerization of the representative primary allyl silyl ethers (Table 4).

Both catalysts readily achieved complete conversion within 20 min at room temperature, providing (*E*)-**4** in high yields and with high selectivity (entries 1–4). The concentration of the catalyst often affects the selectivity. Thus, the isomerization of the crotyl ether in the presence of 3 mol % of **3** resulted in $E/Z = 97/3$, but a similar reaction with 1 mol % of **3** gave 99% (*E*)-selectivity (entry 2). The use of a low concentration of **3** was also advantageous to achieve 99% (*E*)-selectivity in the reaction of the 2-hexenyl ether (entry 4). The (*E*)-selectivity was not significantly affected either by the bulkiness of the silyl ligands (entries 4–7) or by the stereochemistry of the starting allyl ether (entry 9), but the MOM (CH_3OCH_2) ether, which has potential ligating ability to the iridium metal center, gave a mixture of two stereoisomers (entry 8). The reaction of the prenyl ether was very slow, presumably due to its steric hindrance during the coordination to the iridium metal, but tripropylphosphine complex **3** was active enough to induce the isomerization (entry 11). The reaction was very slow in acetone, but an 85% yield was readily achieved in a mixed solvent of CH_2Cl_2 /acetone.

The results of the isomerization of various secondary allyl ethers are summarized in Table 5.

The Ir-arylphosphine complex **2** exceptionally catalyzed the isomerization of **5c** and **5d** ($R^4 = Me$) with the predominating (*E*)-isomer when the reaction was carried out in CH_2Cl_2 /acetone (80/1) (entries 2 and 3). A bulky tri(isopropyl)silyl ether gave 96% (*E*)-selectivity as the result of its large steric difference between the methyl and siloxy groups (entry 3). The catalyst **2** was not effective for other secondary allyl ethers (entries 5, 10, and 14), but **3** apparently demonstrated a higher catalytic efficiency for secondary allyl ethers. Thus, a complete conversion within 30 min at 20 °C was readily achieved with the Ir-tripropylphosphine complex **3** (entries 1–6, 8–10, and 12–15). The reaction predominantly produced the (*Z*)-isomer, the yield of which exceeded 99% when R^4 was the secondary alkyls (entries 5, and 8–10). On the other hand, the equilibrium mixture of three or four possible isomers was formed when R^4 was methyl (entries 1–3 and Scheme 4) and pentyl (entry 12 and Scheme 5).

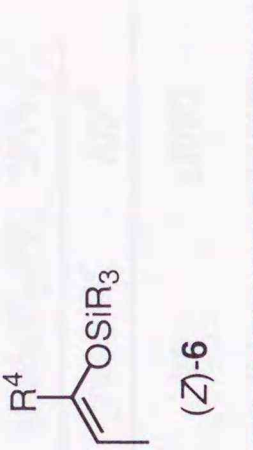
Table 4. Isomerization of Primary Allyl Silyl Ethers (**1**)



entry	substrate	R ¹	R ²	R ³	SiR ₃	time (min)	product	[Ir(cod)(PPh ₂ Me) ₂]PF ₆ ^a		[Ir(cod) ₂]PF ₆ -2PPr ₃ ^b	
								yield/% ^c	E/Z ^d	yield/% ^c	E/Z ^d
1	1b	H	H	H	Si ⁱ BuMe ₂	10	4b	78	99/1	74	99/1
2	1c	CH ₃	H	H	Si ⁱ BuMe ₂	20	4c	84	97/3	92 ^e	99/1
3	1d	H	H	CH ₃	Si ⁱ BuMe ₂	20	4d	91	-		
4	1e	<i>n</i> -C ₃ H ₇	H	H	Si ⁱ BuMe ₂	20	4e	93	88/12	97 ^e	99/1
5	1f	<i>n</i> -C ₃ H ₇	H	H	SiPh ₂ Me	20	4f	87	94/6		
6	1g	<i>n</i> -C ₃ H ₇	H	H	SiPhMe ₂	20	4g	81	93/7		
7	1h	<i>n</i> -C ₃ H ₇	H	H	SiMe ₃	20	4h	64	95/5		
8	1i	<i>n</i> -C ₃ H ₇	H	H	CH ₂ OCH ₃	20	4i	84	68/32		
9	1j	H	<i>n</i> -C ₃ H ₇	H	Si ⁱ BuMe ₂	10	4e	74	95/5		
10	1k	Ph	H	H	Si ⁱ BuMe ₂	30	4j	76	98/2	77	96/4
11	1l	CH ₃	CH ₃	H	Si ⁱ BuMe ₂	240	4k	<10	-	85 ^f	88/12

^a A solution of [Ir(cod)(PPh₂Me)₂]PF₆ (0.015 mmol) and **5** (0.5 mmol) in THF (3 ml) was treated with catecholborane (0.015 mmol) and then stirred at 20 °C. ^b A solution of [Ir(cod)₂]PF₆ (0.015 mmol) and PPr₃ (0.03 mmol) in acetone (3 ml) treated with H₂ to prepare the catalyst, which was then stirred with **1** at 20 °C. ^c Isolated yields. ^d Determined by ¹H NMR. ^e The reaction was carried out for 10 min in the presence of 1 mol% of the catalyst. ^f The reaction was carried out in CH₂Cl₂/acetone (80/1). An 8% yield of **1l** was recovered with an accompanying 2% of 2-methyl-4-(*tert*-butyldimethylsilyloxy)-1-butene.

Table 5. Isomerization of Secondary Allyl Silyl Ethers (**5**)

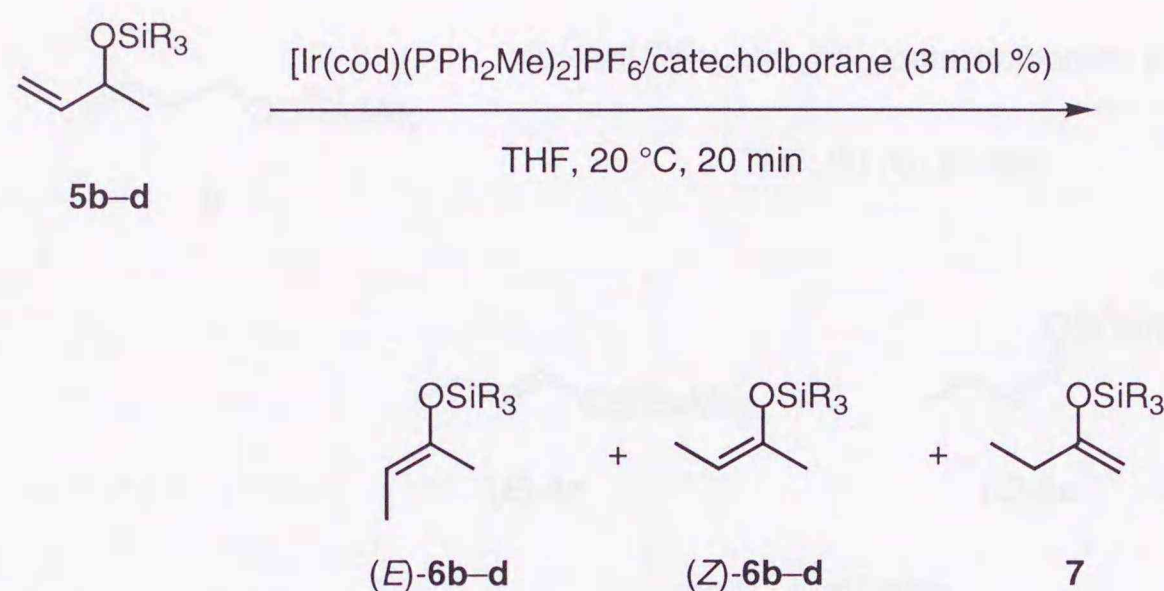
								
entry	substrate	R ⁴	SiR ₃	product	[Ir(cod)(PPh ₂ Me) ₂]PF ₆ ^a		[Ir(cod) ₂]PF ₆ -2PPr ₃ ^b	
					yield/% ^c	E/Z ^d	yield/% ^c	E/Z ^d
1	5b	CH ₃	SiMe ₃	6b			71 ^e	26/74
2	5c	CH ₃	Si ⁱ BuMe ₂	6c	82	72/28	89 ^e	28/72
3	5d	CH ₃	Si ⁱ Pr ₃	6d	96	96/4	95 ^e	63/37
4	5e	CH ₂ CH ₃	SiMe ₃	6e			83	12/88
5	5f	CH(CH ₃) ₂	SiMe ₃	6f	trace	-	89	Z>99
6	5g	CH(CH ₃) ₂	Si ⁱ BuMe ₂	6g			82 ^f	4/96
7	5h	CH(CH ₃) ₂	Si ⁱ Pr ₃	6h			trace	-
8	5i	CH(CH ₃)CH ₂ CH ₂ CH ₃	SiMe ₃	6i			93	Z>99
9	5j	CH(CH ₂ CH ₃)CH ₂ CH ₃	SiMe ₃	6j			92	Z>99
10	5k	<i>cyclo</i> -C ₆ H ₁₁	SiMe ₃	6k	trace	-	96	Z>99
11	5l	<i>tert</i> -C ₄ H ₉	SiMe ₃	6l			3	-
12	5m	CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	SiMe ₃	6m			82	g

Continued

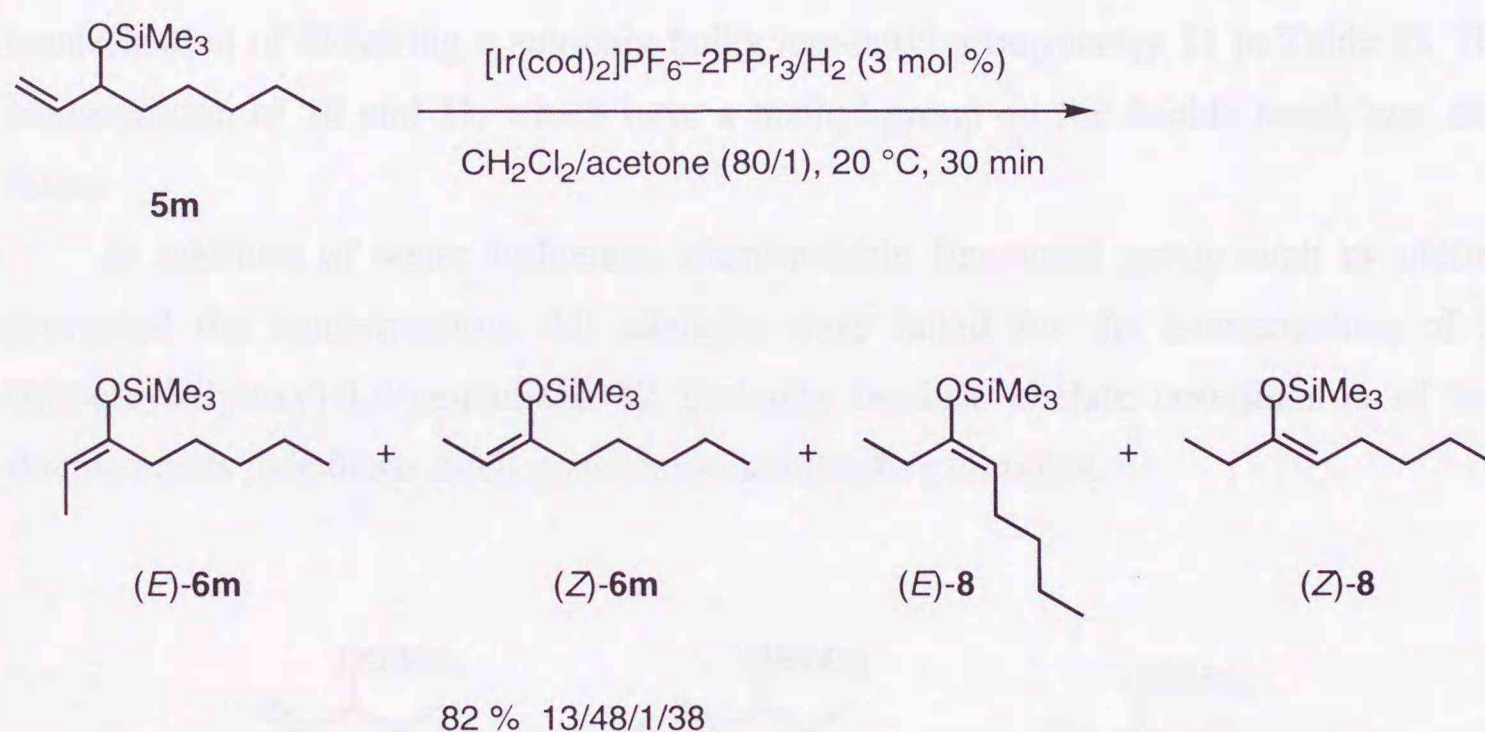
Table 5. Continued

entry	substrate	R ⁴	SiR ₃	product	[Ir(cod)(PPh ₂ Me) ₂]PF ₆ ^a		[Ir(cod) ₂]PF ₆ -2PPr ₃ ^b	
					yield/% ^c	E/Z ^d	yield/% ^c	E/Z ^d
13	5n	Ph	SiMe ₃	6n			96	18/82
14	5a	Ph	Si ⁱ BuMe ₂	6a	trace	-	92	12/88
15	5o	Ph	Si ⁱ Pr ₃	6o			98 ^h	42/58

^a A solution of [Ir(cod)(PPh₂Me)₂]PF₆ (0.015 mmol) and **5** (0.5 mmol) in CH₂Cl₂ (3 ml)/acetone (0.037 ml, 0.5 mmol) was treated with catecholborane (3 mol %) and then stirred at 20 °C for 30 min. ^b A solution of [Ir(cod)₂]PF₆ (0.015 mmol) and PPr₃ (0.03 mmol) in CH₂Cl₂ (3 ml)/acetone (0.037 ml, 0.5 mmol) treated with H₂ to prepare the catalyst, which was then stirred at 20 °C for 30 min. ^c Isolated yields. ^d Determined by ¹H NMR. ^e The reaction was accompanied with 2-silyloxy-1-butene (5–6 %). ^f [Ir(cod)₂]PF₆ (0.03 mmol) and PPr₃ (0.06 mmol) was used and reacted for 1h. ^g See the text. ^h [Ir(cod)₂]PF₆ (0.05 mmol) and PPr₃ (0.10 mmol) was used and reacted for 1h.



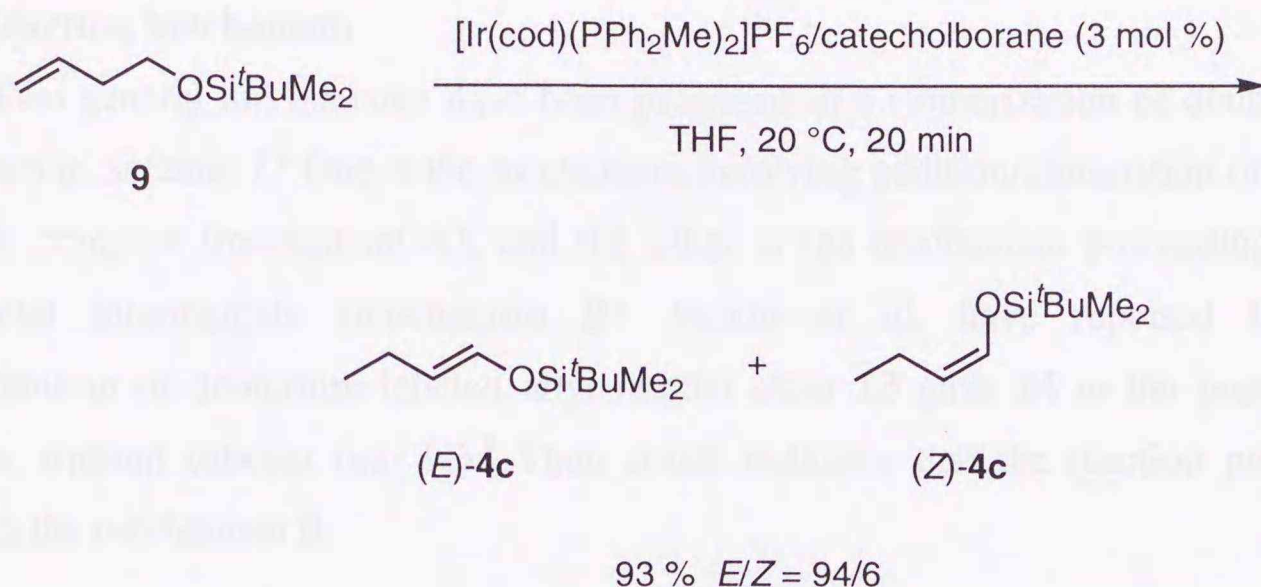
Scheme 4. Isomerization of **5b-d**



Scheme 5. Isomerization of **5m**

The iridium catalysts also isomerized homoallyl silyl ethers to silyl enol ethers. In the presence of Ir-arylphosphine complex **2**, the isomerization of homoallyl silyl ether **9** proceeded smoothly and gave **4c** with high yield and excellent *E* selectivity (Scheme 6).

The **2** and **3** are highly effective for the isomerization of secondary allyl silyl ethers to silyl enol ethers described above, but the isomerization is highly sensitive to



Scheme 6. Isomerization of Homoallyl Silyl Ether **9**

the alkyl substituent on the starting allyl ethers. All attempts were failed for the isomerization of **5l** having a sterically bulky *tert*-butyl group (entry 11 in Table 5). The isomerization of **10** and **11**, which have a methyl group on the double bond, was also failed.

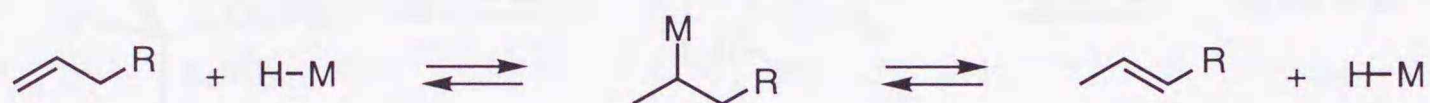
In addition of steric influence, coordinatable functional group such as olefine prevented the isomerization. All attempts were failed for the isomerization of 3-(trimethylsilyloxy)-1,4-pentadiene **12** probably because chelate coordination of two double bonds to iridium metal gave stable and inactive complex.



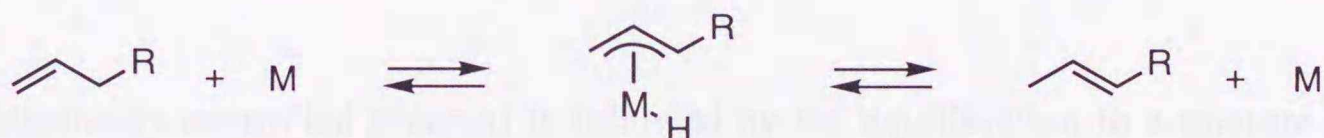
2-3. Reaction Mechanism

Two general mechanisms have been proposed in a isomerization of double bond as shown in Scheme 7.⁶ One is the mechanism involving addition/elimination of a metal hydride complex (mechanism A), and the other is the mechanism proceeding via π -allylmetal intermediate (mechanism B). Felkin *et al.* have reported that the isomerization of deuterium labeled allyl methyl ether **13** gave **14** in the presence of cationic iridium catalyst (eq. 11).⁸ Their result indicates that the reaction proceeded through the mechanism B.

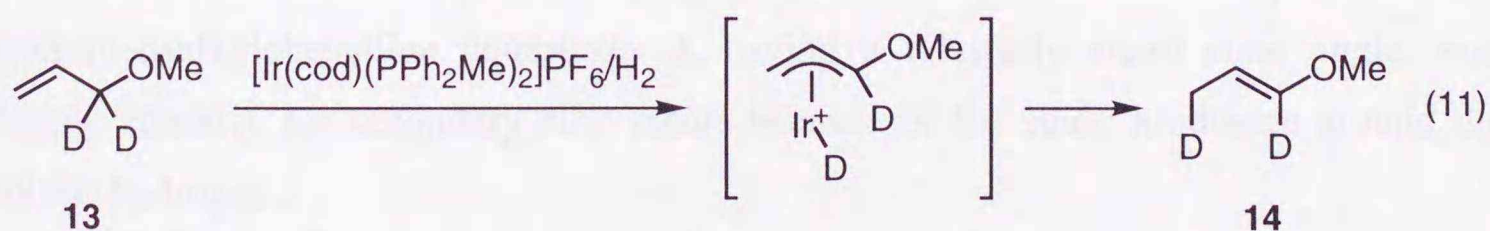
Mechanism A



Mechanism B

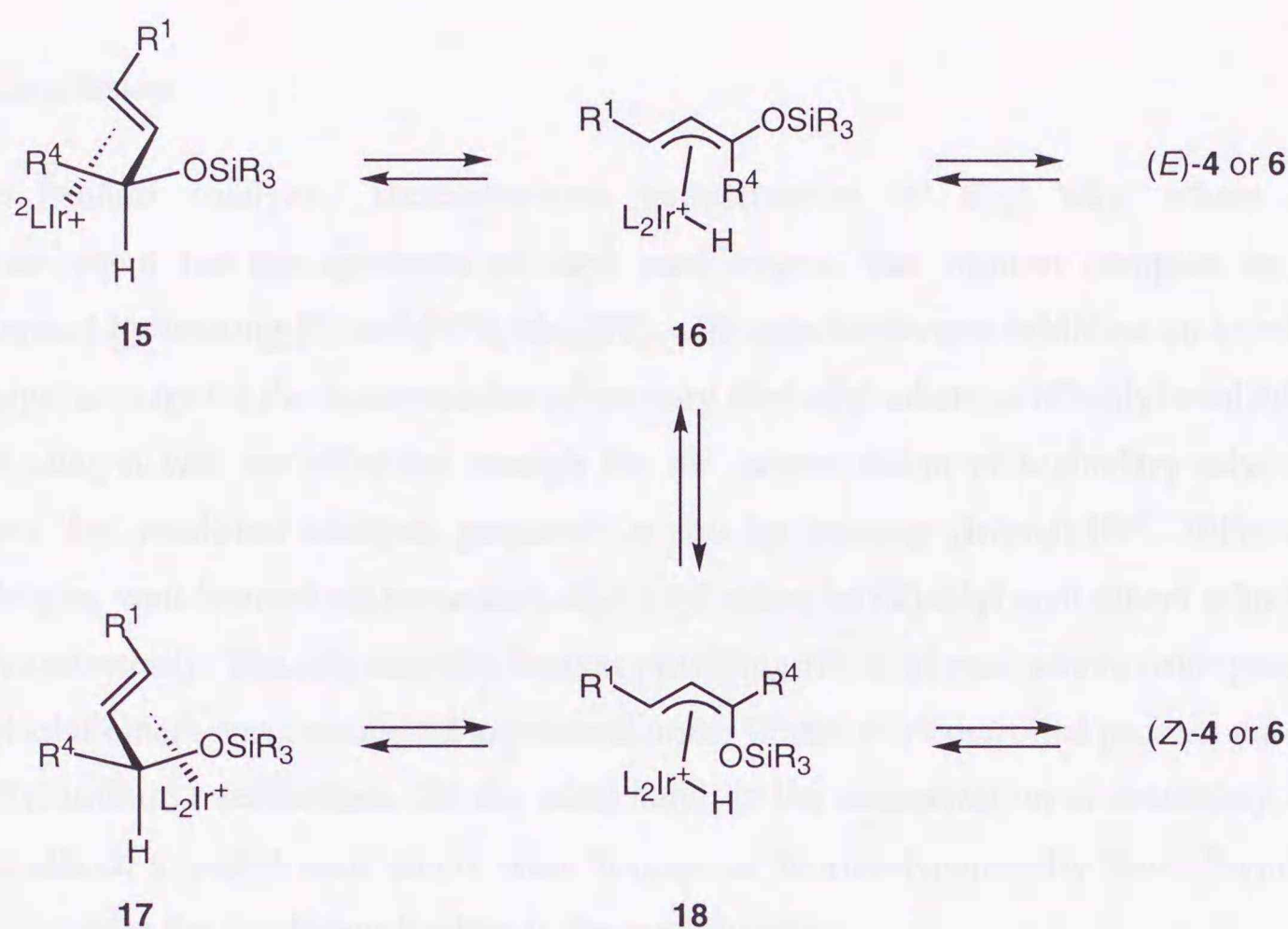


Scheme 7. Two General Mechanisms in Isomerization of Alkenes



The isomerization mechanism involving π -allyl intermediate is shown in Scheme 8. The oxidative addition of an allylic C-H bond to the iridium(I) complex to give π -allyliridium species (**16** and **18**), followed by reductive elimination to afford enol ether **4** or **6**.

The isomerization involves two processes: the first and selective formation of (*E*)-



Scheme 8. Mechanism of Isomerization

4 (kinetically controlled process) is followed by the equilibration to a mixture of (*E*)- and (*Z*)- **4** through the anti- π -allyl intermediate (thermodynamically controlled process). Both the oxidative addition and equilibration processes can be retarded in a solvent that strongly coordinates to the iridium metal, but they are very fast in CH_2Cl_2 . Acetone, having a medium donor strength, allows the smooth oxidative addition of a primary allyl ether to **2** or **3** with retarding the *cis*, *trans*-isomerization process. The iridium-trialkylphosphine complexes **3**, having a relatively small cone angle, was highly effective for secondary allyl ethers because of the steric hindrance around the allylic hydrogen.

Thus, the stereochemistry of **4** was highly dependent on the catalyst, the solvent, reaction time, and the substrate. When primary allyl ethers were reacted in acetone, the kinetic products ((*E*)-**4**) were obtained through the *syn*- π -allyl intermediate (**15** $\rightarrow$ **16** $\rightarrow$ (*E*)-**4**). On the other hand, high (*Z*)-selectivity was achieved for secondary allyl ethers under the conditions leading to the equilibration because the steric difference between the R^4 and R_3Si groups controls the stereochemistry of the products (**15** $\rightarrow$ **16** $\rightarrow$ **18** or **17** $\rightarrow$ **18** $\rightarrow$ (*Z*)-**6**).

3. Conclusion

Iridium catalyzed stereoselective isomerization of allyl silyl ethers was demonstrated for the synthesis of silyl enol ethers. The iridium complex *in situ* generated by treating $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ with catecholborane exhibited an excellent catalyst activity for the isomerization of primary allyl silyl ethers to (*E*)-silyl enol ethers. The catalyst was not effective enough for the isomerization of secondary allyl silyl ethers, but modified catalyst, prepared *in situ* by treating $[\text{Ir}(\text{cod})_2]\text{PF}_6-2\text{PPr}_3$ with hydrogen, well isomerized secondary allyl silyl ethers to (*Z*)-silyl enol ethers with high stereoselectivity. The reaction mechanism providing (*E*)-silyl enol ethers from primary allyl silyl ethers was considered to proceed under kinetically controlled process via *syn*- π -allyl iridium intermediate. On the other hand, in the isomerization of secondary allyl silyl ethers, (*Z*)-silyl enol ethers were formed as thermodynamically more favorable isomer under the conditions leading to the equilibration.

4. Experimental Section

General

All the experiments were carried out under argon atmosphere. ^1H NMR spectra were recorded by a JEOL JNM-A400II (400 MHz) spectrometer using CDCl_3 as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra in CDCl_3 were taken on JEOL JNM-A400II (100 MHz) spectrometer. Chemical shifts in ^{13}C NMR spectra were measured relative to CDCl_3 and converted to $\delta_{\text{Me}_4\text{Si}}$ values by using δ_{CDCl_3} 77.0 ppm. IR spectra were determined on a HITACHI 260-10 spectrometer. Mass spectra were obtained on a Finnigan MAT GCQTM apparatus. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-FABmate or a JMS-700TZ apparatus in the Instrumental Analysis Center of the Graduate School of Pharmaceutical Sciences, Hokkaido University.

Iridium Catalysts

$[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ and $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$ were prepared from $[\text{Ir}(\text{cod})\text{Cl}]_2$ and corresponding phosphines by reported literature.¹⁷ $[\text{Ir}(\text{cod})_2]\text{PF}_6$ was synthesized by a similar procedures for the preparation of $[\text{Rh}(\text{cod})_2]\text{BF}_4$ reported literature.¹⁸ All phosphines used as the ligand were obtained commercially. PPr_3 , PMe_3 , PEt_3 , and PBu_3 were distilled before use.

Allyl Silyl Ethers

All allyl silyl ethers were prepared from corresponding allylic alcohols with trisubstituted chlorosilanes and imidazole in DMF.

Solvents and Other Materials

CH_2Cl_2 , DMF, and CH_3CN were distilled over calcium hydride. Anhydrous THF was purchased from KANTO CHEMICAL CO., INC. Acetone was distilled before use and dried with MS 4A. CD_2Cl_2 and acetone- d_6 were purchased from MERCK.

Catecholborane was prepared from borane-methyl sulfide complex by the methods reported in the literature.¹⁹ 9-BBN, DIBAL-H, HSiCl_3 , HSiEt_3 , and HSnBu_3 were obtained commercially.

Preparation of Catalyst (Table 1)

Procedure using H₂ as a reducing agent (entry 1): A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with [Ir(cod)(PPh₂Me)₂]PF₆ (0.013 g, 0.015 mmol) and then flushed with argon. THF (3 ml) was added and stirring was started. Hydrogen gas was bubbled for 1 min into the solution through a needle to give a light yellow solution. The excess hydrogen was thoroughly replaced with argon by passing for 1 min into the solution. To the catalyst solution thus obtained was added **1a** (0.5 mmol) and the mixture was stirred at 20 °C for 30 min. The reaction was quenched with ethylenediamine (2 µl, 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ¹H NMR. After column chromatography on silica gel, **4a** was isolated as colorless liquid.

Procedure using hydrometal compounds as a reducing agent (entries 2–7): A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with [Ir(cod)(PPh₂Me)₂]PF₆ (0.013 g, 0.015 mmol) and then flushed with argon. Addition of THF (3 ml) gave a red suspension. Then **1a** (0.5 mmol) and hydrometal compounds (0.015 mmol) were successively added. The solution turned to clear red within 3 min and was stirred for 30 min at 20 °C. The reaction was quenched with ethylenediamine (2 µl, 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ¹H NMR. After column chromatography on silica gel, **4a** was isolated as colorless liquid.

Effect of Solvent and Reaction Time on the Iridium-Catalyzed Isomerization of **1a** (entries 1–7 in Table 2)

A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with [Ir(cod)(PPh₂Me)₂]PF₆ (0.013 g, 0.015 mmol) and then flushed with argon. Solvent (3 ml), **1a** (0.5 mmol), and catecholborane (1.6 µl, 0.015 mmol) were successively added. The solution was stirred for 30–1440 min at 20 °C. The reaction was quenched with ethylenediamine (2 µl, 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ¹H NMR to determine the conversion of **1a** and *E/Z* ratio of **4a**.

¹H NMR Study of the Iridium-Catalyzed Isomerization of **1a** (entries 8–12 in Table 2)

A dry NMR tube, equipped with a rubber septum cup, was charged with [Ir(cod)(PPh₂Me)₂]₂PF₆ (0.002 g, 0.002 mmol) and then flushed with argon. CD₂Cl₂ (0.7 ml), acetone-*d*₆ (14 μl, 0.2 mmol), and **1a** (23 μl, 0.1 mmol) were successively added. The tube was cooled to 0 °C, and CD₂Cl₂ solution of catecholborane (0.002 mmol) was then injected to initiate the isomerization. The integration of vinylic protons of (*E*)-**4a** at 4.98 and 6.22 ppm and (*Z*)-**4a** at 4.50 and 6.19 ppm gave the *E/Z* ratio shown in Table 2.

E/Z Isomerization of **4a** (Scheme 3)

A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with [Ir(cod)(PPh₂Me)₂]₂PF₆ (0.013 g, 0.015 mmol) and then flushed with argon. Addition of CH₂Cl₂ (3 ml) and acetone (37 μl, 0.5 mmol) gave a clear-red solution in CH₂Cl₂. Then isomerically pure (*E*)-**4a** or (*Z*)-**4a** (0.5 mmol) and catecholborane (1.6 μl, 0.015 mmol) were successively added. The solution turned to clear red within 3 min and was stirred for 30 min at 20 °C. The reaction was quenched with ethylenediamine (2 μl, 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ¹H NMR. The same ratio of *E/Z* mixture (33/67) of **4a** was obtained starting from both (*E*)-**4a** and (*Z*)-**4a**.

Effects of Catalyst on the Isomerization of **5a** (Table 3)

Procedure using H₂ as a reducing agent (entries 1 and 4–9): A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with [Ir(cod)(PPh₂Me)₂]₂PF₆ (0.013 g, 0.015 mmol) or [Ir(cod)₂]₂PF₆ (0.008 g, 0.015 mmol), and then flushed with argon. CH₂Cl₂ (3 ml), acetone (37 μl, 0.5 mmol), and phosphine ligand (0.03 mmol of trialkylphosphine or 0.015 mmol of dppe) were added with stirring. Hydrogen gas was bubbled for 1 min into the solution through a needle. The excess hydrogen was thoroughly replaced with argon by passing for 1 min into the solution. To the catalyst solution thus obtained was added **5a** (0.5 mmol) and stirred at 20 °C for 30 min. The reaction was quenched with ethylenediamine (2 μl, 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ¹H NMR. After column chromatography on silica gel, **6a** was isolated as

colorless liquid.

Procedure using catecholborane as a reducing agent (entries 2 and 3): A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (0.013 g, 0.015 mmol) and then flushed with argon. Addition of THF (3 ml) gave a red suspension. Then **5a** (0.5 mmol) and hydrometal compounds (0.015 mmol) were successively added. The resulting solution was stirred for 30 min at 20 °C. The reaction was quenched with ethylenediamine (2 μl , 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ^1H NMR. After column chromatography on silica gel, **6a** was isolated as colorless liquid.

General Procedure for The Isomerization of Primary Allyl Silyl Ethers (Table 4)

The isomerization with $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ /catecholborane in THF: A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (0.013 g, 0.015 mmol) and then flushed with argon. Addition of THF (3 ml) gave a red suspension. An primary allyl silyl ether (0.5 mmol) and catecholborane (1.6 μl , 0.015 mmol) were successively added. The solution turned to clear red within 3 min and was stirred for 30 min at 20 °C. The reaction was quenched with ethylenediamine (2 μl , 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ^1H NMR. The analytically pure product was isolated by column chromatography on silica gel for **4a–4f** and **4h–4k**, or by kugelrohr distillation for **4g**.

The isomerization with $[\text{Ir}(\text{cod})_2]\text{PF}_6$ –2PPr₃/H₂ in acetone: A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with $[\text{Ir}(\text{cod})_2]\text{PF}_6$ (0.008 g, 0.015 mmol) and then flushed with argon. Acetone (3 ml) and tripropylphosphine (0.03 mmol) were added. Hydrogen gas was bubbled for 1 min into the solution through a needle to give a light yellow solution. The excess hydrogen was thoroughly replaced with argon by passing for 1 min into the solution. To the catalyst solution thus obtained was added an primary allyl silyl ether (0.5 mmol) and the mixture was stirred at 20°C for the time shown in the table. The reaction was quenched with ethylenediamine (2 μl , 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ^1H NMR. The analytically pure product was isolated by column chromatography on silica gel.

General Procedure for The Isomerization of Secondary Allyl Silyl Ethers (Table 5)

The isomerization with $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ /catecholborane in CH_2Cl_2 /acetone (80/1): A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (0.013 g, 0.015 mmol) and then flushed with argon. Addition of CH_2Cl_2 (3 ml) and acetone (37 μl , 0.5 mmol) gave a red suspension clear-red solution. An secondary allyl silyl ether (0.5 mmol) and catecholborane (1.6 μl , 0.015 mmol) were successively added. The solution turned to clear red within 3 min and was stirred for 30 min at 20 °C. The reaction was quenched with ethylenediamine (2 μl , 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ^1H NMR. The analytically pure product was isolated by column chromatography on silica gel.

The isomerization with $[\text{Ir}(\text{cod})_2]\text{PF}_6$ -2PPr₃/H₂ in CH_2Cl_2 /acetone (80/1): A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with $[\text{Ir}(\text{cod})_2]\text{PF}_6$ (0.008 g, 0.015 mmol) and then flushed with argon. CH_2Cl_2 (3 ml), acetone (37 μl , 0.5 mmol), and tripropylphosphine (0.03 mmol) were added. Hydrogen gas was bubbled for 1 min into the solution through a needle to give a light yellow solution. The excess hydrogen was thoroughly replaced with argon by passing for 1 min into the solution. To the catalyst solution thus obtained was added an secondary allyl silyl ether (0.5 mmol) and was stirred at 20°C for the time shown in the table. The reaction was quenched with ethylenediamine (2 μl , 0.03 mmol) to deactivate the catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ^1H NMR. The analytically pure product was isolated by column chromatography on silica gel for **6a**, **6c**, **6d**, **6g**, **6h** and **6o**, or by kugelrohr distillation for **6b**, **6e**, **6f**, and **6i-6n**.

The Isomerization of Homoallyl Silyl Ether **9** (Scheme 6)

A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with $[\text{Ir}(\text{cod})(\text{PPh}_2\text{Me})_2]\text{PF}_6$ (0.013 g, 0.015 mmol) and then flushed with argon. Addition of THF (3 ml) gave a red suspension. An homoallyl silyl ether **9** (0.5 mmol) and catecholborane (1.6 μl , 0.015 mmol) were successively added. The solution turned to clear red within 3 min and was stirred for 20 min at 20 °C. The reaction was quenched with ethylenediamine (2 μl , 0.03 mmol) to deactivate the

catalyst. After evaporation of volatile materials, the crude mixture was analyzed by ^1H NMR. The analytically pure **4c** (93%, $E/Z = 94/6$) was isolated by column chromatography on silica gel.

(E)-1-[(tert-Butyldimethylsilyl)oxy]-1-hexene [(E)-4a]: ^1H NMR (400 MHz, CDCl_3): δ 6.22 (d, $J = 11.7$ Hz, 1H), 4.98 (dt, $J = 11.7, 7.6$ Hz, 1H), 1.85–1.92 (m, 2H), 1.27–1.32 (m, 4H), 0.92 (s, 9H), 0.8–0.9 (m, 3H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.0, 111.7, 32.6, 27.0, 25.8, 25.6, 22.1, 13.9, -5.2. MS (EI): m/z 214 (M^+ , 10), 157 ($\text{M}^+ - \text{CMe}_3$, 80), 115 (45), 75 (100), 73 (47), 59 (24). HRMS calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$ 214.1753, found 214.1753.

(Z)-1-[(tert-Butyldimethylsilyl)oxy]-1-hexene [(Z)-4a]: ^1H NMR (400 MHz, CDCl_3): δ 6.17 (d, $J = 5.9$ Hz, 1H), 4.44 (dt, $J = 5.9, 7.2$ Hz, 1H), 2.03–2.12 (m, 2H), 1.27–1.35 (m, 4H), 0.92 (s, 9H), 0.12 (s, 6H).

(E)-1-[(tert-Butyldimethylsilyl)oxy]propene [(E)-4b]: ^1H NMR (400 MHz, CDCl_3): δ 6.22 (dq, $J = 11.8, 1.5$ Hz, 1H), 4.98 (dq, $J = 11.8, 6.8$ Hz, 1H), 1.51 (dd, $J = 6.8, 1.5$ Hz, 3H), 0.91 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.5, 105.7, 25.7, 18.3, 12.1, -5.2. IR (neat): 1668 cm^{-1} . MS (EI): m/z 172 (M^+ , 14), 115 ($\text{M}^+ - \text{CMe}_3$, 100), 85 (59), 75 (45), 73 (31), 59 (47). HRMS calcd for $\text{C}_9\text{H}_{20}\text{OSi}$ 172.1283, found 172.1282.

(Z)-1-[(tert-Butyldimethylsilyl)oxy]propene [(Z)-4b]: ^1H NMR (400 MHz, CDCl_3): δ 6.19 (dq, $J = 5.9, 1.7$ Hz, 1H), 4.50 (dq, $J = 6.6, 5.9$ Hz, 1H), 1.57 (dd, $J = 6.6, 1.7$ Hz, 3H), 0.93 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.3, 104.8, 25.6, 18.3, 8.9, -5.4.

(E)-1-[(tert-Butyldimethylsilyl)oxy]-1-butene [(E)-4c]: ^1H NMR (400 MHz, CDCl_3): δ 6.23 (d, $J = 12.0$ Hz, 1H), 5.02 (dt, $J = 12.0, 7.1$ Hz, 1H), 1.90 (dq, $J = 7.4, 7.1$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H), 0.92 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.5, 113.4, 25.7, 20.7, 18.3, 15.1, -5.2. MS (EI): m/z 186 (M^+ , 11), 147 (13), 129 ($\text{M}^+ - \text{CMe}_3$, 45), 75 (100), 73 (21), 59 (16). HRMS calcd for $\text{C}_{10}\text{H}_{22}\text{OSi}$ 186.1440, found 186.1431.

(Z)-1-[(tert-Butyldimethylsilyl)oxy]-1-butene [(Z)-4c]: ^1H NMR (400 MHz, CDCl_3): δ 6.14 (d, $J = 5.9$ Hz, 1H), 4.45 (dt, $J = 7.1, 5.9$ Hz, 1H), 2.10 (dq, $J = 7.6, 7.1$ Hz, 2H), 0.95 (t, $J = 7.6$ Hz, 3H), 0.92 (s, 9H), 0.12 (s, 6H).

1-[(tert-Butyldimethylsilyl)oxy]-2-methylpropene (4d): ^1H NMR (400 MHz, CDCl_3): δ 6.03 (s, 1H), 1.60 (s, 3H), 1.53 (s, 3H), 0.92 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (100 MHz,

CDCl₃): δ 133.5, 113.3, 25.7, 19.3, 18.2, 14.7, -5.3. IR (neat): 1690 cm⁻¹. MS (EI): m/z 186 (M⁺, 17), 129 (M⁺-CMe₃, 54), 75 (100), 73 (19), 59 (19). HRMS calcd for C₁₀H₂₂OSi 186.1440, found 186.1444.

(E)-1-[(*tert*-Butyldimethylsilyl)oxy]-3-phenyl-1-propene [(E)-4j]: ¹H NMR (400 MHz, CDCl₃): δ 7.16–7.29 (m, 5H), 6.34 (d, J = 11.7 Hz, 1H), 5.16 (dt, J = 11.7, 7.3 Hz, 1H), 3.23 (d, J = 7.3 Hz, 2H), 0.92 (s, 9H), 0.14 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 141.5, 141.4, 128.3, 128.2, 125.8, 110.2, 33.6, 25.7, 18.3, -5.2. IR (neat): 1667 cm⁻¹. MS (EI): m/z 248 (M⁺, 7), 191 (M⁺-CMe₃, 97), 135 (100), 117 (66), 75 (68), 73 (47), 59 (38). HRMS calcd for C₁₅H₂₄OSi 248.1597, found 248.1596.

(E)-1-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-1-butene [(E)-4k]: ¹H NMR (400 MHz, CDCl₃): δ 6.21 (d, J = 12.0 Hz, 1H), 4.96 (dd, J = 12.0, 7.8 Hz, 1H), 2.21 (m, 1H), 0.97 (d, J = 6.6 Hz, 6H), 0.92 (s, 9H), 0.12 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 138.4, 119.4, 27.2, 25.7, 23.6, 18.4, -5.2. IR (neat): 1668 cm⁻¹. MS (EI): m/z 200 (M⁺, 7), 143 (M⁺-CMe₃, 28), 75 (100), 73 (26), 59 (11). HRMS calcd for C₁₁H₂₄OSi 200.1596, found 200.1583.

(E)-1-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-1-propene [(E)-6a]: ¹H NMR (400 MHz, CDCl₃): δ 7.22–7.43 (m, 5H), 5.11 (q, J = 7.3 Hz, 1H), 1.70 (d, J = 7.3 Hz, 3H), 0.91 (s, 9H), 0.03 (s, 6H).

(Z)-1-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-1-propene [(Z)-6a]: ¹H NMR (400 MHz, CDCl₃): δ 7.22–7.43 (m, 5H), 5.20 (q, J = 6.8 Hz, 1H), 1.74 (d, J = 6.8 Hz, 3H), 0.99 (s, 9H), -0.04 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 139.8, 127.9, 127.2, 125.7, 105.8, 18.3, 11.7, -4.0. MS (EI): m/z 248 (M⁺, 16), 233 (M⁺-CH₃, 7), 191 (M⁺-CMe₃, 58), 117 (44), 75 (100), 73 (34), 57 (28), 41 (32). HRMS calcd for C₁₅H₂₄OSi 248.1597, found 248.1593.

(E)-2-[(Trimethylsilyl)oxy]-2-butene [(E)-6b]: ¹H NMR (400 MHz, CDCl₃): δ 4.67 (q, J = 6.8 Hz, 1H), 1.72 (s, 3H), 1.52 (d, J = 6.8 Hz, 3H), 0.17 (s, 9H).

(Z)-2-[(Trimethylsilyl)oxy]-2-butene [(Z)-6b]: ¹H NMR (400 MHz, CDCl₃): δ 4.49 (q, J = 6.6 Hz, 1H), 1.76 (s, 3H), 1.49 (dd, J = 6.6, 1.0 Hz, 3H), 0.19 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 147.3, 102.8, 22.6, 10.7, 0.6. MS (EI): m/z 144 (M⁺, 25), 129 (M⁺-CH₃, 30), 75 (95), 73 (68), 43 (100). HRMS calcd for C₇H₁₆OSi 144.0970, found 144.0984.

(E)-2-[(*tert*-Butyldimethylsilyl)oxy]-2-butene [(E)-6c]: ¹H NMR (400 MHz, CDCl₃): δ 4.67 (q, J = 6.6 Hz, 1H), 1.72 (s, 3H), 1.5 (m, 3H), 0.92 (s, 9H), 0.11 (s, 6H). ¹³C NMR

(100 MHz, CDCl_3): δ 148.2, 101.9, 25.7, 22.7, 17.3, 12.1, -4.5. MS (EI): m/z 186 (M^+ , 11), 129 ($\text{M}^+ - \text{CMe}_3$, 54), 75 (100), 73 (15), 59 (9). HRMS calcd for $\text{C}_{10}\text{H}_{22}\text{OSi}$ 186.1440, found 186.1436.

(Z)-2-[(*tert*-Butyldimethylsilyl)oxy]-2-butene [(Z)-6c]: ^1H NMR (400 MHz, CDCl_3): δ 4.46 (q, $J = 6.6$ Hz, 1H), 1.76 (s, 3H), 1.5 (m, 3H), 0.95 (s, 9H), 0.13 (s, 6H).

(E)-2-[(Triisopropylsilyl)oxy]-2-butene [(Z)-6d]: ^1H NMR (400 MHz, CDCl_3): δ 4.67 (q, $J = 6.8$ Hz, 1H), 1.76 (s, 3H), 1.51 (d, $J = 6.8$ Hz, 2H), 1.1-1.2 (m, 21H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.5, 100.9, 18.0, 17.4, 12.6, 12.1. IR (neat): 1684 cm^{-1} . MS (EI): m/z 228 (M^+ , 18), 185 ($\text{M}^+ - \text{CHMe}_2$, 100), 157 (45), 115 (32), 75 (41), 73 (10), 61 (30), 59 (17), 45 (21). HRMS calcd for $\text{C}_{13}\text{H}_{28}\text{OSi}$ 228.1910, found 228.1926.

(Z)-3-[(Trimethylsilyl)oxy]-2-pentene [(Z)-6e]: ^1H NMR (400 MHz, CDCl_3): δ 4.52 (q, $J = 6.6$ Hz, 1H), 2.02 (q, $J = 7.3$ Hz, 2H), 1.51 (d, $J = 6.6$ Hz, 3H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.7, 101.0, 29.5, 11.7, 10.7, 0.6. MS (EI): m/z 158 (M^+ , 33), 143 ($\text{M}^+ - \text{CH}_3$, 36), 115 (41), 75 (100), 73 (84), 45 (20), 43 (23). HRMS calcd for $\text{C}_8\text{H}_{18}\text{OSi}$ 158.1127, found 158.1121.

(Z)-4-Methyl-3-[(trimethylsilyl)oxy]-2-pentene [(Z)-6f]: ^1H NMR (400 MHz, CDCl_3): δ 4.54 (dq, $J = 6.6, 0.9$ Hz, 1H), 2.12-2.19 (m, 1H), 1.51 (dd, $J = 6.6, 1.2$ Hz, 3H), 1.02 (d, $J = 6.6$ Hz, 6H), 0.20 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.7, 99.3, 34.4, 20.7, 10.9, 0.7. MS (EI): m/z 172 (M^+ , 28), 157 ($\text{M}^+ - \text{CH}_3$, 30), 75 (92), 73 (100), 45 (22), 43 (51), 41 (22). HRMS calcd for $\text{C}_9\text{H}_{20}\text{OSi}$ 172.1283, found 172.1269.

(Z)-3-[(*tert*-Butyldimethylsilyl)oxy]-4-methyl-2-pentene [(Z)-6g]: ^1H NMR (400 MHz, CDCl_3): δ 4.51 (dq, $J = 6.6, 1.0$ Hz, 1H), 2.13 (septet, $J = 6.8$ Hz, 1H), 1.53 (dd, $J = 6.6, 1.3$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 6H), 0.92 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.9, 98.7, 34.1, 25.9, 20.8, 18.4, 10.9, -4.0. MS (EI): m/z 214 (M^+ , 8), 157 ($\text{M}^+ - \text{CMe}_3$, 15), 75 (100), 73 (16), 59 (7). HRMS calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$ 214.1753, found 214.1755.

(Z)-4-Methyl-3-[(trimethylsilyl)oxy]-2-heptene [(Z)-6i]: ^1H NMR (400 MHz, CDCl_3): δ 4.50 (q, $J = 6.6$ Hz, 1H), 1.98-2.03 (m, 1H), 1.51 (d, $J = 6.6$ Hz, 3H), 1.43-1.50 (m, 1H), 1.16-1.35 (m, 3H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.6, 100.0, 39.6, 36.8, 20.4, 18.5, 14.2, 10.9, 0.8. MS (EI): m/z 200 (M^+ , 7), 171 (7), 158 (80), 143 (56), 115 (9), 75 (71), 73 (100). HRMS calcd for $\text{C}_{11}\text{H}_{24}\text{OSi}$ 200.1596, found 200.1604.

(Z)-4-Ethyl-3-[(trimethylsilyl)oxy]-2-hexene [(Z)-6j]: ^1H NMR (400 MHz, CDCl_3): δ

4.46 (q, $J = 6.6$ Hz, 1H), 1.71 (quintet, $J = 6.6$ Hz, 1H), 1.53 (d, $J = 6.6$ Hz, 3H), 1.31–1.43 (m, 4H), 0.84 (t, $J = 7.3$ Hz, 6H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.9, 101.6, 49.2, 24.8, 11.7, 11.0, 1.0. MS (EI): m/z 200 (M^+ , 100), 186 (24), 172 (56), 158 (25), 144 (21), 76 (18), 73 (16). HRMS calcd for $\text{C}_{11}\text{H}_{24}\text{OSi}$ 200.1596, found 200.1578.

(Z)-1-Cyclohexyl-1-[(trimethylsilyl)oxy]-1-propene [(Z)-6k]: ^1H NMR (400 MHz, CDCl_3): δ 4.49 (q, $J = 6.6$ Hz, 1H), 1.65–1.86 (m, 6H), 1.51 (d, $J = 6.6$ Hz, 3H), 1.03–1.27 (m, 5H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.9, 99.5, 44.4, 31.1, 26.4, 10.8, 0.7. MS (EI): m/z 212 (M^+ , 18), 197 ($\text{M}^+ - \text{CH}_3$, 7), 157 (53), 75 (56), 73 (100), 55 (25), 45 (31), 41 (33). HRMS calcd for $\text{C}_{12}\text{H}_{24}\text{OSi}$ 212.1596, found 212.1602.

(Z)-3-[(Trimethylsilyl)oxy]-2-octene [(Z)-6m]: ^1H NMR (400 MHz, CDCl_3): δ 4.51 (q, $J = 6.6$ Hz, 1H), 1.93–2.01 (m, 2H), 1.50 (dt, $J = 6.6, 1.2$ Hz, 3H), 1.24–1.32 (m, 6H), 0.89 (t, $J = 7.1$ Hz, 3H), 0.19 (s, 9H).

(E)-1-Phenyl-1-[(trimethylsilyl)oxy]—propene [(E)-6n]: ^1H NMR (400 MHz, CDCl_3): δ 7.20–7.47 (m, 5H), 5.10 (q, $J = 7.1$ Hz, 1H), 1.70 (d, $J = 7.1$ Hz, 3H), 0.12 (s, 9H).

(Z)-1-Phenyl-1-[(trimethylsilyl)oxy]-1-propene [(Z)-6n]: ^1H NMR (400 MHz, CDCl_3): δ 7.20–7.47 (m, 5H), 5.33 (q, $J = 6.8$ Hz, 1H), 1.74 (d, $J = 6.8$ Hz, 3H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 139.2, 128.0, 127.3, 125.2, 105.3, 11.7, 0.6. MS (EI): m/z 206 (M^+ , 27), 191 ($\text{M}^+ - \text{CH}_3$, 10), 105 (53), 77 (81), 75 (71), 73 (100), 45 (73), 43 (54). HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{OSi}$ 206.1127, found 206.1125.

(E)-1-Phenyl-1-[(triisopropylsilyl)oxy]-1-propene [(E)-6o]: ^1H NMR (400 MHz, CDCl_3): δ 7.21–7.45 (m, 5H), 5.09 (q, $J = 7.3$ Hz, 1H), 1.70 (d, $J = 7.3$ Hz, 3H), 1.04–1.17 (m, 21H). MS (EI): m/z 290 (M^+ , 16), 247 ($\text{M}^+ - \text{CHMe}_2$, 100), 219 (17), 117 (47), 115 (39), 103 (32), 91 (38), 75 (79), 61 (53), 59 (34). HRMS calcd for $\text{C}_{18}\text{H}_{30}\text{OSi}$ 290.2066, found 290.2065.

(Z)-1-Phenyl-1-[(triisopropylsilyl)oxy]-1-propene [(Z)-6o]: ^1H NMR (400 MHz, CDCl_3): δ 7.21–7.45 (m, 5H), 5.06 (q, $J = 6.8$ Hz, 1H), 1.77 (d, $J = 6.8$ Hz, 3H), 1.04–1.17 (m, 21H).

Abbreviations

cod	1,5-cyclooctadiene
Cy	cyclohexyl
9-BBN	9-borabicyclo-[3.3.1]nonan
DIBAL-H	diisobutylaluminium hydride
MOM	methoxymethyl
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
THF	tetrahydrofuran
DMF	N,N-dimethylformamide

References and Notes

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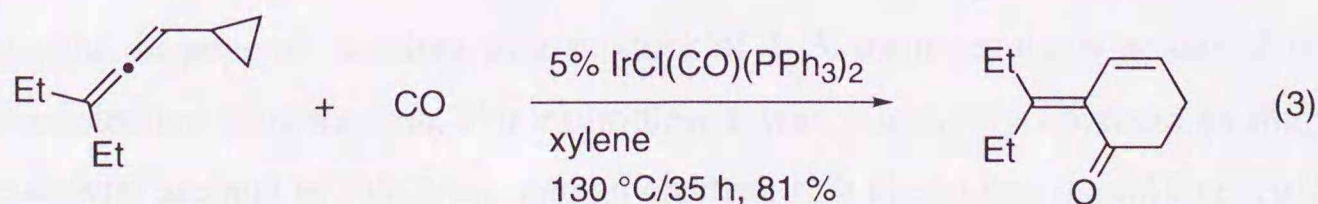
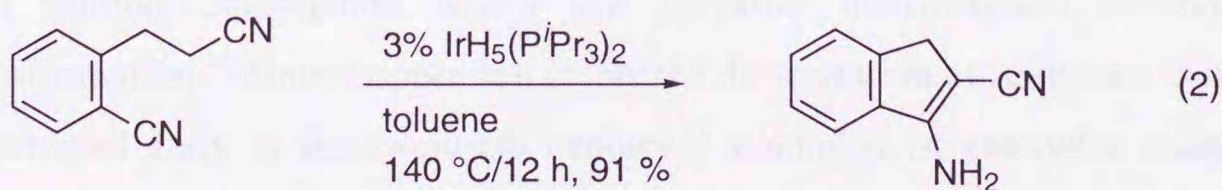
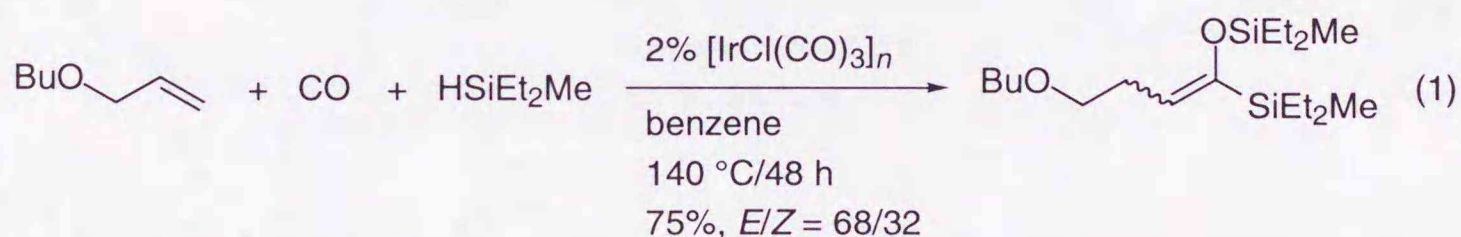
Chapter 2

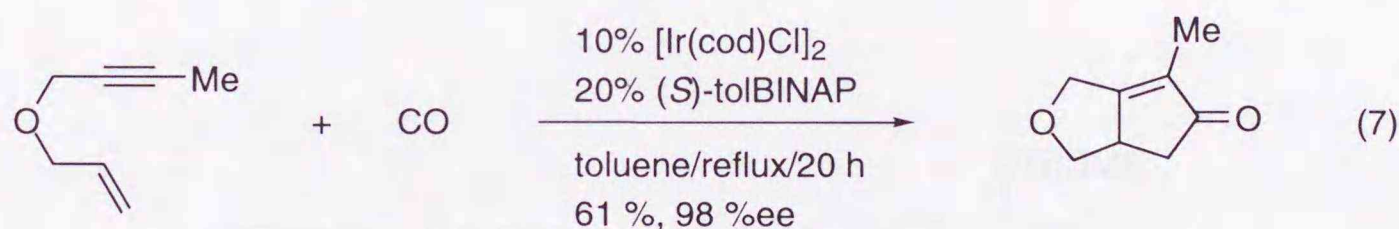
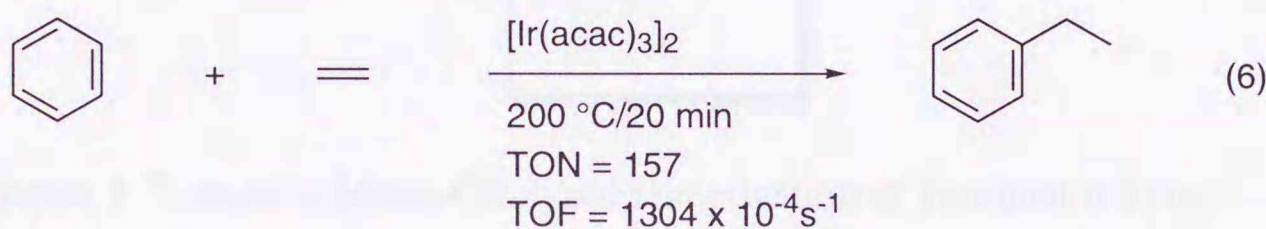
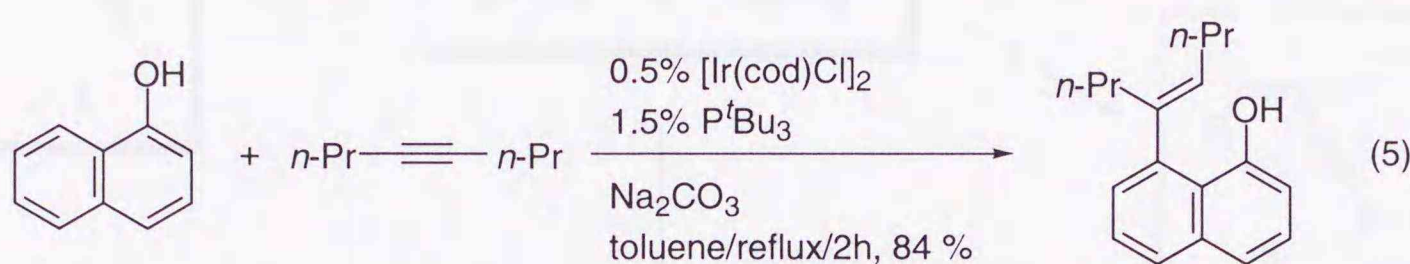
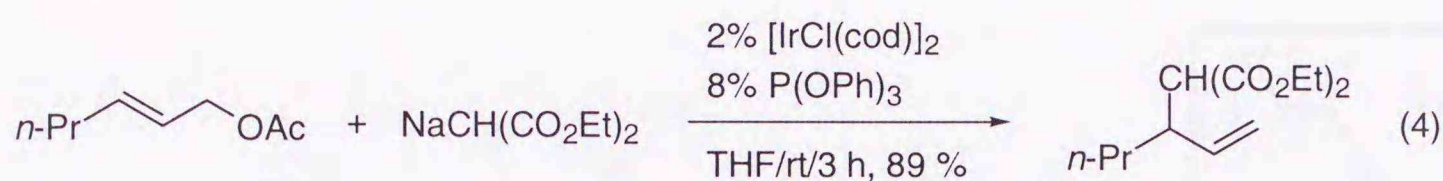
Iridium-Catalyzed Dimerization of Terminal Alkynes to (*E*)-Enynes, (*Z*)-Enynes, or 1,2,3-Butatrienes

Abstract: The iridium complex *in situ* generated from $[\text{Ir}(\text{cod})\text{Cl}]_2$ and a phosphine ligand catalyzed the dimerization of terminal alkynes to give (*E*)-enynes, (*Z*)-enynes, or 1,2,3-butatriene derivatives in the presence of triethylamine. The triarylphosphine complex selectively yielded linear (*E*)-enynes for silylethynes, while the tripropylphosphine complex provided linear (*Z*)-enynes for silylalkynes or 1,2,3-butatrienes for *tert*-alkylethynes.

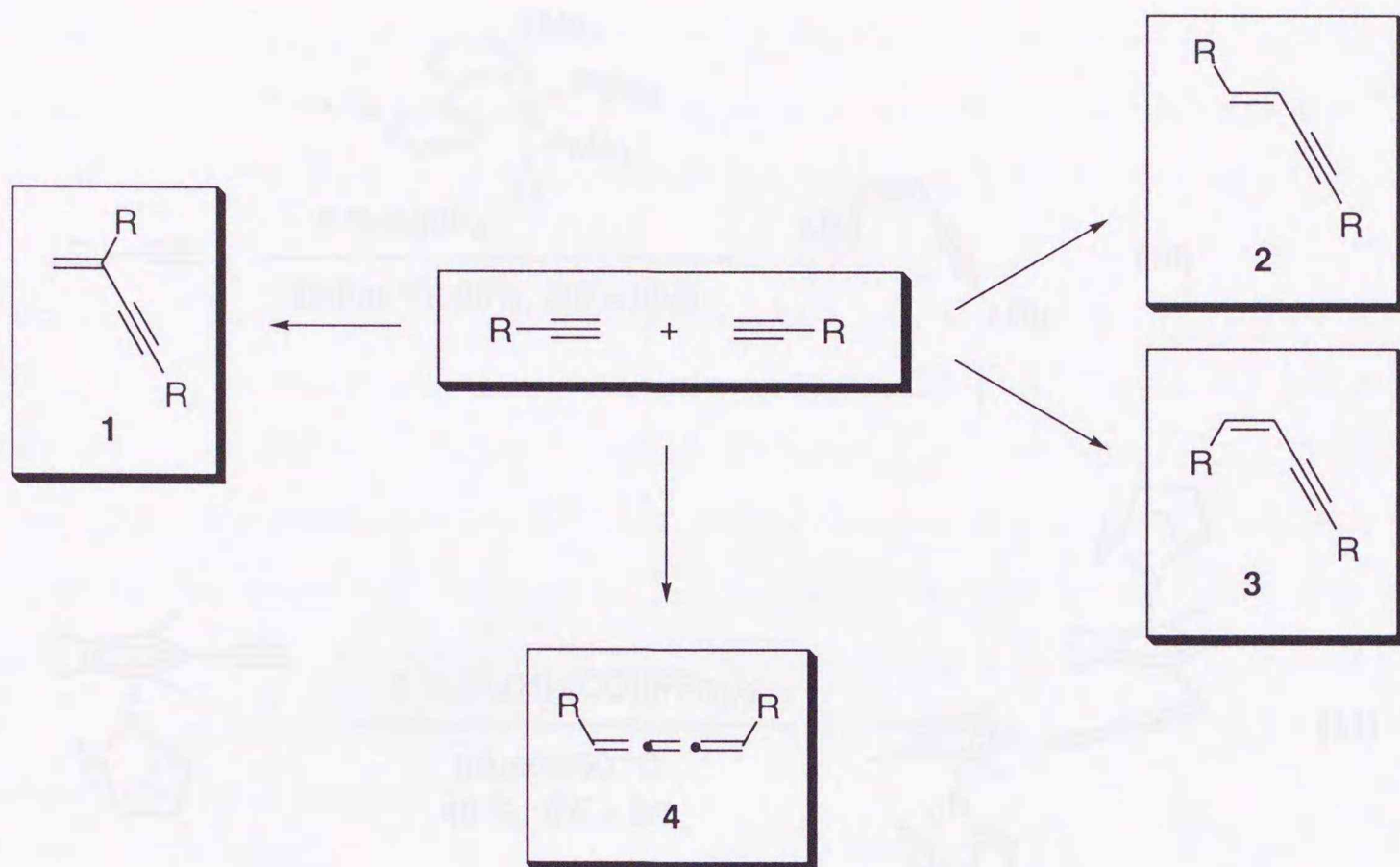
1. Introduction

The transition metal catalyzed or mediated carbon–carbon bond forming reactions, including cross-coupling reaction between organic electrophiles and organometallic compounds, have been recognized as one of the most powerful tools for the synthesis of complex organic molecules.¹ A wide variety of transition metal complexes have been studied extensively as reagents or catalysts for such reactions. Although iridium complexes have received much attention as highly active catalyst for hydrogenation² and isomerization³ of alkene, iridium catalysts have been limitedly used for carbon–carbon bond forming reactions. However, several groups recently reported a synthetically useful regio- and stereocontrolled carbon–carbon bond formation reactions catalyzed by iridium complexes. For examples, silylcarbonylation of alkenes and alkynyl hydrazones (eq. 1),⁴ addition reaction of nitriles (eq. 2),⁵ ring opening carbonylation of allenylcyclopropane (eq. 3),⁶ allylic alkylation of allyl and dienyl ester (eq. 4),⁷ addition of aromatic carbon–hydrogen bond to alkyne⁸ and alkene⁹ (eq. 5 and 6), and asymmetric Pauson-Khand reaction (eq. 7).¹⁰ The developments of these reactions opened the door to practical use of potential catalyst ability in iridium complexes.

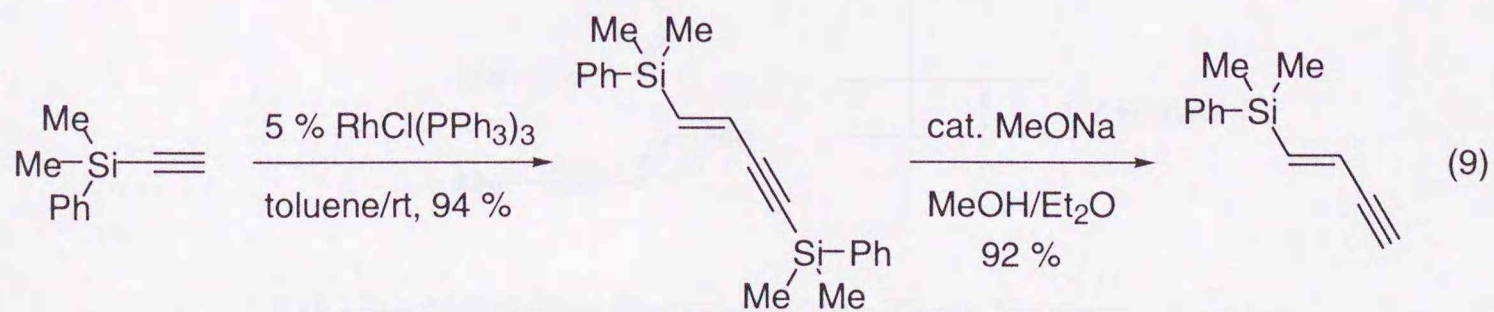
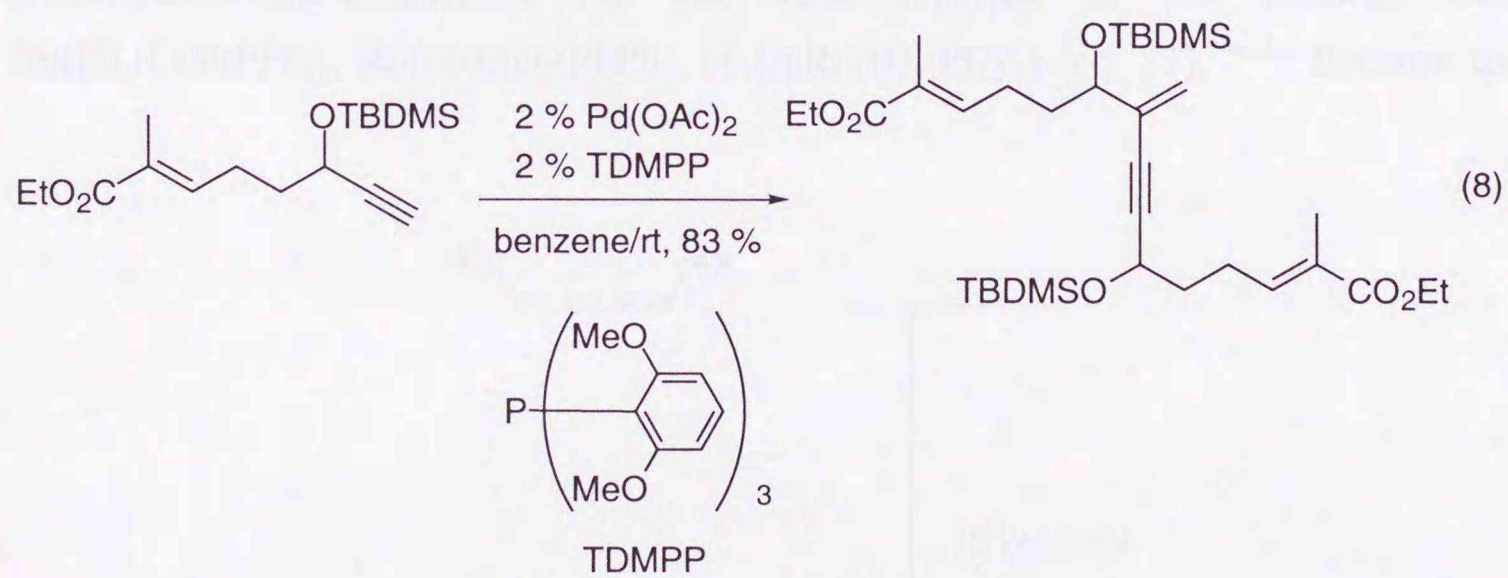


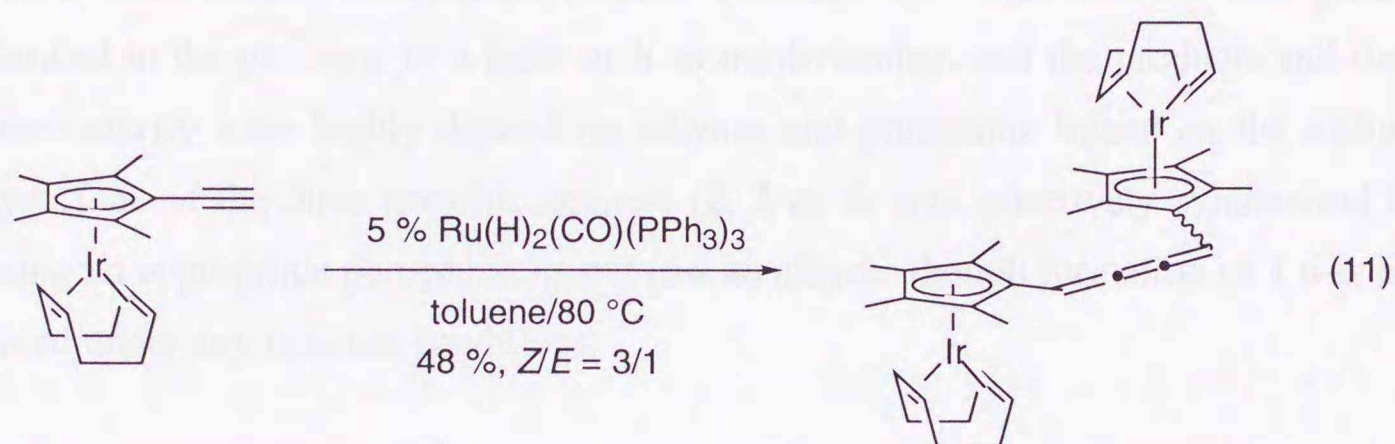
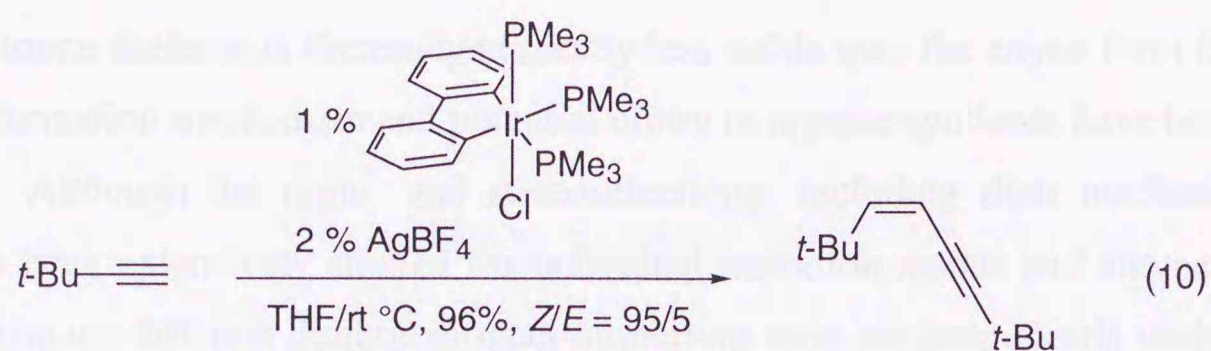


A great deal of attention has been focused on the transition metal-catalyzed dimerization of terminal alkynes as an efficient method for the synthesis of unsaturated four carbon compounds which are versatile intermediates to further organic transformation.¹¹ Since copper salt catalyzed dimerization of acetylene to vinylacetylene discovered early in the twentieth century,¹² a number of examples using early-¹³ and late-transition metal catalysts^{14,15,16,17} have been reported. In general, the dimerization of terminal alkynes gives 1,3-disubstituted enynes (**1**) from head-to-tail coupling and 1,4-disubstituted enynes (**2** and **3**) from head-to-head coupling (Scheme 1). Although the reactions, in general, resulted in a mixture of **1–3**, some catalysts achieved regio- and stereoselective dimerization. For examples, **1** was selectively obtained in the presence of catalytic amount of $\text{Pd}(\text{OAc})_2$ and an electron rich phosphine ligand like tris(2,6-

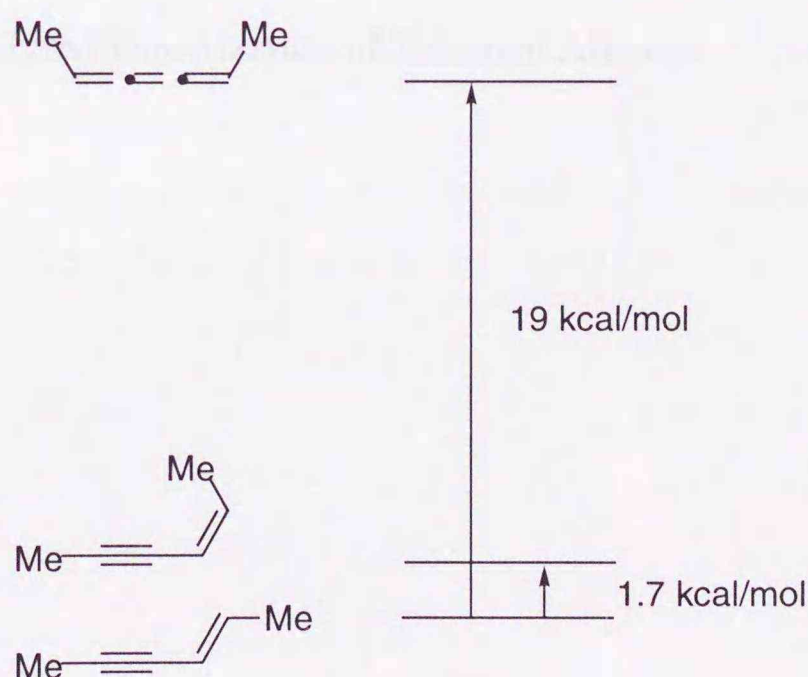


Scheme 1. Transition Metal-Catalyzed Dimerization of Terminal Alkynes





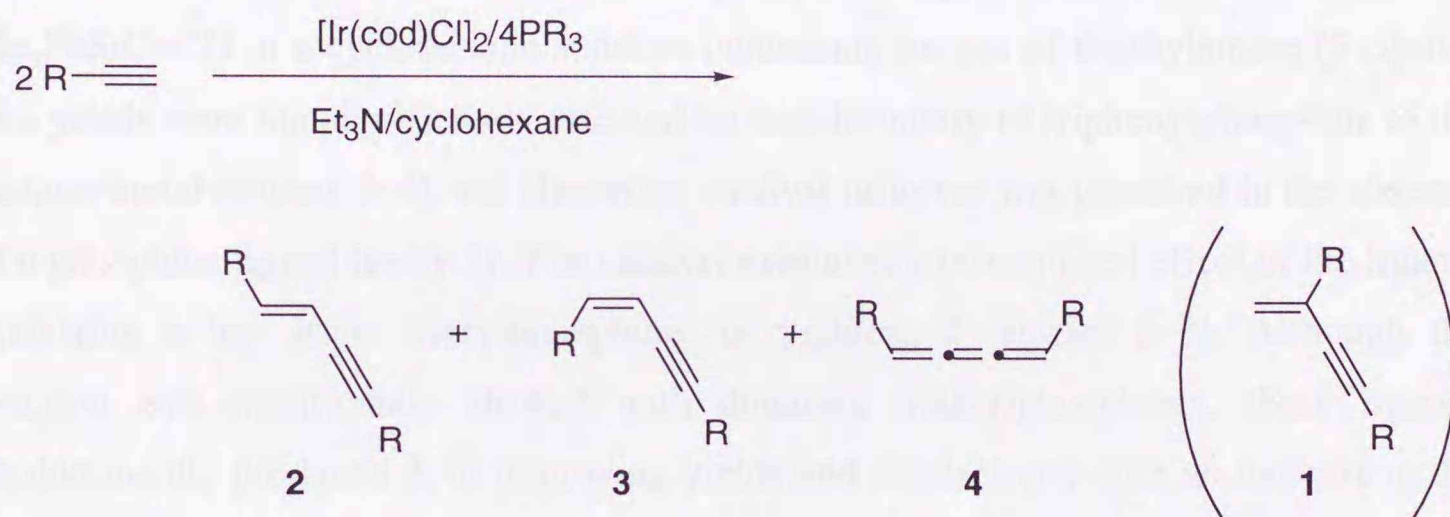
dimethoxyphenyl) phosphine (eq. 8), while $\text{RhCl(PPh}_3)_3$,^{15c} $\text{Ir(biphenyl-2,2'-diyl)(PMe}_3)_3\text{Cl}$,^{15f} and $[\text{RuP(CH}_2\text{CH}_2\text{PPh}_2)_3(\text{C}\equiv\text{CSiMe}_3)]\text{BPh}_4$ ^{14d} provide **2** or **3** with high stereoselectivity (eqs. 9 and 10). On the other hand, the selective formation of 1,4-disubstituted-1,2,3-butatrienes (**4**) has been reported in the reaction with $\text{Ru(H)}_2\text{(CO)(PPh)}_3$, $\text{Ru(cod)(cot)/PPh}_3$, or $\text{CpRu(H)}_3(\text{PCy}_3)$ (eq. 11).^{14a,e,i,o} Because the



Scheme 2. Relative Energies of the Three Isomers

butatriene skeleton is thermodynamically less stable than the enyne form (Scheme 2),^{14a} its formation mechanism and potential utility in organic synthesis have been of interest.

Although the regio- and stereoselectivity, including their mechanistic aspects, have been extensively studied for individual transition metals and alkynes, the factors influencing different dimeric product formations have not been clearly understood. Here, I wish to report regio- and stereoselectivity, scope and limitation in the iridium-catalyzed dimerization of terminal alkynes (Scheme 3).¹⁸ The reaction was greatly accelerated in the presence of a base such as triethylamine, and the products and their stereoselectivity were highly depend on alkynes and phosphine ligand on the iridium catalyst. One of the three possible isomers (**2**, **3** or **4**) was selectively synthesized by choosing an appropriate phosphine ligand and an alkyne, though formation of **1** was not observed under any reaction conditions.



Scheme 3. Iridium-Catalyzed Dimerization of Terminal Alkynes

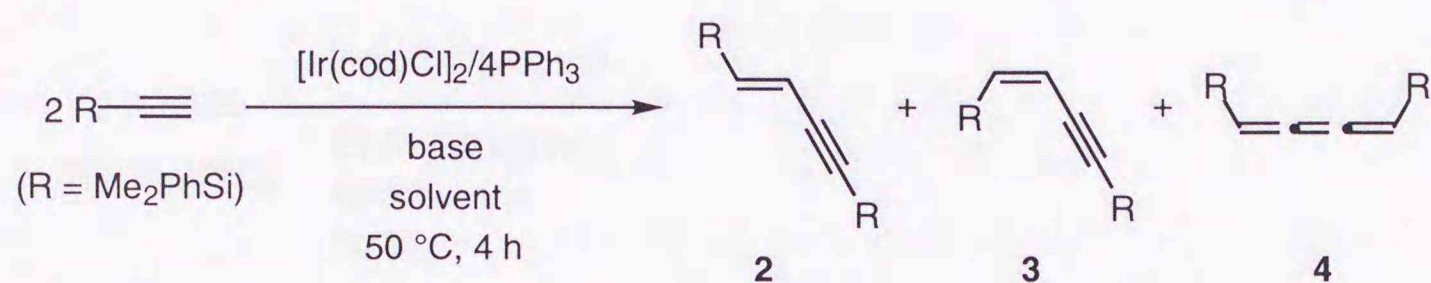
2. Results and Discussions

2-1. Reaction Conditions

The effects of base and solvent on the dimerization of $\text{Me}_2\text{PhSiC}\equiv\text{CH}$ in the presence of $[\text{Ir}(\text{cod})\text{Cl}]_2/\text{PPh}_3$ catalyst are summarized in Table 1. The reaction suffered from low yields and low stereoselectivity (entry 1), but the presence of a catalytic amount or large excess of triethylamine greatly improved the yields and the (*E*)-selectivity ($E:Z = 96:4$) completing the reaction within 4 h at 50 °C (entries 2–4). Diethylamine and diisopropylethylamine similarly gave good results (entries 5 and 6), but cyclohexylamine and less basic pyridine were not effective (entries 7 and 8). The reaction was fast in the less polar solvents such as cyclohexane and toluene (entry 9), but it was very slow in THF, 1,2-dichloroethane, and acetonitrile (entries 10–12). The reaction also gave good results when using triethylamine as the solvent (entry 13).

Table 2 shows the effects of a phosphine ligand on the dimerization of $\text{Me}_2\text{PhSiC}\equiv\text{CH}$ in a cyclohexane solution containing excess of triethylamine (5 equiv). The yields were not significantly affected by stoichiometry of triphenylphosphine to the iridium metal (entries 2–4), but almost no catalyst turnover was observed in the absence of a phosphine ligand (entry 1). The catalyst exhibited a pronounced effect of the ligand, preferring a less basic triarylphosphine for yielding **2** (entries 2–7). Although the reaction was significantly slowed with donating trialkylphosphines, these ligands predominantly produced **3**, in improving yields and *Z* selectivity with an increase in the carbon numbers of the phosphine ligand (entries 9–11). Finally, the best *Z* selectivity exceeding over 96% was achieved by the tripropylphosphine complex (entry 11), whereas bulky trialkylphosphines such as triisopropylphosphine and tricyclohexylphosphine, which have been recommended for the ruthenium-catalyzed dimerization,^{14a,i} resulted in low yields or low selectivity (entries 12–14).

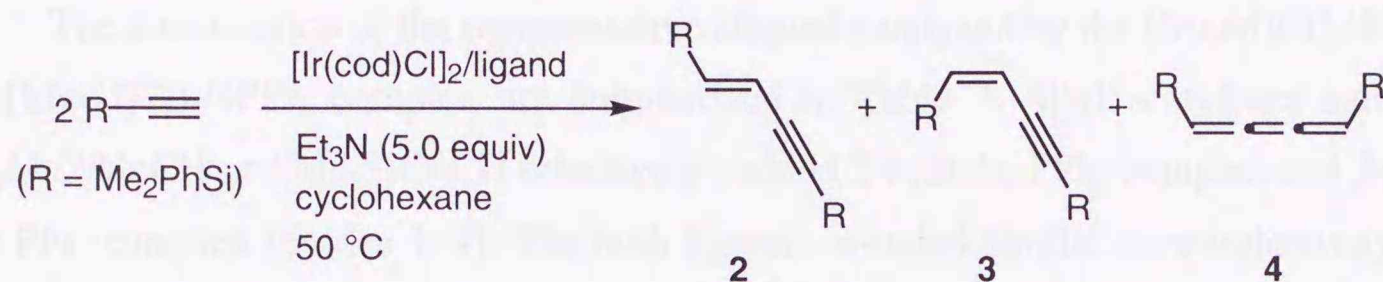
Table 1. Effects of Base and Solvent on Dimerization of Me₂PhSiC≡CH^a



entry	solvent	base (amt, equiv)	yield/% ^b	isomer ratio ^c		
				2	3	4
1	cyclohexane	-	26 ^d	75	25	0
2	cyclohexane	Et ₃ N (0.03)	92	96	4	0
3	cyclohexane	Et ₃ N (1.0)	93	96	4	0
4	cyclohexane	Et ₃ N (5.0)	93	96	4	0
5	cyclohexane	Et ₂ NH (5.0)	89	95	5	0
6	cyclohexane	<i>i</i> -Pr ₂ NEt (5.0)	64	95	5	0
7	cyclohexane	CyNH ₂ (5.0)	29	96	4	0
8	cyclohexane	pyridine (5.0)	23	96	4	0
9	toluene	Et ₃ N (5.0)	80	95	5	0
10	THF	Et ₃ N (5.0)	54	95	5	0
11	ClCH ₂ CH ₂ Cl	Et ₃ N (5.0)	49	94	6	0
12	CH ₃ CN	Et ₃ N (5.0)	49	98	2	0
13	Et ₃ N	-	79	95	5	0

^a A mixture of [Ir(cod)Cl]₂ (0.015 mmol), PPh₃ (0.06 mmol), (dimethylphenylsilyl)ethyne (1 mmol) in solvent (5 mL) was stirred at 50 °C in the presence or absence of a base. ^b Isolate yields by chromatography over silica gel. ^c Determined by ¹H NMR. ^d After 36h.

Table 2. Effects of Ligand on Dimerization of $\text{Me}_2\text{PhSiC}\equiv\text{CH}^a$



entry	ligand (L/Ir)	time/h	yield/% ^b	isomer ratio ^c		
				2	3	4
1	none	4	trace	-	-	-
2	PPh_3 (1)	4	85	95	5	0
3	PPh_3 (2)	4	93	96	4	0
4	PPh_3 (3)	4	85	96	4	0
5	$\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$ (2)	2	99	96	4	0
6	$\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3$ (2)	2	94	94	6	0
7	PMePh_2 (2)	4	71	95	5	0
8	PMe_2Ph (2)	4	23	87	12	1
9	PMe_3 (2)	26	18	51	49	0
10	PEt_3 (2)	26	45	20	78	2
11	PPr_3 (2)	26	75	2	96	2
12	PBu_3 (2)	26	51	16	84	0
13	P^iPr_3 (2)	26	trace	-	-	-
14	PCy_3 (2)	26	trace	-	-	-

^a A mixture of $[\text{Ir(cod)Cl}]_2$ (0.015 mmol), a phosphine ligand (0.03 - 0.09 mmol), Et_3N (5 mmol), (dimethylphenylsilyl)ethyne (1 mmol) in cyclohexane (5 mL) was stirred at 50 °C. ^b Isolate yields by chromatography over silica gel.

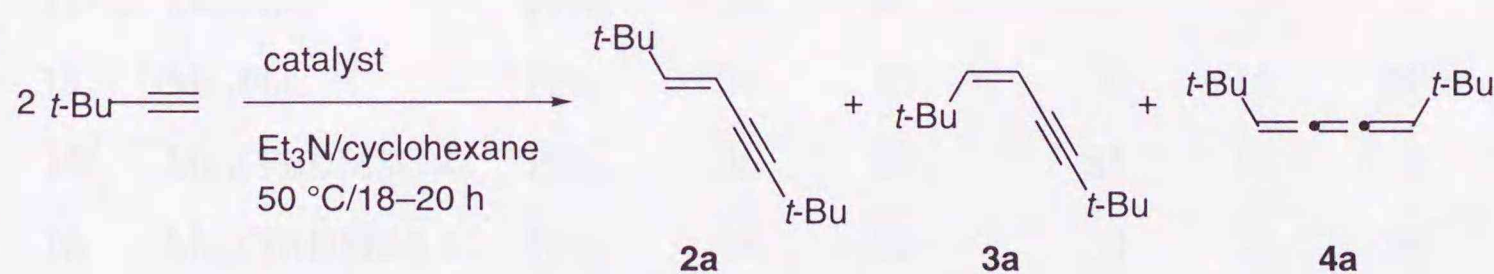
^c Determined by ^1H NMR.

2-2. Dimerization of Terminal Alkynes

The dimerization of the representative alkynes catalyzed by the $[\text{Ir}(\text{cod})\text{Cl}]_2/4\text{PPh}_3$ or $[\text{Ir}(\text{cod})\text{Cl}]_2/4\text{PPr}_3$ complex are summarized in Table 3. Silyl acetylenes such as $\text{Ph}_2\text{MeSiC}\equiv\text{CH}$ and $\text{Me}_3\text{SiC}\equiv\text{CH}$ selectively yielded **2** with the PPh_3 complex and **3** with the PPr_3 complex (entries 1–4). The both ligands revealed similar stereoselectivity for $t\text{-Pr}_3\text{SiC}\equiv\text{CH}$, 2-MeC₆H₄C $\equiv$ CH, and 4-MeC₆H₄C $\equiv$ CH, though these reactions resulted in low yields and low selectivity due to the slow reaction even at 80 °C (entries 5–10).

In contrast to the ligand-controlled reaction shown in entries 1–10, tertiary alkylacetylenes exclusively produced 1,4-disubstituted 1,2,3-butatrienes **4** with the PPr_3 complex, whereas the PPh_3 complex did not change the selectivity giving **2**. (entries 12–16). The formation of **4** can be exclusive in bulky and presumably electron-rich alkynes since the formations of which were negligibly small amount in silylacetylenes and arylacetylenes. On the other hand, all attempts at the dimerization of alkylacetylenes having propargylic hydrogens were unsuccessful (entry 17).

To compare the reactivity and selectivity between iridium and rhodium catalysts, the dimerization of *tert*-butylacetylene was carried out by using rhodium complex under similar reaction conditions used for the iridium catalyst (Scheme 4). The dimerization proceeded smoothly in the presence of catalytic amount of $[\text{Rh}(\text{cod})\text{Cl}]_2/\text{PPr}_3$ complex and triethylamine at 50 °C. However, in contrast to $[\text{Ir}(\text{cod})\text{Cl}]_2/4\text{PPr}_3$ system, **2a** was selectively obtained without accompanying with **4a**.



catalyst	yield (%)	2a	3a	4a
$[\text{Rh}(\text{cod})\text{Cl}]_2/4\text{PPr}_3$	67	100	0	0
$[\text{Ir}(\text{cod})\text{Cl}]_2/4\text{PPr}_3$	74	0	7	93

Scheme 4. Comparison of Selectivity in Dimerization of *tert*-Butylacetylene

Table 3. Dimerization of Terminal Alkynes^a

$2 \text{ R}-\text{C}\equiv\text{CH} \xrightarrow[\text{cyclohexane, 50-80 } ^\circ\text{C, 4-60 h}]{[\text{Ir}(\text{cod})\text{Cl}]_2 (1)\text{-ligand, Et}_3\text{N (5.0 equiv)}}$

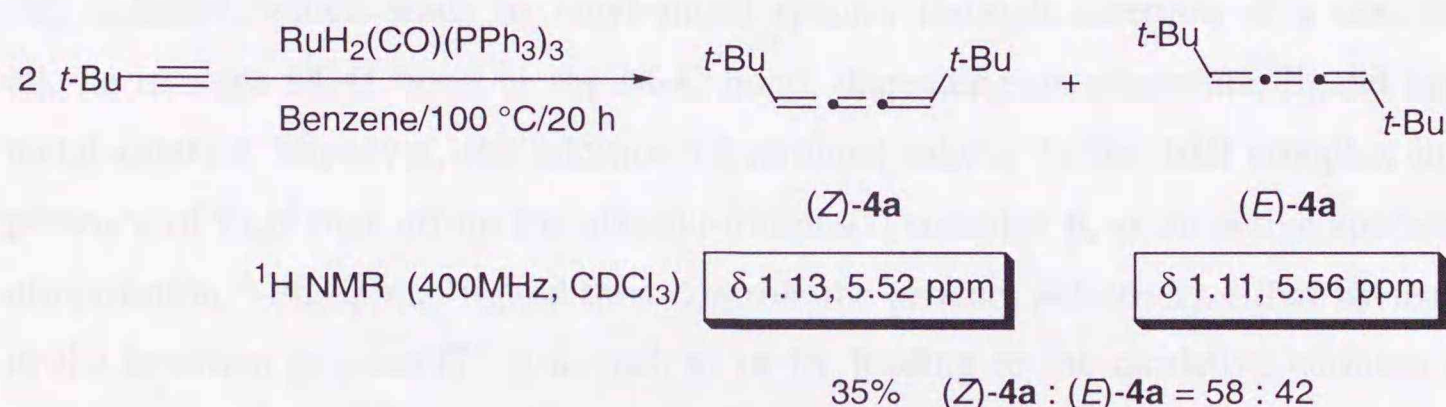
$\text{2} \quad \text{3} \quad \text{4}$

entry	R	ligand	time/h	yield/% ^b	isomer ratio ^c		
					2	3	4
1	Ph ₂ MeSi	PPh ₃	4	95	98	2	0
2	Ph ₂ MeSi	PPr ₃	20	62	11	89	0
3	Me ₃ Si	PPh ₃	6	83	94	6	0
4	Me ₃ Si	PPr ₃	24	70	8	91	1
5 ^d	ⁱ Pr ₃ Si	PPh ₃	12	50	86	14	0
6 ^d	ⁱ Pr ₃ Si	PPr ₃	60	70	14	86	0
7 ^d	2-MeC ₆ H ₄	PPh ₃	9	55	81	19	0
8 ^d	2-MeC ₆ H ₄	PPr ₃	24	78	13	87	0
9 ^d	4-MeC ₆ H ₄	PPh ₃	6	19	66	34	0
10 ^d	4-MeC ₆ H ₄	PPr ₃	24	67	24	76	0
11 ^d	^t C ₄ H ₉	PPh ₃	18	36	94	4	2
12	^t C ₄ H ₉	PPr ₃	18	74	0	7	93 ^e
13 ^d	Me ₂ PhC	PPh ₃	36	53	85	10	5
14	Me ₂ PhC	PPr ₃	24	83	0	16	84 ^f
15 ^d	Me ₂ (TBDMSO)C	PPh ₃	36	23	81	16	3
16	Me ₂ (TBDMSO)C	PPr ₃	36	71	0	22	78 ^f
17 ^d	ⁿ C ₆ H ₁₃	PPh ₃	36	<10			

^a A mixture of [Ir(cod)Cl]₂ (0.015 mmol), a phosphine ligand (0.06 mmol), an alkyne (1 mmol), Et₃N (5 mmol), and cyclohexane (3 mL) was stirred at 50 °C, unless otherwise noted. ^b Isolate yields by chromatography over silica gel. ^c Determined by ¹H NMR. ^d Reactions were conducted at 80 °C in a sealed tube. ^e Reaction gave (Z)-4. ^f The stereochemistry was not determined.

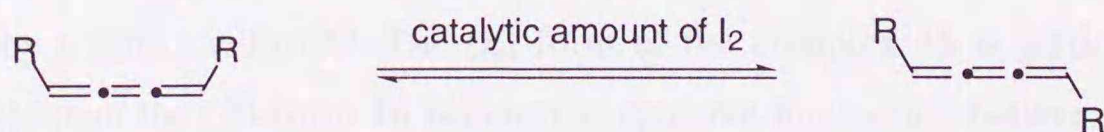
2-3. Stereochemistry of 1,4-Disubstituted-1,2,3-butatrienes

The stereochemistry of the 1,4-di-*tert*-butylbutatriene, obtained by the dimerization of *tert*-butylacetylene ($R = 'C_4H_9$; entry 12 in Table 3), was assigned by 1H NMR spectra of the corresponding *E* and *Z* isomer. The two isomers were prepared by the catalytic dimerization of *t*-butylacetylene with $RuH_2(CO)(PPh_3)_3$,^{14a} giving a mixture of (*Z*)- and (*E*)-1,4-di-*tert*-butylbutatriene (35 % yield, *Z*:*E* = 58:42; Scheme 5). The 1H NMR spectra (400 MHz, $CDCl_3$) showed two sets of two singlets, one at δ 1.13 and 5.52 (*Z* isomer) and the other at δ 1.11 and 5.56 (*E* isomer).¹⁹ The former signals of *Z* isomer were in good agreement with the spectra of the product formed by the iridium-catalyzed dimerization.



Scheme 5. Synthesis of 1,4-Di-*tert*-butylbutatriene Catalyzed by $RuH_2(CO)(PPh_3)_3$

On the other hand, the stereochemistry of 2,7-dimethyl-2,7-diphenylocta-3,4,5-triene ($R = Me_2PhC$; entry 14 in Table 3) and 2,7-bis[(*tert*-butyldimethylsilyl)oxy]-2,7-dimethylocta-3,4,5-triene [$R = Me_2(TBDMSO)C$; entry 16 in Table 3] were not exactly determined because no comparison data for geometry has been reported. But, the treatment of these butatrienes with catalytic amount of iodine resulted in a fast isomerization to a *Z/E* mixture²⁰ giving a geometrical information (Scheme 6). A new



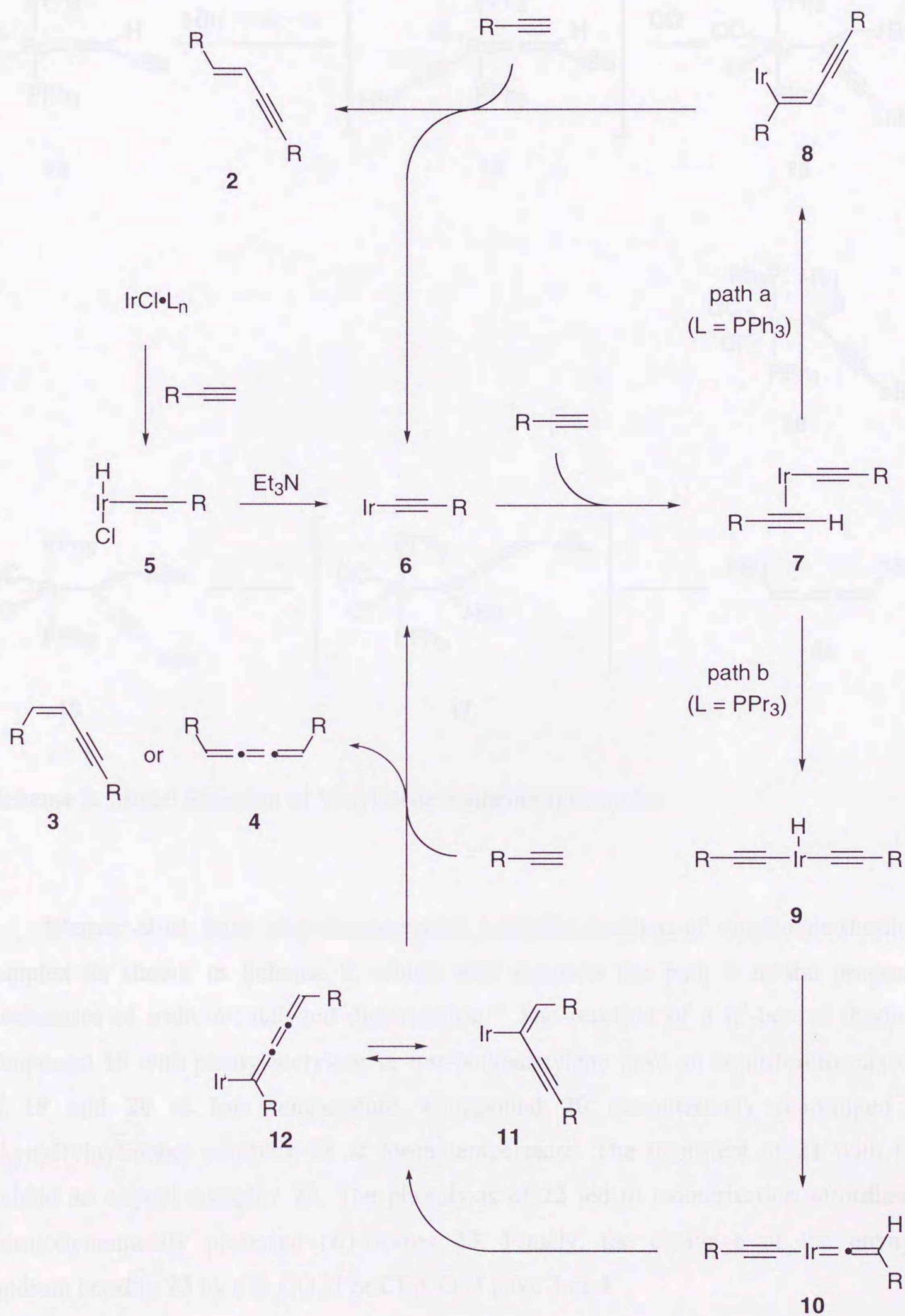
Scheme 6. Isomerization Between (*Z*)- and (*E*)-Butatriene in the Presence of I_2

singlet of vinyl proton was observed by ^1H NMR analysis in addition to original singlet when catalytic amount of iodine was added to a CDCl_3 solution of the butatriene. This result indicated that one of the two isomers of butatriene, presumably *Z* isomer, was also selectively formed in the iridium-catalyzed dimerization of these alkynes.

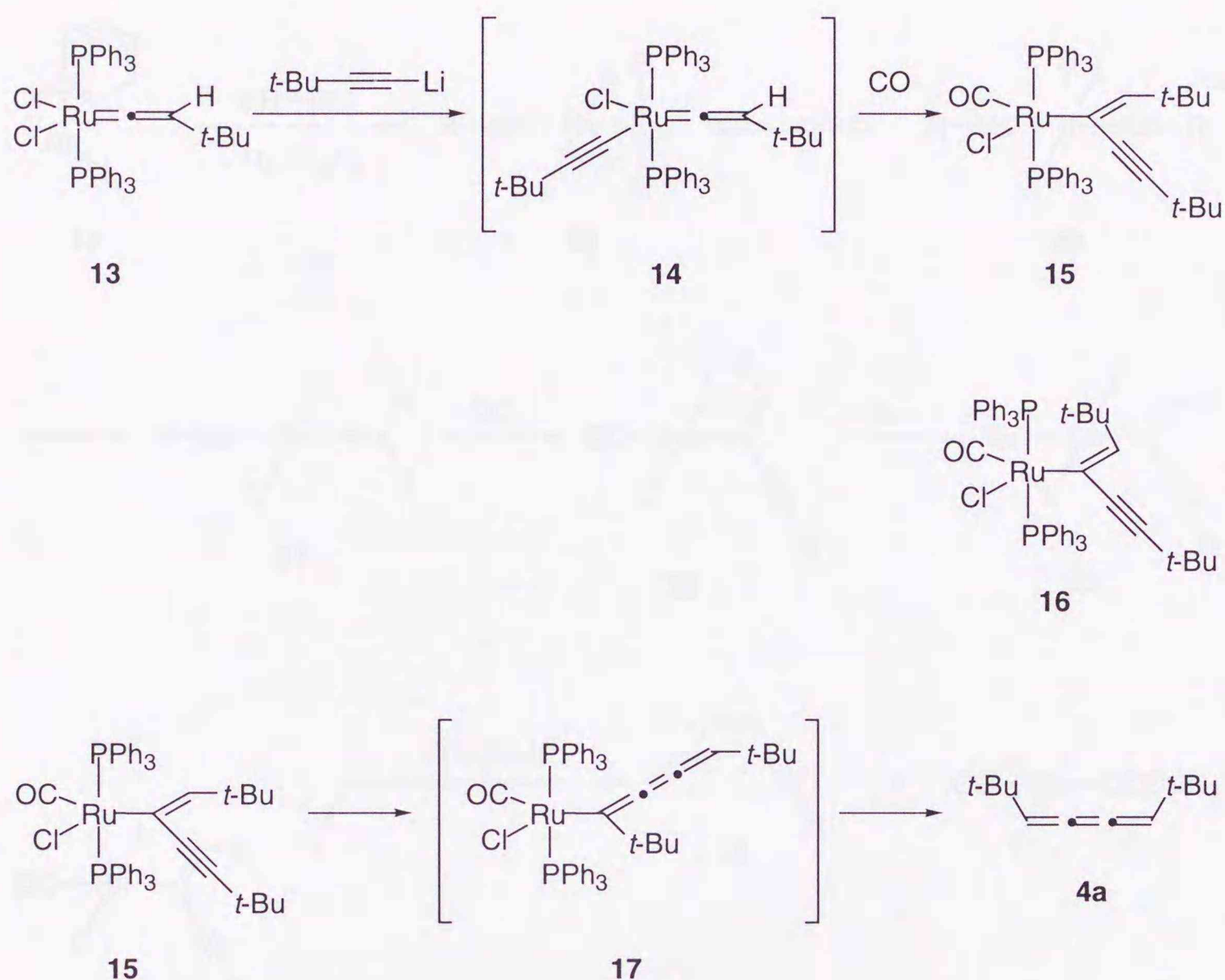
2-4. Reaction Mechanism

A plausible mechanism involving two catalytic cycles (path a and b) is shown in Scheme 7. Although the related dimerization reactions have been carried out under neutral conditions,¹²⁻¹⁶ phosphine ligand and the presence of base were significant for achieving both product selectivity and fast reaction rate. The oxidative addition of the alkyne C-H bond to a low valent transition metal yields $\text{RC}\equiv\text{C}-\text{M}-\text{H}$ ($\text{M} = \text{Rh}, \text{Ir}, \text{Ru}, \text{Pd}$) complex, which leads to vinyl-metal species through insertion of a coordinate alkyne into the M-H bond or the M-C bond, depending on phosphine ligand on the metal catalyst. However, the addition of terminal alkyne to the IrCl complex in the presence of Et_3N may afford the alkynyl-iridium(I) complex **6**, as an active species for dimerization.²¹ Phosphine ligand then controls the product selectivity either by leading to the insertion process (**7** $\rightarrow$ **8**, path a) or by leading to the oxidative addition of a coordinate alkyne (**7** $\rightarrow$ **9**, path b). The "path a" giving **2** is predominant when using the PPh_3 complex, whereas the high electron-donating property of trialkylphosphines such as PPr_3 favors the oxidative addition of the terminal C-H bond (path b) rather than the insertion process. The formation of **3** through the alkynyl(vinylidene) complex **10** and the specific formation of **4** in *tert*-butylacetylene from same intermediate have been amply demonstrated by Wakatsuki^{14a} and Werner²² in the ruthenium and rhodium complexes described below.

Wakatsuki *et al.* have reported a model reaction for the transformation of alkynyl(vinylidene) complex **10** to enynyl complex **11** using a vinylidene ruthenium complex as shown in scheme 8.^{14a} The reaction of the vinylidene complex **13** with *tert*- $\text{BuC}\equiv\text{CLi}$ afforded alkynyl(vinylidene) intermediate **14** which was led to enynyl complex **15** by treating with CO. The (*E*)-form of the complex **15** is sterically much more favorable than the (*Z*)-form **16** because a repulsive interaction between the bulky *tert*-butyl group and other ligands makes the (*Z*)-form **16** unstable. The complex **15** slowly decomposed under heating condition giving **4** through the butatrienyl intermediate **17**.

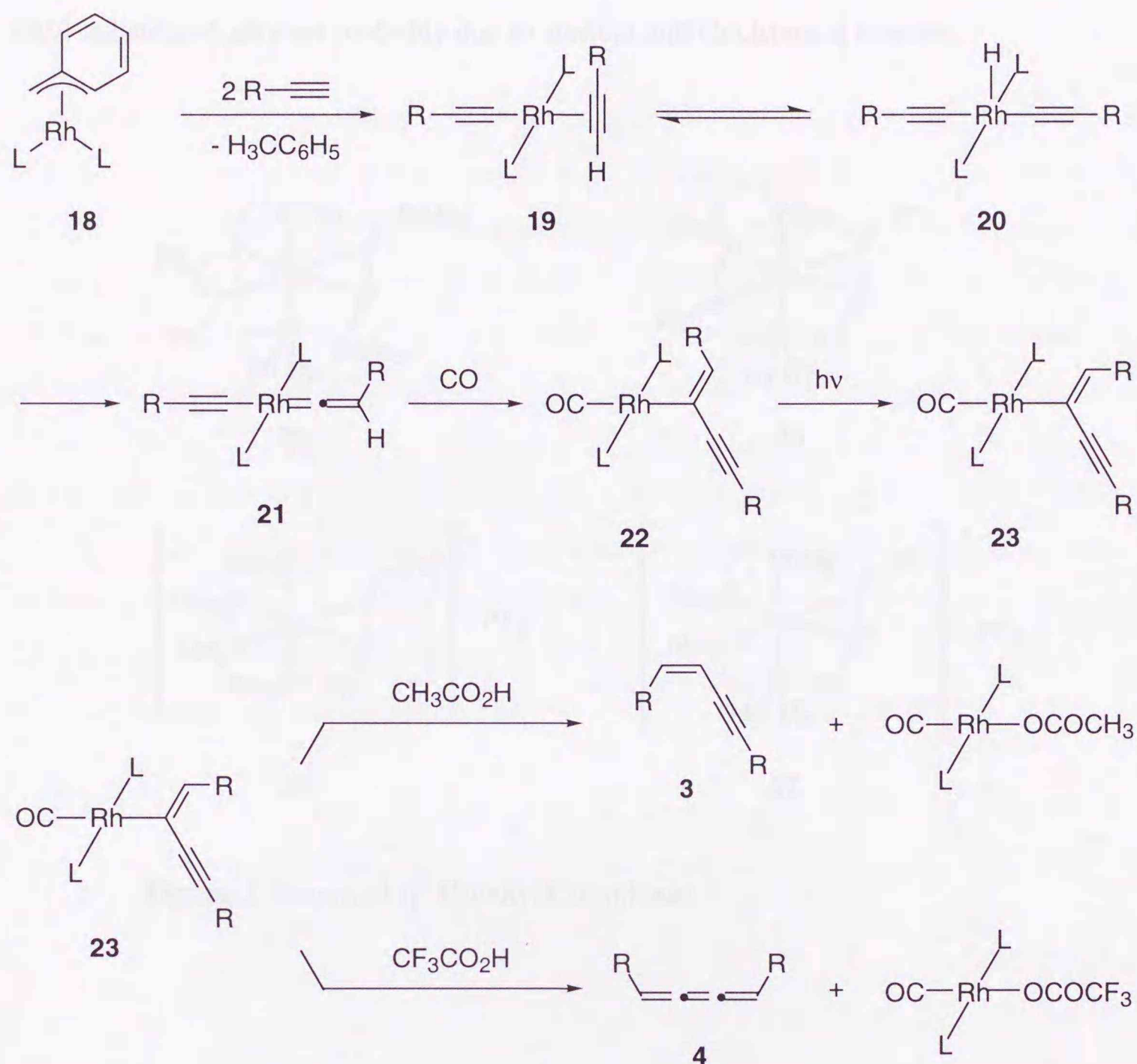


Scheme 7. Proposed Catalytic Cycle



Scheme 8. Model Reaction of Vinylidene Ruthenium Complex

Werner *et al.* have also demonstrated a similar reaction of vinylidene-rhodium complex as shown in Scheme 9, which well supports the path b in the proposed mechanism of iridium-catalyzed dimerization.²² The reaction of a η^3 -benzyl rhodium compound **18** with phenylacetylene or *tert*-butylacetylene gave an equilibrium mixture of **19** and **20** at low temperature. Compound **20** quantitatively rearranged to alkynyl(vinylidene) complex **21** at room temperature. The treatment of **21** with CO yielded an enynyl complex **22**. The photolysis of **22** led to isomerization affording a thermodynamically preferred (*E*)-isomer **23**. Finally, the cleavage of the enynyl-rhodium bond in **23** by $\text{CH}_3\text{CO}_2\text{H}$ or $\text{CF}_3\text{CO}_2\text{H}$ gave **3** or **4**.

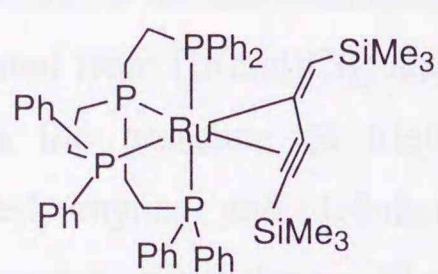


Scheme 9. Model Reaction of Vinylidene Rhodium Complex ($\text{R} = \text{Ph}, ^t\text{Bu}$; $\text{L} = \text{P}^i\text{Pr}_3$)

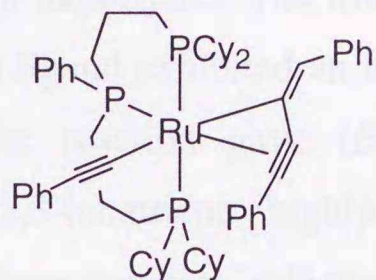
The rearrangement of **11** to **12** may occur by a 1,3-shift of the iridium metal to the acetylenic carbon presumably via η^3 -butenyl intermediate. Some groups have isolated indeed η^3 -butenyl ruthenium,^{14d,23} osmium,²⁴ and iron complexes²⁵ such as **24** – **27** shown in Figure 1. The reported structure of these complexes can be regarded as the transient form of the isomerization of **11** to **12**.

At the final step of the catalytic cycle, the oxidative addition of a next alkyne followed by reductive elimination (or protonation by acetylenic hydrogen) affords either **3** from **11** or **4** from **12**. The equilibrium between **11** and **12** lies to **11** in the reaction of silyl- and aryl-substituted alkynes, while **12** is a more favorable intermediate for tertiary

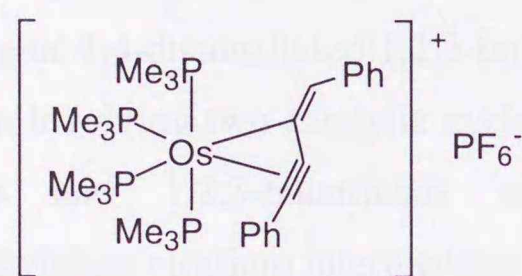
alkyl-substituted alkynes probably due to sterical and electronical reasons.



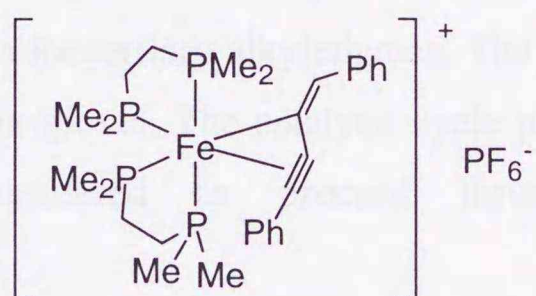
24



25



26



27

Figure 1. Reported η^3 -Butenyl Complexes

3. Conclusion

An iridium catalyzed regio- and stereoselective dimerization of terminal alkynes was demonstrated for the synthesis of enynes and butatrienes. The iridium complex *in situ* generated from $[\text{Ir}(\text{cod})\text{Cl}]_2$ and a phosphine ligand exhibited an excellent catalyst activity in the presence of triethylamine. The reaction gave (*E*)- and (*Z*)-1,4-disubstituted enynes and 1,4-disubstituted 1,2,3-butatriene highly depending on phosphine and starting alkyne. The triarylphosphine complex selectively yielded (*E*)-1,4-disubstituted enynes for silyl-, aryl-, and tertiary alkylethynes, while the tripropylphosphine complex provided (*Z*)-1,4-disubstituted enynes for silyl- and arylalkynes or 1,4-disubstituted 1,2,3-butatrienes for tertiary alkylethynes. The reaction mechanism involving two catalytic cycles was proposed. The catalytic cycle providing (*Z*)-enynes and 1,2,3-butatrienes was considered to proceed through an alkynyl(vinylidene) iridium intermediate.

4. Experimental Section

General.

All the experiments were carried out under argon atmosphere. ^1H NMR spectra were recorded by a JEOL JNM-A400II (400 MHz) spectrometer using CDCl_3 as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra in CDCl_3 were taken on JEOL JNM-A400II (100 MHz) spectrometer. Chemical shifts in ^{13}C NMR spectra were measured relative to CDCl_3 and converted to $\delta_{\text{Me}_4\text{Si}}$ values by using δ_{CDCl_3} 77.0 ppm. IR spectra were determined on a HITACHI 260-10 spectrometer. Mass spectra were obtained on a Finnigan MAT GCQTM apparatus. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-FABmate or a JMS-700TZ apparatus in the Instrumental Analysis Center of the Graduate School of Pharmaceutical Sciences, Hokkaido University.

Solvents and Amines.

Cyclohexane was distilled over lithium aluminum hydride. Toluene was distilled over sodium. 1,2-Dichloroethane, acetonitrile, triethylamine, diethylamine, N, N-diisopropylethylamine, cyclohexylamine, and pyridine were distilled over calcium hydride. Anhydrous THF was purchased from KANTO CHEMICAL CO., INC.

Catalysts and Ligands.

$[\text{Ir}(\text{cod})\text{Cl}]_2$ was prepared from IrCl_3 and 1,5-cyclooctadiene in $\text{EtOH}/\text{H}_2\text{O}$ by the reported procedure.²⁶ $[\text{Rh}(\text{cod})\text{Cl}]_2$ was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 1,5-cyclooctadiene, and sodium carbonate in $\text{EtOH}/\text{H}_2\text{O}$ by the reported procedure.²⁷ $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ was prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ by the reported procedure.²⁸ All phosphines used as the ligand were obtained commercially. PPr_3 , PMe_3 , PEt_3 , PBu_3 , P^iPr_3 , PMePh_2 , and PMe_2Ph were distilled before use.

Alkynes.

All silylethynes used as the starting compounds were synthesized by the reaction of ethynylmagnesium bromide with the corresponding chlorosilanes.²⁹ Two arylethynes were prepared by the method reported in the literature.³⁰ 3-(*tert*-Butyldimethylsilyl)oxy-3-methylbut-1-yne was synthesized by the silylation of 3-methylbut-1-yn-3-ol with *tert*-

butylchlorodimethylsilane and imidazole in DMF. 3,3-Dimethylbut-1-yne was obtained commercially.

Preparation of 3-methyl-3-phenylbut-1-yne: 3-Methyl-3-phenylbut-1-yne was prepared by the similar method reported in the literature.³¹ A solution of phenylmagnesium bromide (101 mmol) in THF (70 ml) was added at 0°C to a stirred solution of LiCuBr₂ (100 mmol), prepared from cuprous bromide (100 mmol) and lithium bromide (100 mmol) in THF (150 ml) with stirring at room temperature for 30 min. Stirring was continued at 0°C during 30 min, then the reaction mixture was cooled at -70°C, and 1-bromo-3-methyl-1,2-butadiene³² (53.6 mmol) was added over a period of 10 min. After stirring was continued at -70°C for 20 min, the cooling bath was removed, and the mixture was allowed to warm to room temperature. The reaction mixture was quenched with aqueous ammonium chloride solution at 0°C, and the organic materials were extracted with ether (three times). The combined extracts were washed with additional aqueous ammonium chloride (five times) and water (three times), dried with anhydrous magnesium sulfate. The solution was contained a mixture of 3-methyl-3-phenylbut-1-yne and 1-phenyl-3-methyl-1,2-butadiene (ca 1 : 1). After concentration by rotary evaporator, the residual oil was distilled under reducing pressure (~65 °C / 5 mmHg), and purified by column chromatography (hexane : benzene = 10 : 1, R_f = 0.6) to afford 1.6 g (11.1 mmol, 21 %) of the 3-methyl-3-phenylbut-1-yne as clear oil; ¹H NMR (400 MHz, CDCl₃): δ 7.21-7.58 (m, 5H), 2.34 (s, 1H), 1.61 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 146.2, 128.3, 126.5, 125.4, 91.0, 69.7, 35.7, 31.5. MS (EI): *m/z* 144 (M⁺, 7), 143 (14), 129 (97), 128 (100).

Reaction Conditions (Table 1 and 2).

A dry 25 ml two-neck flask, equipped with a magnetic stirrer bar and rubber septum cup, was charged with [Ir(cod)Cl]₂ (0.010 g, 0.015 mmol) and then flushed with argon. Anhydrous solvent (5 ml), a phosphine (0.06 mmol), an additive (0.03–5.0 mmol), and Me₂PhSiC≡CH (1.0 mmol) were successively added and the mixture was stirred at 50 °C for 4 h. Evaporation of volatile materials followed by chromatography over silica gel afforded the dimerization product. The product was characterized by the ¹H NMR, ¹³C NMR, IR, and MS analysis. The stereochemistry was assigned by ³J_{HH} values of the olefinic proton, *E* isomer (*J* = 19.3 Hz) and *Z* isomer (*J* = 15.3 Hz), and the isomer ratio was determined by integration values of these peaks.

General Procedure for Iridium-Catalyzed Dimerization of Terminal Alkynes (Table 3).

A dry 25 ml two-neck flask (entries 1–4) or a 10 ml sealed tube (entries 5–17), equipped with a magnetic stirrer bar, was charged with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.010 g, 0.015 mmol) and then flushed with argon. Cyclohexane (3 ml), a phosphine (0.06 mmol), Et_3N (0.7 ml, 5.0 mmol), and an alkyne (1.0 mmol) were successively added. The mixture was stirred at 50 °C (entries 1–4, 12, 14, and 16) or 80 °C (entries 5–11, 13, and 15) for prescribed time. Evaporation of volatile materials followed by chromatography over silica gel afforded the dimeric products **2**, **3**, or **4**.

Rhodium Catalyzed Dimerization of *tert*-butylacetylene (Scheme 4).

A dry 10 ml sealed tube, equipped with a magnetic stirrer bar, was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.007 g, 0.015 mmol) and then flushed with argon. Cyclohexane (5 ml), tripropylphosphine (12 μl , 0.06 mmol), triethylamine (0.7 ml, 5.0 mmol), and *tert*-butylacetylene (0.082 g, 1.0 mmol) were successively added and sealed with screw cup. The mixture was stirred at 50 °C for 20 h. Evaporation of volatile materials followed by chromatography over silica gel afforded the **2a** (0.110 g, 67 %).

Synthesis of (*Z*)- and (*E*)-1,4-Di-*tert*-butylbutatriene catalyzed by $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (Scheme 5).^{14a}

A dry 10 ml sealed tube, equipped with a magnetic stirrer bar, was charged with $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (0.028 g, 0.03 mmol) and then flushed with argon. Benzene (3 ml) and *tert*-butylacetylene (0.079 g, 0.96 mmol) were added and sealed with screw cup. The mixture was stirred at 100 °C for 20 h. Evaporation of volatile materials followed by Kugelrohr distillation (70 °C/7 mmHg) afforded the mixture of (*Z*)- and (*E*)-1,4-di-*tert*-butylbutatriene (0.110 g, 67 %, *Z/E* = 58/42).

I_2 Catalyzed Isomerization of 1,4-Disubstituted-1,2,3-butatrienes (Scheme 6)

To a CDCl_3 solution of 2,7-Dimethyl-2,7-diphenylocta-3,4,5-triene ($\text{R} = \text{Me}_2\text{PhC}$, 0.07 mmol) was added small piece of I_2 and the resulting solution was shaken for several min. The ^1H NMR spectra of the solution showed two sets of vinyl proton peaks and methyl proton peaks, one at δ 1.49 and 5.79 and the other at δ 1.50 and 5.80. The

former was assigned as starting butatriene, and the latter as other isomer. The ratio of the two isomers was 62/38.

Similar experiment for 2,7-Bis[(*tert*-butyldimethylsilyl)oxy]-2,7-dimethylocta-3,4,5-triene [R = Me₂(TBSO)C] gave two methyl proton peaks at δ 1.37 and 1.39. The former was assigned as the peak of new isomer, the ratio of new/original was 45/55. The peak of vinyl proton did not shift after treatment with I₂.

(*E*)-1,4-Bis(dimethylphenylsilyl)but-1-en-3-yne (2: R = Me₂PhSi): ¹H NMR (400 MHz, CDCl₃): δ 7.61-7.63 (m, 2H), 7.49-7.51 (m, 2H), 7.35-7.38 (m, 6H), 6.66 (d, *J* = 19.3Hz, 1H), 6.02 (d, *J* = 19.3Hz, 1H), 0.42 (s, 6H), 0.36 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 145.1, 137.1, 136.8, 133.9, 133.7, 129.4, 129.3, 127.9 (2C), 124.9, 106.7, 93.3, -1.0, -3.0. IR (neat): $\nu_{\text{C}\equiv\text{C}}$ 2170 cm⁻¹. MS (EI): *m/z* 320 (M⁺, 46), 319 (100), 305 (28), 245 (27), 243 (11), 185 (15), 135 (27). HRMS (EI) calcd for C₂₀H₂₄Si₂ 320.1417, found 320.1407.

(*Z*)-1,4-Bis(dimethylphenylsilyl)but-1-en-3-yne (3: R = Me₂PhSi): ¹H NMR (400 MHz, CDCl₃): δ 7.54-7.58 (m, 4H), 7.30-7.38 (m, 6H), 6.42 (d, *J* = 15.3Hz, 1H), 6.32 (d, *J* = 15.3Hz, 1H), 0.46 (s, 6H), 0.39 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 144.2, 138.3, 136.6, 133.8, 133.7, 129.4, 129.0, 127.9, 127.8, 125.9, 106.4, 97.3, -1.2, -2.2. IR (neat): $\nu_{\text{C}\equiv\text{C}}$ 2160 cm⁻¹. MS (EI): *m/z* 320 (M⁺, 80), 319 (100), 305 (71), 245 (88), 243 (88), 185 (15), 135 (27). HRMS (EI) calcd for C₂₀H₂₄Si₂ 320.1417, found 320.1440.

(*E*)-1,4-Bis(trimethylsilyl)but-1-en-3-yne (2: R = Me₃Si): ¹H NMR (400 MHz, CDCl₃): δ 6.51 (d, *J* = 19.4Hz, 1H), 5.97 (d, *J* = 19.4Hz, 1H), 0.18 (s, 9H), 0.08 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 146.9, 123.3, 105.3, 94.7, -0.1, -1.7. IR (neat): $\nu_{\text{C}\equiv\text{C}}$ 2160 cm⁻¹. MS (EI): *m/z* 196 (M⁺, 15), 181 (71), 155 (16), 123 (15), 83 (18), 73 (100). HRMS (EI) calcd for C₁₀H₂₀Si₂ 196.1104, found 196.1081.

(*Z*)-1,4-Bis(trimethylsilyl)but-1-en-3-yne (3: R = Me₃Si): ¹H NMR (400 MHz, CDCl₃): δ 6.26 (d, *J* = 15.1, 1H), 6.16 (d, *J* = 15.1, 1H), 0.19 (s, 9H), 0.19(s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 146.2, 124.5, 105.1, 98.6, -0.3, -1.2. IR (neat): $\nu_{\text{C}\equiv\text{C}}$ 2155 cm⁻¹. MS (EI): *m/z* 196 (M⁺, 29), 181 (100), 155 (18), 123 (10), 73 (46). HRMS (EI) calcd for C₁₀H₂₀Si₂ 196.1104, found 196.1101.

(*E*)-1,4-Bis(diphenylmethylsilyl)but-1-en-3-yne (2: R = MePh₂Si): ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.64 (m, 4H), 7.50-7.52 (m, 4H), 7.33-7.39 (m, 12H), 6.88 (d, *J* = 19.3Hz, 1H), 6.08 (d, *J* = 19.3Hz, 1H), 0.70 (s, 3H), 0.64 (s, 3H). ¹³C NMR (100 MHz,

CDCl_3): δ 143.3, 135.1 (2C), 134.9, 134.5, 129.7, 129.6, 128.0, 127.9, 126.8, 108.0, 92.2, -2.1, -4.1. IR (neat): $\nu_{\text{C}\equiv\text{C}}$ 2160 cm^{-1} . MS (EI): m/z 444 (M^+ , 44), 443 (100), 365 (21), 309 (13), 247 (24), 197 (58), 105 (61). HRMS (EI) calcd for $\text{C}_{30}\text{H}_{27}\text{Si}_2$ ($\text{M}^+ - \text{H}$) 443.1651, found 443.1673.

(Z)-1,4-Bis(diphenylmethylsilyl)but-1-en-3-yne (3: R = MePh₂Si): ^1H NMR (400 MHz, CDCl_3): δ 7.53-7.55 (m, 4H), 7.45-7.47 (m, 4H), 7.27-7.39 (m, 12H), 6.61 (d, J = 15.2Hz, 1H), 6.55 (d, J = 15.2Hz, 1H), 0.72 (s, 3H), 0.54 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.5, 136.2, 134.8, 134.7, 134.5, 129.6, 129.3, 127.8 (2C), 127.4, 107.4, 96.6, -2.4, -3.2. IR (neat): $\nu_{\text{C}\equiv\text{C}}$ 2145 cm^{-1} . MS (EI): m/z 444 (M^+ , 50), 443 (95), 384 (20), 366 (100), 351 (17), 309 (16), 263 (11), 247 (12), 197 (24), 105 (16). HRMS (EI) calcd for $\text{C}_{30}\text{H}_{27}\text{Si}_2$ ($\text{M}^+ - \text{H}$) 443.1651, found 443.1628.

(E)-1,4-Bis(triisopropylsilyl)but-1-en-3-yne (2: R = $i\text{Pr}_3\text{Si}$): ^1H NMR (400 MHz, CDCl_3): δ 6.37 (d, J = 19.5Hz, 1H), 6.04 (d, J = 19.5Hz, 1H), 1.02-1.12 (m, 42H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.0, 125.7, 107.6, 90.3, 18.7, 18.6, 11.4, 10.8. IR (Nujol): $\nu_{\text{C}\equiv\text{C}}$ 2155 cm^{-1} . MS (EI): m/z 364 (M^+ , 26), 321 (100), 279 (48), 157 (30), 115 (27), 83 (57), 73 (44), 59 (47). HRMS (EI) calcd for $\text{C}_{22}\text{H}_{44}\text{Si}_2$ 364.2982, found 364.3010.

(Z)-1,4-Bis(triisopropylsilyl)but-1-en-3-yne (3: R = $i\text{Pr}_3\text{Si}$): ^1H NMR (400 MHz, CDCl_3): δ 6.50 (d, J = 15.9Hz, 1H), 6.03 (d, J = 15.9Hz, 1H), 1.38 (heptet, J = 7.6Hz, 3H), 1.07-1.09 (m, 39H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.2, 126.6, 107.2, 94.9, 18.8, 18.5, 11.6, 11.4. IR (neat): $\nu_{\text{C}\equiv\text{C}}$ 2140 cm^{-1} . MS (EI): m/z 364 (M^+ , 17), 279 (100), 237 (62), 195 (31), 83 (35), 73 (28), 59 (32). HRMS (EI) calcd for $\text{C}_{22}\text{H}_{44}\text{Si}_2$ 364.2982, found 364.3001.

(E)-1,4-Di-*o*-tolylbut-1-en-3-yne (2: R = 2-MeC₆H₄): ^1H NMR (400 MHz, CDCl_3): δ 7.50-7.52 (m, 1H), 7.45 (d, J = 7.6Hz, 1H), 7.27 (d, J = 16.1Hz, 1H), 7.13-7.22 (m, 6H), 6.34 (d, J = 16.1Hz, 1H), 2.49 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.1, 138.6, 135.8, 135.3, 131.9, 130.5, 129.4, 128.4, 128.2, 126.2, 125.6, 124.9, 123.2, 109.3, 93.0, 90.3, 20.8, 19.8. MS (EI): m/z 232 (M^+ , 100), 217 (53), 202 (23), 115 (14). HRMS (EI) calcd for $\text{C}_{18}\text{H}_{16}$ 232.1252, found 232.1248.

(Z)-1,4-Di-*o*-tolylbut-1-en-3-yne (3: R = 2-MeC₆H₄): ^1H NMR (400 MHz, CDCl_3): δ 8.26-8.27 (m, 1H), 7.39 (d, J = 7.3Hz, 1H), 7.12-7.22 (m, 6H), 6.90 (d, J = 12.0Hz, 1H), 6.02 (d, J = 12.0Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.2, 136.5, 136.4, 135.3, 132.1, 130.1, 129.4, 128.3 (2C), 128.2, 125.5 (2C), 123.3, 108.5, 93.9, 91.6, 20.8, 19.8. MS (EI): m/z 232 (M^+ , 100), 231 (20), 217 (48), 202 (18).

HRMS (EI) calcd for $C_{18}H_{16}$ 232.1252, found 232.1251.

(E)-1,4-Di-*p*-tolylbut-1-en-3-yne (**2**: $R = 4\text{-MeC}_6\text{H}_4$): ^1H NMR (400 MHz, CDCl_3): δ 7.36 (d, $J = 8.1\text{Hz}$, 2H), 7.32 (d, $J = 8.1\text{Hz}$, 2H), 7.12-7.20 (m, 4H), 7.00 (d, $J = 16.1\text{Hz}$, 1H), 6.33 (d, $J = 16.1\text{Hz}$, 1H), 2.34 (s, 6H).

(Z)-1,4-Di-*p*-tolylbut-1-en-3-yne (**3**: $R = 4\text{-MeC}_6\text{H}_4$): ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 8.1\text{Hz}$, 2H), 7.38 (d, $J = 8.1\text{Hz}$, 2H), 7.19 (d, $J = 8.1\text{Hz}$, 2H), 7.15 (d, $J = 8.1\text{Hz}$, 2H), 6.64 (d, $J = 12.0\text{Hz}$, 1H), 5.85 (d, $J = 12.0\text{Hz}$, 1H), 2.37 (s, 6H). MS (EI): m/z 232 (M^+ , 100), 217 (49), 202 (40). HRMS (EI) calcd for $C_{18}H_{16}$ 232.1252, found 232.1253.

(E)-1,4-Di-*tert*-butylbut-1-en-3-yne (**2**: $R = \text{'C}_4\text{H}_9$): ^1H NMR (400 MHz, CDCl_3): δ 6.09 (d, $J = 16.1\text{Hz}$, 1H), 5.41 (d, $J = 16.1\text{Hz}$, 1H), 1.24 (s, 9H), 1.02 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.3, 105.2, 97.3, 77.7, 33.8, 31.1, 29.1, 27.9. MS (EI): m/z 164 (M^+ , 100), 149 (60), 121 (31), 107 (27). HRMS (EI) calcd for $C_{12}H_{20}$ 164.1565, found 164.1567.

(Z)-1,4-Di-*tert*-butylbutatriene (**4**: $R = \text{'C}_4\text{H}_9$): ^1H NMR (400 MHz, CDCl_3): δ 5.52 (s, 2H), 1.13 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.5, 118.5, 35.1, 29.8. MS (EI): m/z 164 (M^+ , 70), 149 (56), 135 (46), 121 (100), 107 (92), 94 (69), 91 (64), 79 (49), 57 (63), 41 (56). HRMS (EI) calcd for $C_{12}H_{20}$ 164.1565, found 164.1555.

(E)-2,7-Dimethyl-2,7-diphenyloct-3-en-5-yne (**2**: $R = \text{Me}_2\text{PhC}$): ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.56 (m, 2H), 7.18-7.37 (m, 8H), 6.31 (d, $J = 16.1\text{Hz}$, 1H), 5.55 (d, $J = 16.1\text{Hz}$, 1H), 1.60 (s, 6H), 1.43 (s, 6H).

2,7-Dimethyl-2,7-diphenylocta-3,4,5-triene (**4**: $R = \text{Me}_2\text{PhC}$): ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.42 (m, 4H), 7.30-7.34 (m, 4H), 7.18-7.22 (m, 2H), 5.79 (s, 2H), 1.49 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.8, 148.4, 128.2, 126.0, 118.1, 42.2, 29.1. MS (EI): m/z 288 (M^+ , 32), 273 (100), 245 (40), 231 (38), 215 (21), 197 (21), 167 (18), 156 (19), 141 (21), 119 (39), 91 (40). HRMS (EI) calcd for $C_{22}H_{24}$ 288.1878, found 288.1870. The stereochemistry was not determined.

(E)-2,7-Bis[(*tert*-butyldimethylsilyl)oxy]-2,7-dimethyloct-3-en-5-yne [**2**: $R = \text{Me}_2(\text{TBDMSO})\text{C}$]: ^1H NMR (400 MHz, CDCl_3): δ 6.11 (d, $J = 15.9\text{Hz}$, 1H), 5.67 (d, $J = 15.9\text{Hz}$, 1H), 1.47 (s, 6H), 1.30 (s, 6H), 0.88 (s, 9H), 0.87 (s, 9H), 0.16 (s, 6H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.0, 106.0, 94.8, 81.1, 73.1, 66.6, 32.9, 30.1, 25.8, 25.7, 18.1, 17.9, -2.1, -3.1. MS (EI): m/z 396 (M^+ , 0.1), 381 (5), 339 (100), 207 (13), 173 (20), 147 (26), 75 (61), 73 (50). HRMS (EI) calcd for $C_{18}H_{35}O_2Si_2$ ($M^+ - \text{'C}_4\text{H}_9$)

339.2176, found 339.2169.

2,7-Bis[(*tert*-butyldimethylsilyl)oxy]-2,7-dimethylocta-3,4,5-triene [4: R = Me₂(TBDMSO)C]: ¹H NMR (400 MHz, CDCl₃): δ 5.75 (s, 2H), 1.39 (s, 12H), 0.86 (s, 18H), 0.08 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): 160.4, 117.9, 73.8, 30.5, 25.7, 18.0, -2.3. MS (EI): *m/z* 396 (M⁺, 1), 339 (50), 265 (11), 207 (20), 173 (100), 147 (24), 115 (12), 75 (38), 73 (65). HRMS (EI) calcd for C₁₈H₃₅O₂Si₂ (M⁺-¹C₄H₉) 339.2176, found 339.2150. The stereochemistry was not determined.

Abbreviations

acac	acetylacetonate
Ac	acetyl
cod	1,5-cyclooctadiene
cot	cyclooctatetraene
Cp	cyclopentadienyl
Cy	cyclohexyl
TBDMS	<i>tert</i> -butyldimethylsilyl
TDMPP	tris(2,6-dimethoxyphenyl)phosphine
THF	tetrahydrofuran

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Chapter 3

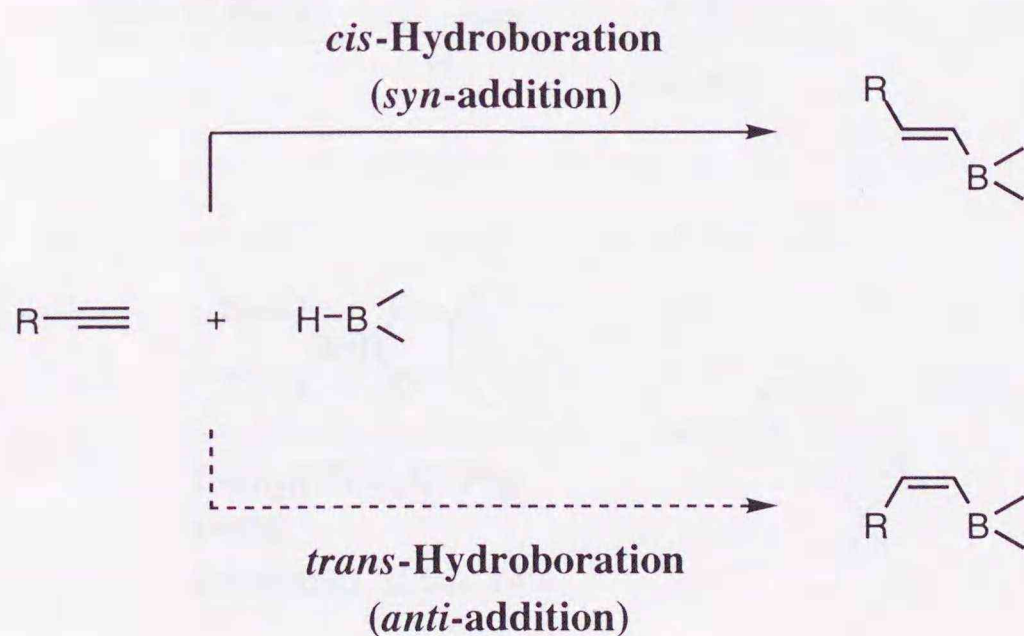
Rhodium- or Iridium-Catalyzed *trans*-Hydroboration of Terminal Alkynes, Giving (Z)-1-Alkenylboronic Esters

Abstract: The complex *in situ* generated from $[M(\text{cod})\text{Cl}]_2$ ($M = \text{Rh}$ or Ir) and P^iPr_3 catalyzed a stereo- and regioselective *trans*-hydroboration of terminal alkynes with catecholborane (**1a**) or pinacolborane (**1b**) in the presence of Et_3N . The reaction yielded the (Z)-1-alkenylboronates with more than 96% selectivity for various terminal alkynes. The mechanism proceeding through a vinylidene complex was proposed since the selective migration of the alkyne terminal hydrogen to the β -carbon was observed in the hydroboration of 1-deuterio-1-octyne with **1a**.

1. Introduction

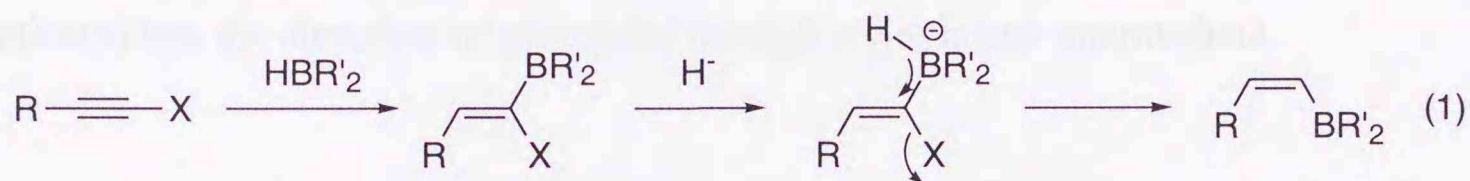
Hydroboration of alkynes and alkenes is a practical route for the syntheses of 1-alkenyl and alkylboron compounds which are a versatile reagent for organic synthesis.^{1,2} Although the method is now most common and convenient for large-scale preparations, the metal-catalyzed reactions are advantageous in terms of efficiency and selectivity of the transformation. However, the catalytic hydroboration did not attract much attention until a report by Männig and Nöth in 1985,³ $\text{RhCl(PPh}_3)_3$ (Wilkinson complex) catalyzes the addition of catecholborane (**1a**) to alkenes or alkynes. Not only the transition-metal complexes significantly accelerate the slow reaction of (dialkoxy)boranes, but the catalytic hydroboration to be a more interesting strategy to realize the different chemo-, regio-, diastereo-, and enantioselectivities, relative to the uncatalyzed reaction.

Although much attention has been recently focused on metal-catalyzed hydroboration with catecholborane (**1a**) or pinacolborane (**1b**), both the uncatalyzed^{1,4} and the catalyzed reaction^{5,6} selectively yields (*E*)-1-alkenylboron compounds through the *anti*-Markovnikov and *syn*-addition of borane to terminal alkynes (Scheme 1). Thus, an alternative, multi-step methods have been developed for the synthesis of (*Z*)-1-alkenylborans. These include the intramolecular $\text{S}_{\text{N}}2$ -type substitution of 1-halo-1-alkenylboronates with metal hydrides (eq. 1),⁷ the catalytic *cis*-hydrogenation of 1-alkynylboronates (eq. 2),⁸ the hydrozirconation of 1-alkynylboronates followed by

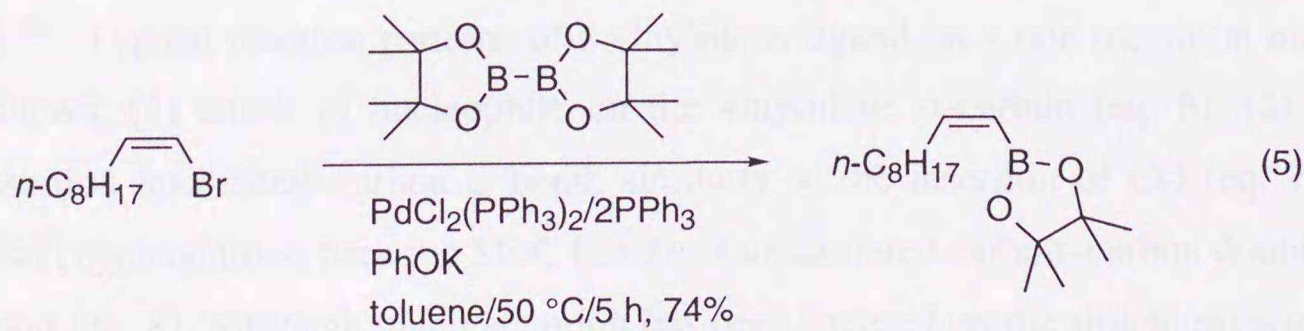
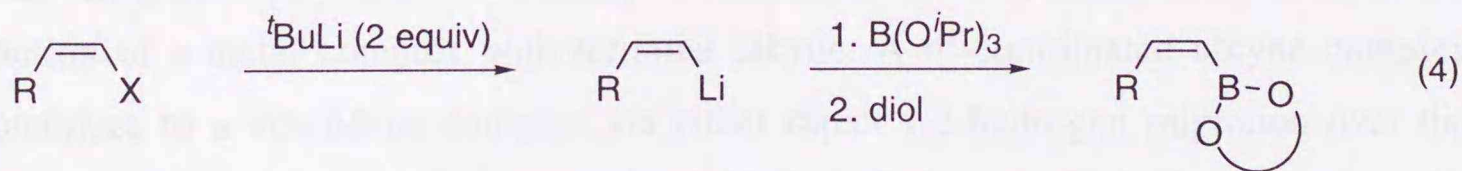
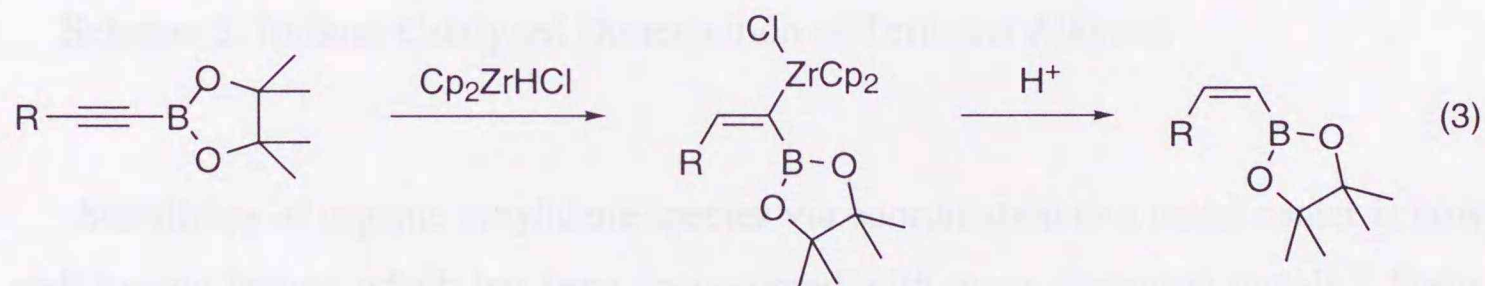
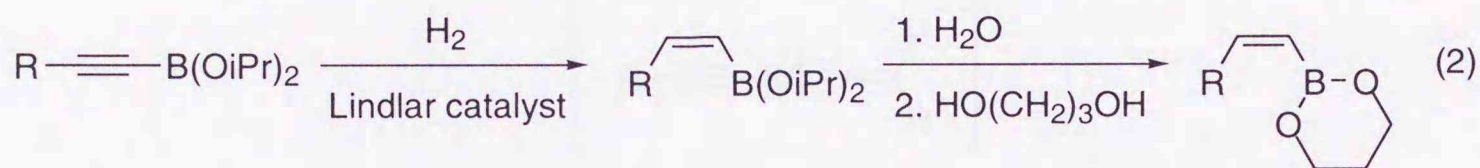


Scheme 1. Hydroboration of Terminal Alkyne

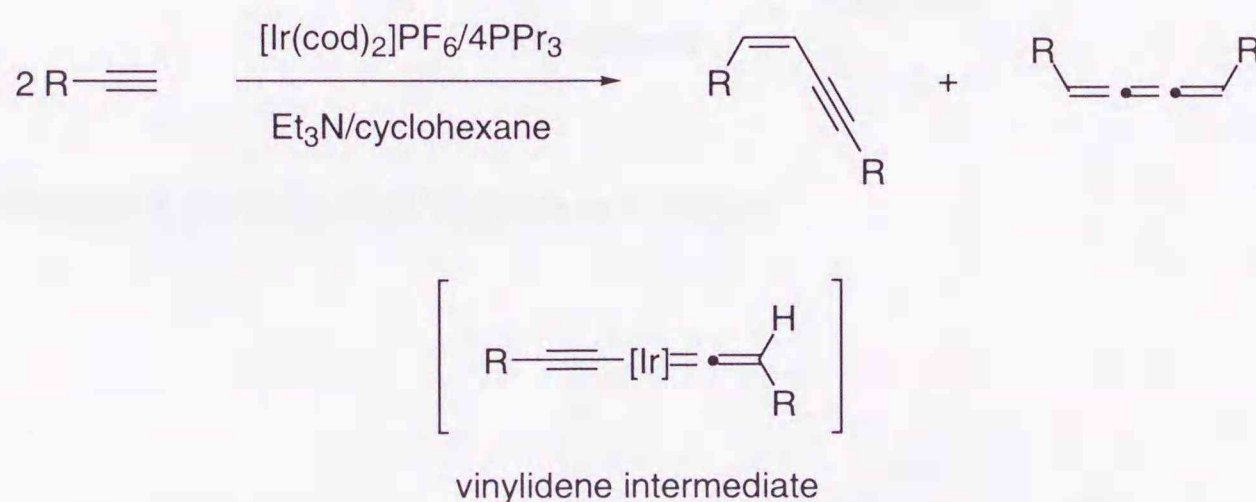
hydrolysis (eq. 3),⁹ and the transmetalation between (Z)-alkenyllithiums and trialkylborates (eq. 4).¹⁰ Very recently, palladium-catalyzed cross-coupling reaction of bis(pinacolate)diboron with (Z)-1-bromo-1-alkenes was developed (eq. 5).^{11,12}



H⁺ source: ^tBuLi, LiEt₃BH, K[(ⁱPrO)₃BH], ⁿBu₃SnH

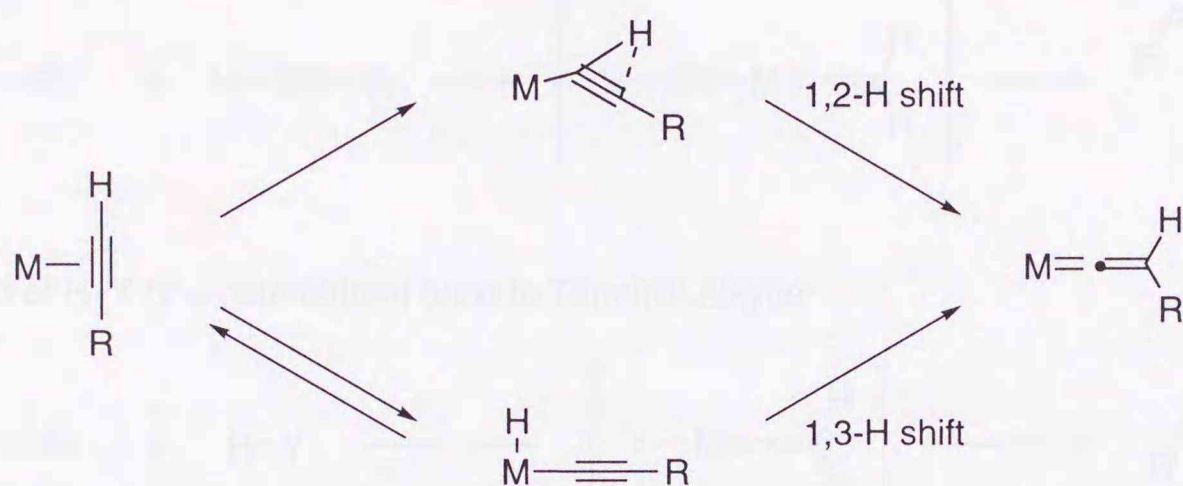


As mentioned in chapter 2, we have recently found the iridium-catalyzed dimerization of terminal alkynes (Scheme 2).¹³ The reaction provided (Z)-1,4-disubstituted enynes or 1,4-disubstituted-1,2,3-butatrienes from sterically hindered terminal alkynes in the presence of an Ir(I)-PPr₃ catalyst. An important information was provided from this research because the formation of (Z)-enynes and 1,2,3-butatrienes indicated that the dimerization proceeded through a vinylidene intermediate.

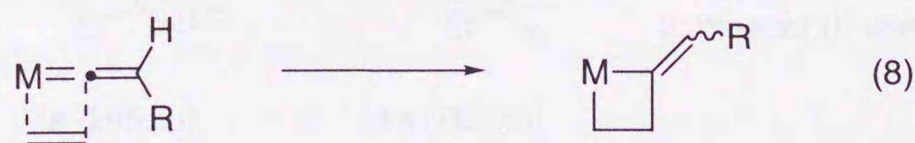
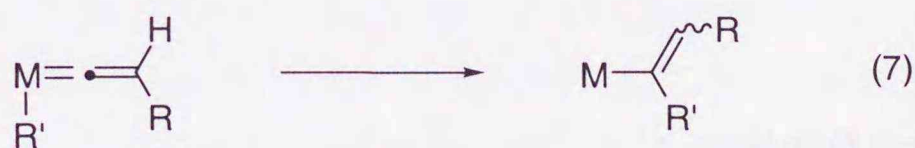
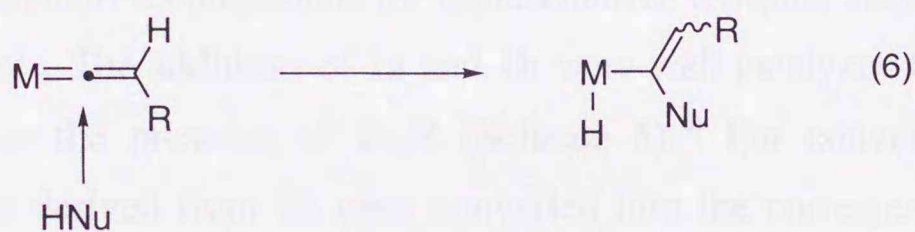


Scheme 2. Iridium-Catalyzed Dimerization of Terminal Alkynes

Stabilizing of organic vinylidene species via coordination to a metal center is now a well-known feature which has been encountered with many transition metals.¹⁴ Some of the different routes to produce metal vinylidene species have been reported, but the most straightforward and catalytically useful route to vinylidene complexes is the reaction of a metal complex with terminal alkyne. A η^2 -coordinated alkyne complex isomerizes to a vinylidene complex via either direct 1,2-hydrogen migration over the carbon-carbon triple bond¹⁵ or oxidative addition of the acetylenic C-H bond to the metal center and subsequent 1,3-shift of the hydride to the alkynyl ligand (Scheme 3).^{16,17} Typical reaction patterns of a vinylidene ligand on a late transition metal are as follows: (1) attack of nucleophile on the vinylidene α -carbon (eq. 6), (2) migratory insertion into metal-carbon σ bond, similarly to the insertion of CO (eq. 7), and (3) [2+2] cycloaddition between M=C bond and unsaturated carbon-carbon double or triple bond (eq. 8). Although much attention has been focused on the stoichiometric reactions of vinylidene complex, the catalytic reactions involving this attractive intermediate have not yet been developed.^{14c,18,19} However, a catalytic activation of terminal alkyne *via*

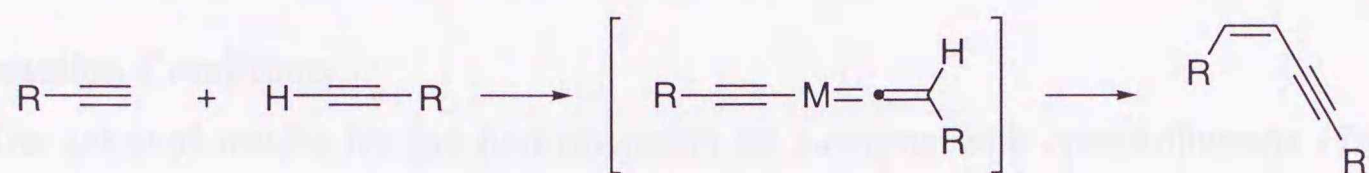


Scheme 3. Formation of Vinylidene Complex

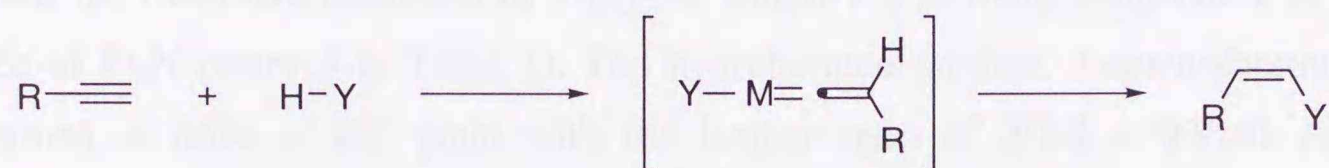


vinylidene complex can be expected to show different reactivity and selectivity from conventional methods. Therefore, we decided to examine the transition metal catalyzed addition reaction of H-Y (Y = heteroatom) bond to terminal alkynes *via* formation of vinylidene complex as a key step (Scheme 4).

Addition of Acetylenic H-C bond to Terminal Alkyne

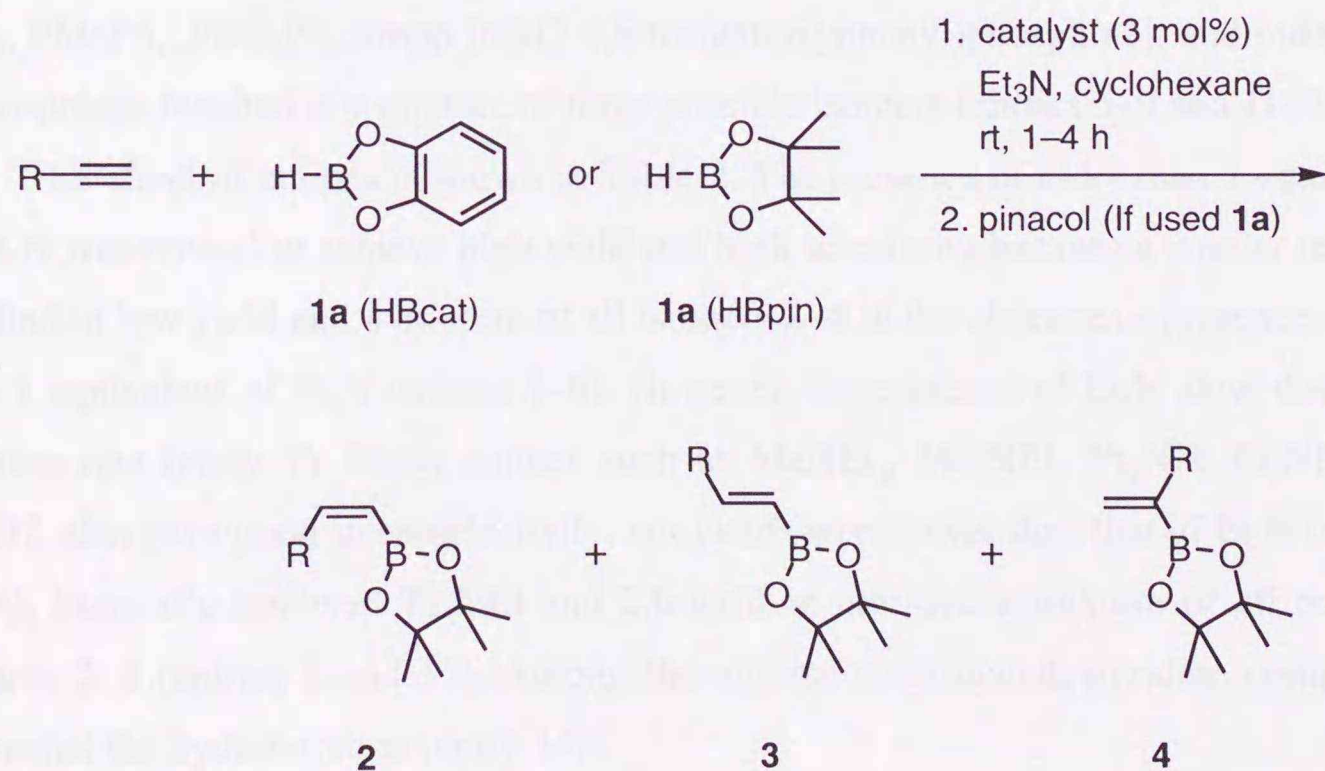


Addition of H-Y (Y = heteroatom) bond to Terminal Alkyne



Scheme 4. Research Concept

I wish to report herein a stereo- and regioselective *trans*-hydroboration directly producing (*Z*)-1-alkenylboron compounds for representative terminal alkynes through a vinylidene intermediate. The additions of **1a** and **1b** were well catalyzed by a Rh(I)- or Ir(I)-P'Pr₃ complex in the presence of Et₃N (Scheme 5).²⁰ For convenience of the analyses, all products derived from **1a** were converted into the corresponding pinacol esters prior to isolation of **2-4**.



Scheme 5. *trans*-Hydroboration of Terminal Alkynes

2. Results and Discussions

2-1. Reaction Conditions

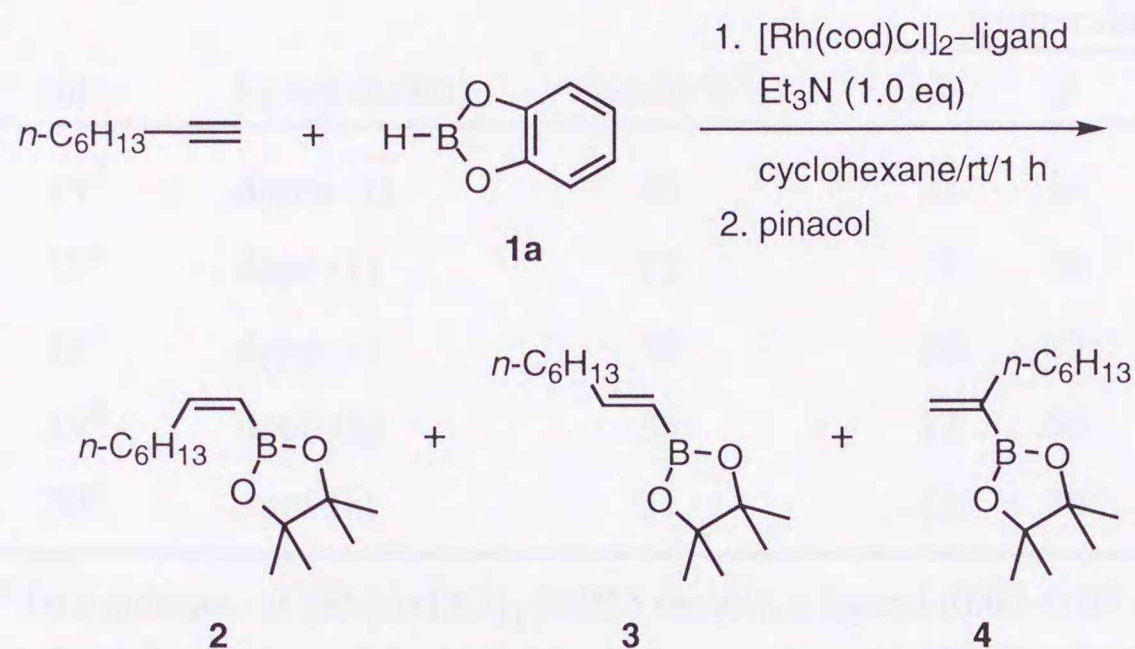
The selected results for the hydroboration of 1-octyne with catecholborane (**1a**) are shown in Table 1-5.

The catalyst *in situ* generated from $[\text{Rh}(\text{cod})\text{Cl}]_2$ (1.5 mol%) and P^iPr_3 (6.0 mol%) completed the *trans*-hydroboration of 1-octyne within 1 h at room temperature in the presence of Et_3N (entry 3 in Table 1). The hydroborated product, 1-octenylboronate, was formed in 86% of GC yield with the isomer ratio of $2/3/4 = 99/1/0$. After chromatographic separation on silica gel, an isomerically pure (*Z*)-1-octenylboronate was obtained in 74% yield.

The effect of phosphine ligands in the hydroboration is shown in Table 1. In the absence of phosphine ligand, only *cis*-hydroboration proceeded and **2** was not formed at all (entry 1). The use of two equivalent of P^iPr_3 per rhodium was recommended for achieving high yield and high stereoselectivity, because one equivalent of P^iPr_3 gave the products with low stereoselectivity and three equivalent of it resulted in low yields (entries 2 and 3). The steric and electronic effects of P^iPr_3 play a major role in influencing the course of the reaction, as evidenced by low product selectivity in other trialkylphosphines and triarylphosphines. Although a PCy_3 complex gave comparable selectivity (entry 10), other rhodium complexes of PMe_3 , PEt_3 , P^nPr_3 , P^nBu_3 , P^iBu_3 , P^nBu_3 , PPh_3 , PMePh_2 , PMe_2Ph , ttmpp [tris(2,4,6-trimethoxyphenyl)phosphine], and bidentated diphosphines resulted in a mixture of three possible isomers (entries 5-9 and 11-20).

The effect of amines is shown in Table 2. The presence of more than 1 equivalent of Et_3N was critical to achieve high yield and high selectivity because a similar reaction resulted in low yield and a mixture of all isomers **2-4** in the absence or presence of less than 1 equivalent of Et_3N (entries 1-6). However, large excess of Et_3N slow down the reaction rate (entry 7). Other amines such as MeNEt_2 , Me_2NEt , $^i\text{Pr}_2\text{NH}$, Et_2NH , and CyNH_2 also gave good stereoselectivity, but yields were lower than that of Et_3N (entries 9-13). Sterically hindered $^i\text{Pr}_2\text{NEt}$ and 2,6-lutidine afforded a mixture of all possible isomers **2-4** (entries 8 and 15). Among the amines investigated, pyridine completely prevented the hydroboration (entry 14).

Table 1. Effect of Ligands in the Hydroboration of 1-Octyne with **1a**^a



entry	ligand (L/Rh)	yield/% ^b	isomer ratio ^c		
			2	3	4
1	none	41	0	72	28
2	P ⁱ Pr ₃ (1)	82	70	23	7
3	P ⁱ Pr ₃ (2)	86 (74)	99	1	0
4	P ⁱ Pr ₃ (3)	72	99	1	0
5	PMe ₃ (2)	59	12	64	24
6	PEt ₃ (2)	65	44	50	6
7	P ⁿ Pr ₃ (2)	60	52	42	6
8	P ⁿ Bu ₃ (2)	56	48	45	7
9	P ⁱ Bu ₃ (2)	62	43	47	10
10	PCy ₃ (2)	86	98	2	0
11	P ⁱ Bu ₃ (2)	34	21	64	15
12	PPh ₃ (2)	60	6	79	15
13	PPh ₂ Me (2)	44	17	69	14
14	PPhMe ₂ (2)	20	30	54	16
15	ttmpp (2)	32	0	65	35

Continued

Table 1. Continued

entry	ligand (L/Rh)	yield/% ^b	isomer ratio ^c		
			2	3	4
16 ^d	dppm (1)	46	24	64	12
17 ^d	dppe (1)	22	7	74	19
18 ^d	dppp (1)	35	18	60	22
19 ^d	dppb (1)	36	12	66	22
20 ^d	dppf (1)	31	11	70	19

^a To a solution of [Rh(cod)Cl]₂ (0.015 mmol), a ligand (0.03–0.09 mmol), Et₃N (1.0 mmol), and **1a** (1.0 mmol) in cyclohexane (3 ml) was added 1-octyne (1.2 mmol). The mixture was then stirred at rt for 1 h, unless otherwise noted. ^b GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. ^c Determined by ¹H NMR of crude product. ^d Reaction was carried out in benzene.

Table 2. Effect of Amines in the Hydroboration of 1-Octyne with **1a**^a

$$n\text{-C}_6\text{H}_{13}\text{—}\equiv + \mathbf{1a} \xrightarrow[\text{2. pinacol}]{\text{1. [Rh(cod)Cl]}_2\text{—}4\text{P}^i\text{Pr}_3, \text{ amine (0.03–5.0 eq)/cyclohexane/rt/1 h}}$$

entry	additive (equiv.)	yield/% ^b	isomer ratio ^c		
			2	3	4
1	none	78	24	60	16
2	Et ₃ N (0.03)	82	21	65	14
3	Et ₃ N (0.2)	89	30	60	10
4	Et ₃ N (0.5)	87	80	17	3
5	Et ₃ N (0.75)	81	95	4	1
6	Et ₃ N (1.0)	86 (74)	99	1	0
7	Et ₃ N (5.0)	63	99	1	0
8	<i>i</i> Pr ₂ NEt (1.0)	86	53	38	9
9	MeNEt ₂ (1.0)	62	96	4	0
10	Me ₂ NEt (1.0)	41	90	10	0
11	<i>i</i> Pr ₂ NH (1.0)	68	96	4	0
12	Et ₂ NH (1.0)	76	99	1	0
13	CyNH ₂ (1.0)	63	99	1	0
14	pyridine (1.0)	4	-	-	-
15	2,6-lutidine (1.0)	80	53	35	12

^a To a solution of [Rh(cod)Cl]₂ (0.015 mmol), P^{*i*}Pr₃ (0.06 mmol), an amine (0.03–5.0 mmol), and **1a** (1.0 mmol) in cyclohexane (3 ml) was added 1-octyne (1.2 mmol). The mixture was then stirred at rt for 1 h, unless otherwise noted. ^b GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. ^c Determined by ¹H NMR of crude product.

Another dominant factor reversing the conventional *cis*-hydroboration to the *trans*-hydroboration was the use of alkyne in excess of the borane reagent. Table 3 shows the effect of stoichiometry of **1a** to 1-octyne. The excellent *Z* selectivity was achieved when 1.2 equivalents of 1-octyne was used (entry 1), but (*E*)-isomer **3** predominated when using a slightly excess of **1a** (entry 3). The reaction initially yields (*Z*)-alkenylboronates **2** (entry 2), but isomerization of **2** to a more stable (*E*)-isomer **3** takes place after completion of hydroboration.

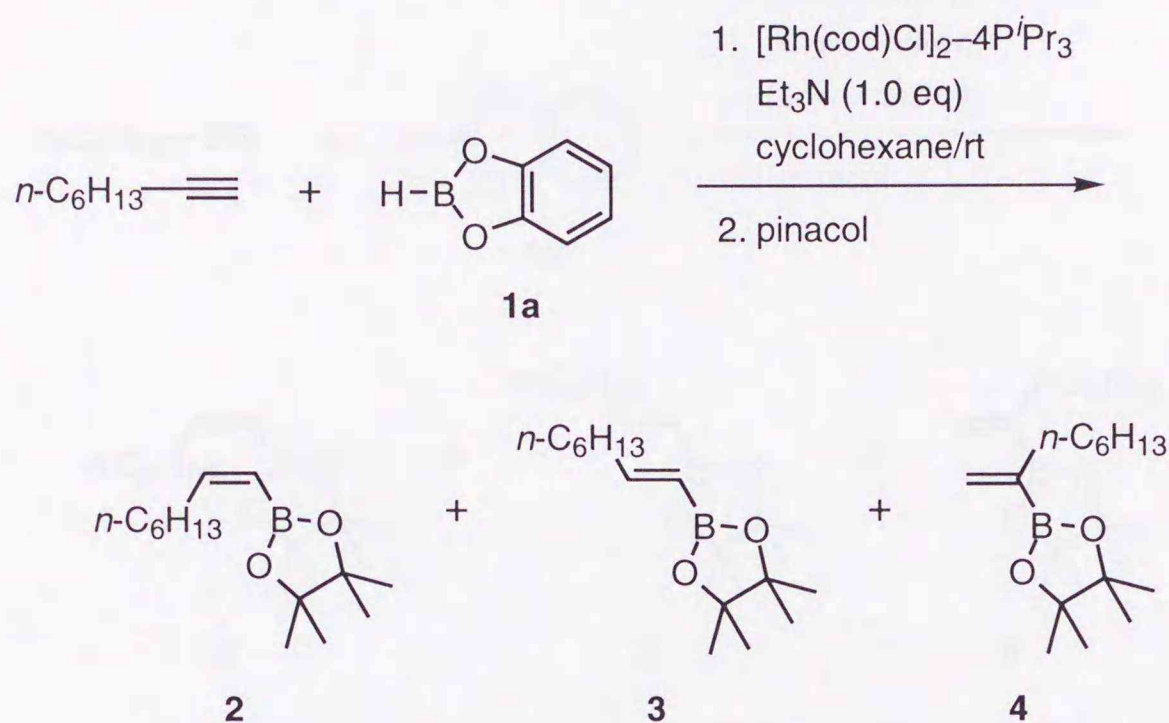
Table 4 shows the effects of solvents. The *trans*-hydroboration was fast in nonpolar solvent such as cyclohexane, hexane, benzene, and toluene (entries 1–4). On the other hand, the reaction was slow and resulted in low selectivity in THF and dichloromethane (entries 5 and 6).

The effect of catalyst precursors for the *trans*-hydroboration of 1-octyne is shown in Table 5. Both the neutral and the cationic rhodium complexes such as $[\text{Rh}(\text{cod})\text{Cl}]_2$, $[\text{Rh}(\text{coe})_2\text{Cl}]_2$, $\text{Rh}(\text{coe})_2(\text{acac})$, and $[\text{Rh}(\text{cod})_2]\text{BF}_4$ showed good catalyst activity for the *trans*-hydroboration to give **2** with high yields and excellent stereoselectivity (entries 1–4). The iridium, ruthenium, palladium, and platinum complexes catalyze various hydrometalations, but these metal complexes of P^iPr_3 and other phosphines failed to achieve selective hydroboration (entries 5–9).

The results of the hydroboration of 1-octyne with pinacolborane (**1b**) is summarized in Table 6.

High (*Z*)-selectivity exceeding 90% was achieved in the presence of 2.0 equivalents of 1-octyne and 5.0 equivalents of Et_3N (entry 1), whereas the reaction again resulted in a mixture of **2**, **3**, and **4** (69/26/5) when using an equivalent of 1-octyne to **1b** (entry 2). The Ir(I)-catalyzed reaction of **1b** was more selective than that of **1a**, though the reaction was accompanied with some dihydroboration product (entries 3 and 4).

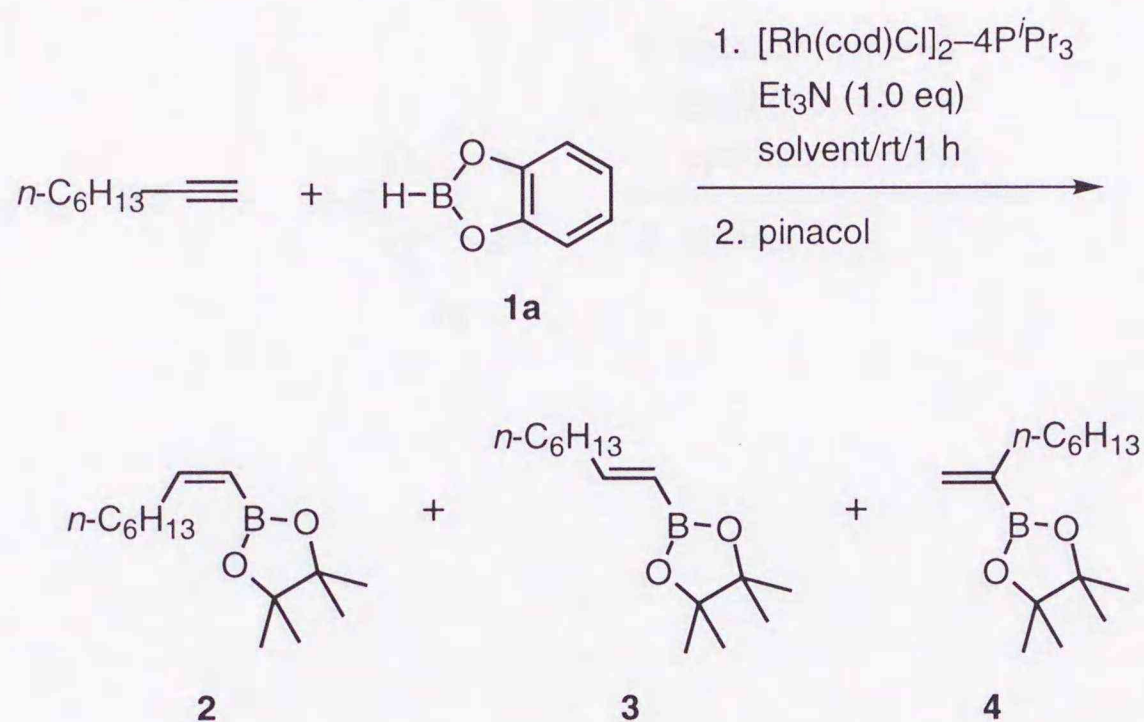
Table 3. Effect of Stoichiometry of Borane in the Hydroboration of 1-Octyne with **1a**^a



entry	1-octyne/ 1a	time/h	yield/% ^b	isomer ratio ^c		
				2	3	4
1	1.2	1	86 (74)	99	1	0
2	0.85	0.25	90 ^d	96	4	0
3	0.85	1	94 ^d	9	90	1

^a To a solution of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.015 mmol), P^iPr_3 (0.06 mmol), Et_3N (1.0 mmol), and **1a** (1.0 mmol) in cyclohexane (3 ml) was added 1-octyne (0.85 or 1.2 mmol). The mixture was then stirred at rt. ^b GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. ^c Determined by ^1H NMR of crude product. ^d GC yield based on 1-octyne.

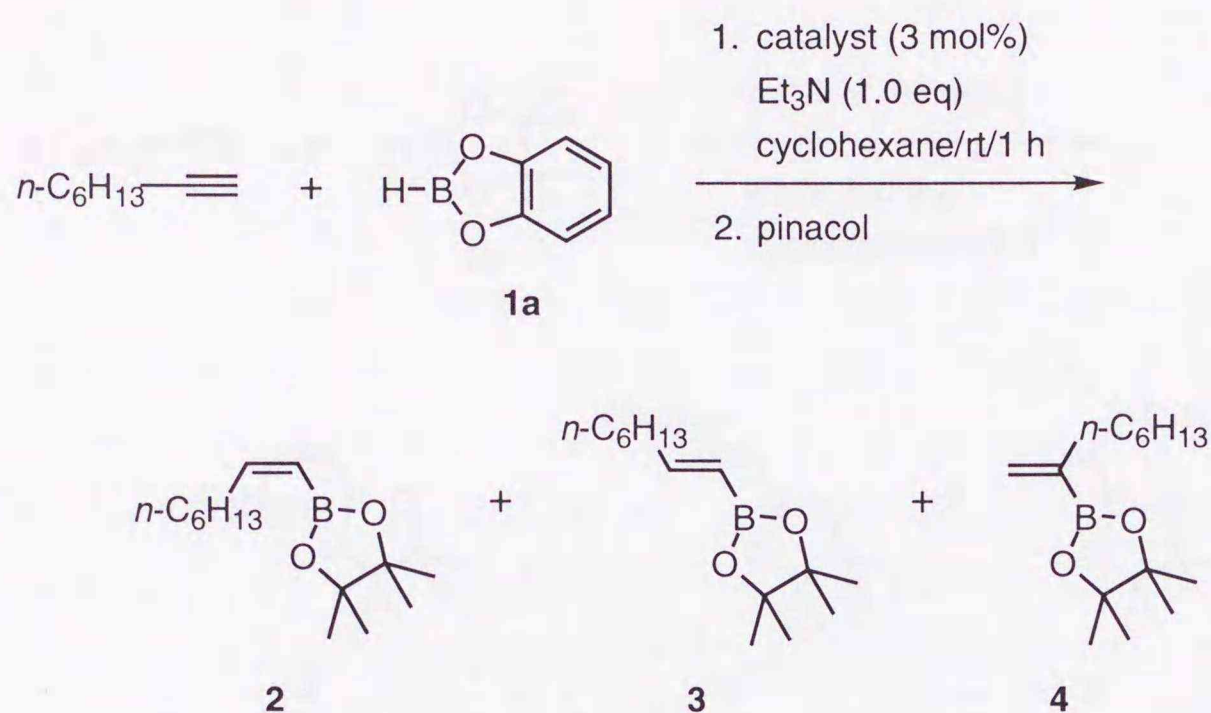
Table 4. Effect of Solvents in the Hydroboration of 1-Octyne with **1a**^a



entry	solvent	yield/% ^b	isomer ratio ^c		
			2	3	4
1	cyclohexane	86 (74)	99	1	0
2	hexane	77	99	1	0
3	benzene	75	99	1	0
4	toluene	71	99	1	0
5	THF	66	86	13	1
6	CH ₂ Cl ₂	58	95	4	1

^a To a solution of [Rh(cod)Cl]₂ (0.015 mmol), PⁱPr₃ (0.06 mmol), Et₃N (1.0 mmol), and **1a** (1.0 mmol) in a solvent (3 ml) was added 1-octyne (1.2 mmol). The mixture was then stirred at rt for 1 h, unless otherwise noted. ^b GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. ^c Determined by ¹H NMR of crude product.

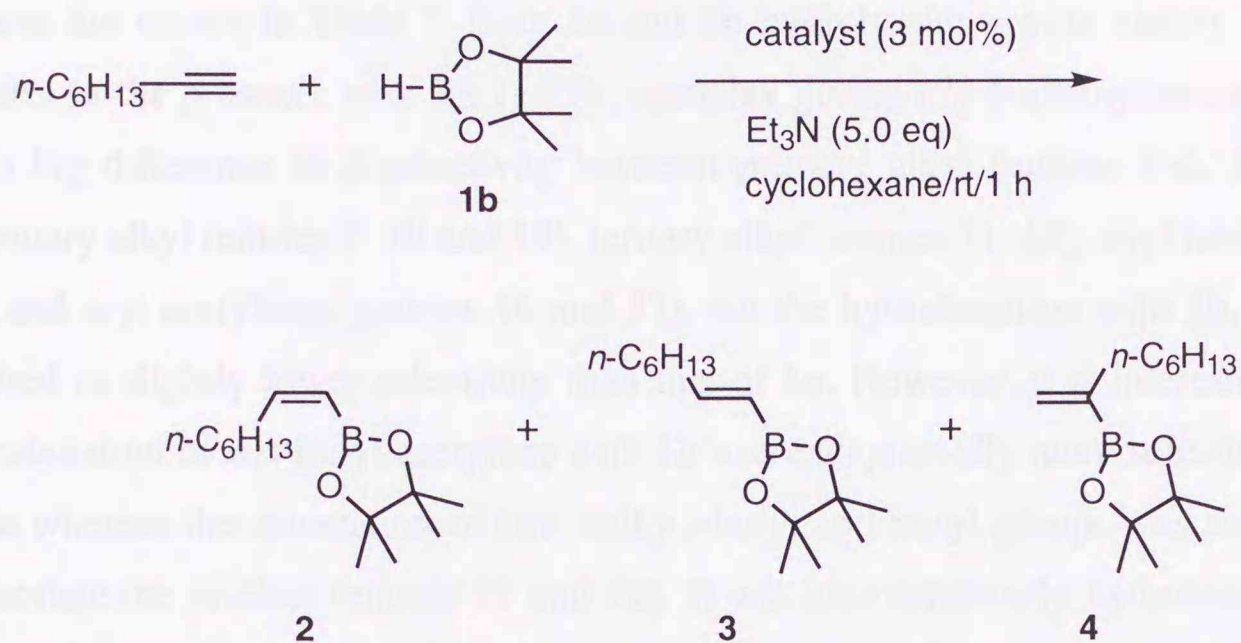
Table 5. Effect of Catalyst Precursors in the Hydroboration of 1-Octyne with **1a**^a



entry	catalyst	yield/% ^b	isomer ratio ^c		
			2	3	4
1	[Rh(cod)Cl] ₂ –4P ⁱ Pr ₃	86 (74)	99	1	0
2	[Rh(coe) ₂ Cl] ₂ –4P ⁱ Pr ₃	78	94	6	0
3	Rh(coe) ₂ (acac)–2P ⁱ Pr ₃	72	96	3	1
4	[Rh(cod) ₂]BF ₄ –2P ⁱ Pr ₃	75	99	1	0
5	[Ir(cod)Cl] ₂ –4P ⁱ Pr ₃	43	58	32	10
6 ^d	RuHCl(CO)(P ⁱ Pr ₃) ₂	7	55	45	0
7	[RuCl ₂ (<i>p</i> -cymene)] ₂ –4P ⁱ Pr ₃	2	–	–	–
8 ^e	Pd(dba) ₂ –2P ⁱ Pr ₃	0	–	–	–
9 ^e	Pt(dba) ₂ –2P ⁱ Pr ₃	2	–	–	–

^a To a solution of catalyst (3 mol%), Et₃N (1.0 mmol), and **1a** (1.0 mmol) in a cyclohexane (3 ml) was added 1-octyne (1.2 mmol). The mixture was then stirred at rt for 1 h, unless otherwise noted. ^b GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. ^c Determined by ¹H NMR of crude product. ^d The reaction carried out in CH₂Cl₂. ^e The reaction carried out in benzene.

Table 6. Hydroboration of 1-Octyne with Pinacolborane (**1b**)^a



entry	catalyst	1-octyne/ 1b	yield/% ^b	isomer ratio ^c		
				2	3	4
1	$[\text{Rh}(\text{cod})\text{Cl}]_2\text{-4P}^i\text{Pr}_3$	2.0	81 (71)	91	7	2
2	$[\text{Rh}(\text{cod})\text{Cl}]_2\text{-4P}^i\text{Pr}_3$	1.0	85	69	26	5
3	$[\text{Ir}(\text{cod})\text{Cl}]_2\text{-4P}^i\text{Pr}_3$	2.0	73 (54)	70	25	5
4	$[\text{Ir}(\text{cod})\text{Cl}]_2\text{-4P}^i\text{Pr}_3$	1.0	62	65	29	6

^a To a solution of catalyst (3 mol%), Et_3N (5.0 mmol), and **1b** (1.0 mmol) in a cyclohexane (3 ml) was added 1-octyne (1.0 or 2.0 mmol). The mixture was then stirred at rt for 1 h, unless otherwise noted. ^b GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. ^c Determined by ^1H NMR of crude product.

2-2. *trans*-Hydroboration of Terminal Alkynes

The results for the rhodium-catalyzed *trans*-hydroboration of various terminal alkynes are shown in Table 7. Both **1a** and **1b** hydroborate a wide variety of terminal alkynes in the presence of a Rh(I)-P^{*i*}Pr₃ complex giving (*Z*)-1-alkenylboronates. There is no big difference in *Z*-selectivity between primary alkyl (entries 1–6, 18 and 20), secondary alkyl (entries 7–10 and 19), tertiary alkyl (entries 11–13), silyl (entries 14 and 15), and aryl acetylenes (entries 16 and 17), but the hydroboration with **1b**, in general, resulted in slightly lower selectivity than that of **1a**. However, it is interesting that the hydroboration of *tert*-butyl acetylene with **1b** was exceptionally more selective than that of **1a** whereas the orientation of two bulky *t*-butyl and boryl groups was anticipated to destabilize the product (entries 11 and 12). It was also selectively hydroborated by the iridium catalyst (entry 13). The reaction was available with the functional groups such as silyl ether (entries 5–10 and 19), ester (entries 3, 4 and 20), ketone (entry 18), aryl bromide (entry 19), and vinyl bromide (entry 20). All attempts at the *trans*-hydroboration of internal alkynes were unsuccessful.

The *trans*-hydroboration was highly chemoselective reaction described above, but some of functional groups were not tolerated. The hydroboration of 4-pentynal **18** with catecholborane gave mainly 4-pentynol **19** under the described conditions (eq. 9). On the other hand, the reaction of 5-hexynenitrile **20** was very slow, probably because of chelate coordination of triple bond and nitrile to the rhodium metal center yielding a stable and inactive complex (eq. 10).

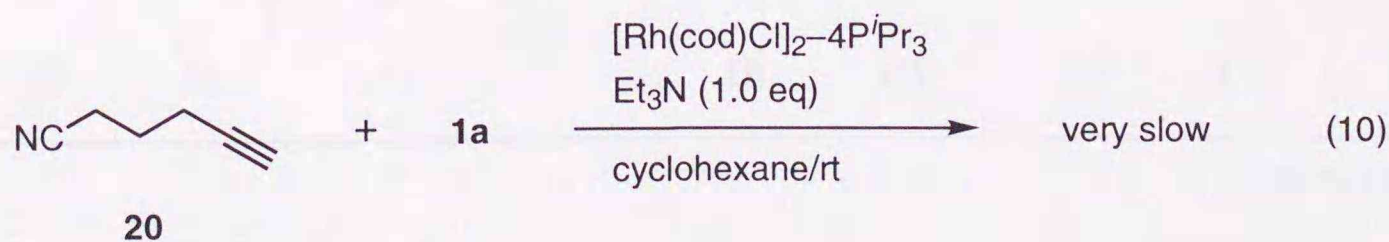
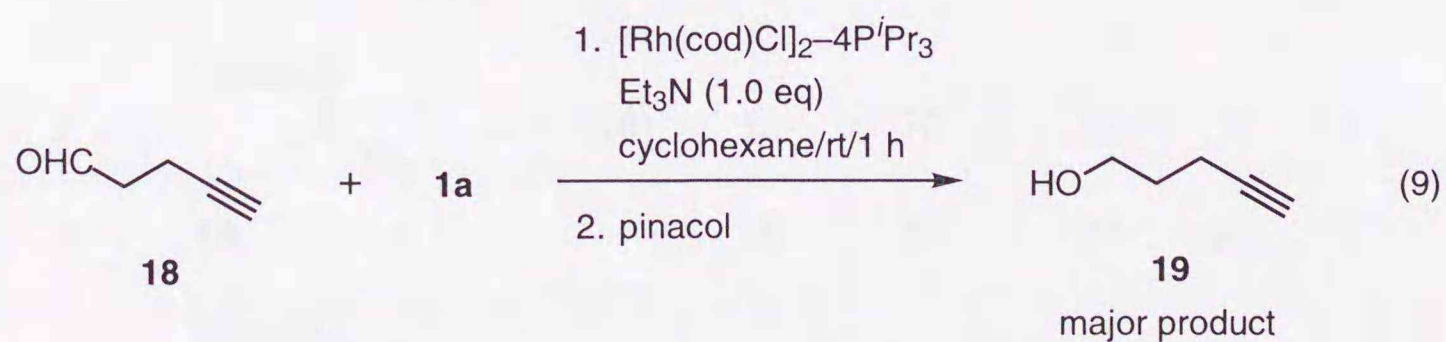


Table 7. Hydroboration of Terminal Alkynes with **1a** and **1b**^a

$$\text{R}-\text{C}\equiv\text{C} + \mathbf{1a} \text{ or } \mathbf{1b} \xrightarrow[\text{2. pinacol (if used 1a)}]{\begin{array}{l} \text{1. [Rh(cod)Cl]}_2\text{-4P}^i\text{Pr}_3 \\ \text{Et}_3\text{N (1.0 eq)} \\ \text{cyclohexane/rt/1-2 h} \end{array}} \begin{array}{c} \text{R} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{B-O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{C(CH}_3)_2 \\ \diagup \quad \diagdown \\ \text{C(CH}_3)_2 \end{array} + \begin{array}{c} \text{R} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{B-O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{C(CH}_3)_2 \\ \diagup \quad \diagdown \\ \text{C(CH}_3)_2 \end{array} + \begin{array}{c} \text{R} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{B-O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{C(CH}_3)_2 \\ \diagup \quad \diagdown \\ \text{C(CH}_3)_2 \end{array}$$

2

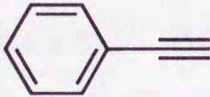
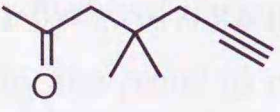
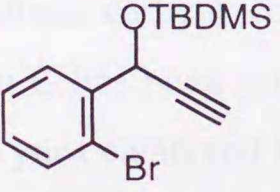
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4

entry	alkyne	borane	yield/% ^b	isomer ratio ^c		
				2	3	4
1	<i>n</i> -C ₈ H ₁₇ -C≡C	(5) 1a	79	99	1	0
2	5	1b	81	91	7	2
3	AcO-CH ₂ -CH ₂ -CH ₂ -C≡C	(6) 1a	79	98	2	0
4	MeO-C(=O)-CH ₂ -CH ₂ -CH ₂ -C≡C	(7) 1a	60	97	3	0
5	TBDMSO-CH ₂ -CH ₂ -CH ₂ -C≡C	(8) 1a	72	98	2	0
6	TBDMSO-CH ₂ -C≡C	(9) 1a	71	>99	<1	0
7	TBDMSO-CH(CH ₃)-C≡C	(10) 1a	70	98	2	1
8	10	1b	59	89	10	1
9	TBDMSO-CH(CH ₃) ₂ -C≡C	(11) 1a	66	96	4	0
10	11	1b	63	96	4	0

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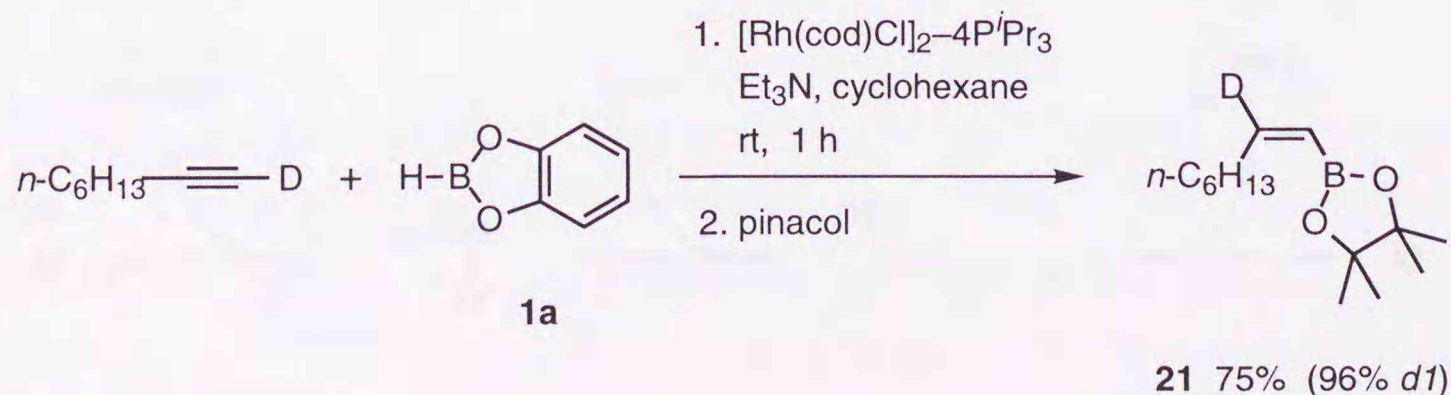
Table 7. Continued

entry	alkyne		borane	yield/% ^b	isomer ratio ^c		
					2	3	4
11	<i>tert</i> -Bu-C≡CH	(12)	1a	62	89	11	0
12	12		1b	69	95	5	0
13 ^d	12		1b	71	97	3	0
14 ^e	Me ₃ Si-C≡CH	(13)	1a	70	98	2	0
15 ^e	13		1b	59	97	3	0
16		(14)	1a	60	99	1	0
17	14		1b	67	97	2	1
18 ^e		(15)	1a	76	>99	<1	0
19 ^e		(16)	1a	76	>99	<1	0
20 ^e	 (E = CO ₂ Me)	(17)	1a	62	>99	<1	0

^a To a solution of [Rh(cod)Cl]₂ (0.015 mmol), P^{*i*}Pr₃ (0.06 mmol), Et₃N (1.0 mmol for **1a** and 5.0 mmol for **1b**), and **1a** or **1b** (1.0 mmol) in cyclohexane (3 ml) was added an alkyne (1.2 mmol for **1a** and 2.0 mmol for **1b**) at rt. The mixture was then stirred at rt for 1-2 h, unless otherwise noted. ^b GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. ^c Determined by ¹H NMR of crude product. ^d [Ir(cod)Cl]₂ (0.015 mmol), P^{*i*}Pr₃ (0.06 mmol), Et₃N (5 mmol), **1b** (1.0 mmol), and *t*-BuC≡CH (1.2 mmol) were used. ^e At rt for 4 h.

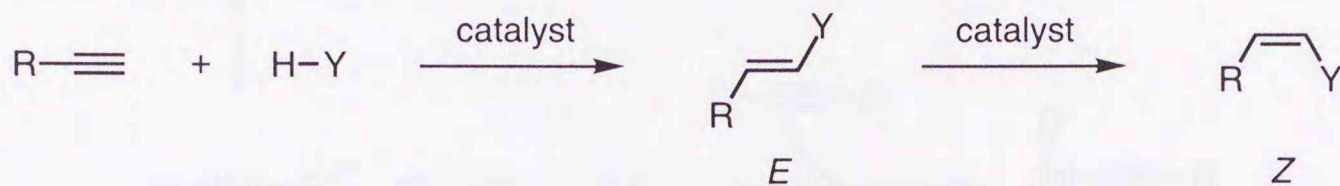
2-3. Reaction Mechanism

The hydroboration of 1-deuterio-1-octyne (96% d_1 incorporation) with **1a** gave mechanistic information for the *trans*-hydroboration (Scheme 6). The β -hydrogen in the *cis*-product unexpectedly does not derive from the borane reagents because the deuterium labeled at the terminal carbon selectively shifted to the β -carbon with 96% deuterium incorporation. Thus, the results do not fit the mechanisms previously proposed in the metal-catalyzed *trans*-hydrometalation of terminal alkynes (Scheme 7). The mechanism A, which is accounted for the *trans*-hydrosilylation by Wilkinson catalyst, involves initial formation of normal *syn*-adducts, the *E*-isomer, followed by *E* to *Z* isomerization.²¹ But the mechanism A should be ruled out because the isomerization of (*Z*)-**2** selectively led to a thermally stable (*E*)-**3** (entries 2 and 3 in Table 3). Ojima and Crabtree proposed the mechanism B for the rhodium- and iridium-catalyzed *trans*-hydrosilylation of terminal alkynes.²² The mechanism directly produces the *Z*-adducts by the *trans* to *cis* isomerization of a vinyl-metal intermediate (**22** $\rightarrow$ **25**) via the zwitterionic carbene complex **23** or metalacyclopropene **24**. On the other hand, the mechanism C has been proposed for the *trans*-hydrostannation and hydrosilylation of terminal alkynes catalyzed by Lewis acid such as $ZrCl_4$ and $AlCl_3$.²³ The mechanism proceeds through the attack of metal hydride to the alkyne coordinated to a Lewis acid, followed by transmetalation of resulting vinyl-metal intermediate **26**. However, both mechanism B and C do not result in the migration of an acetylenic hydrogen. A possible mechanism which might account for both the acetylenic hydrogen migration and the *anti*-addition of the B-H bond is one proceeding through a vinylidene complex **28** as shown in Scheme 8.

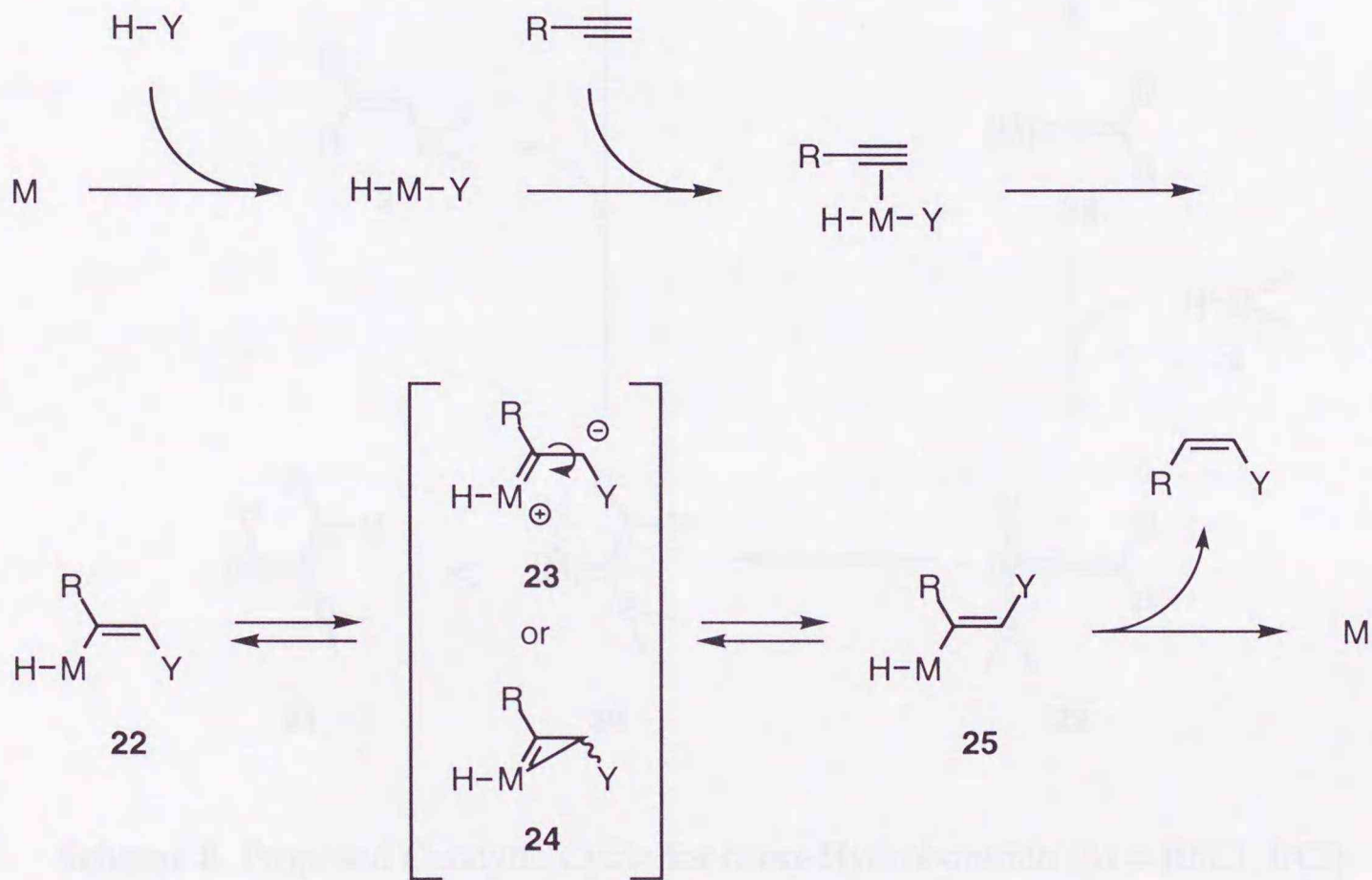


Scheme 6. Deuterium-Labeling Experiment

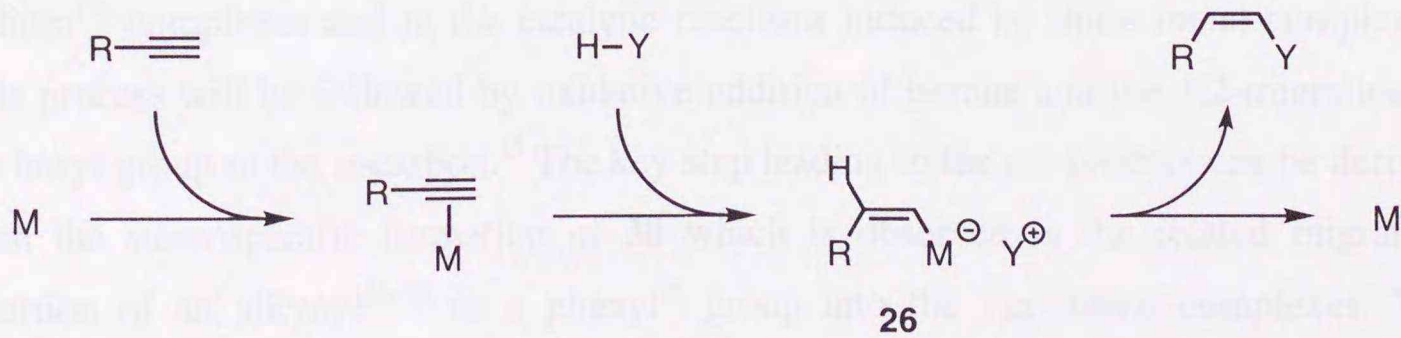
Mechanism A (Isomerization Mechanism)



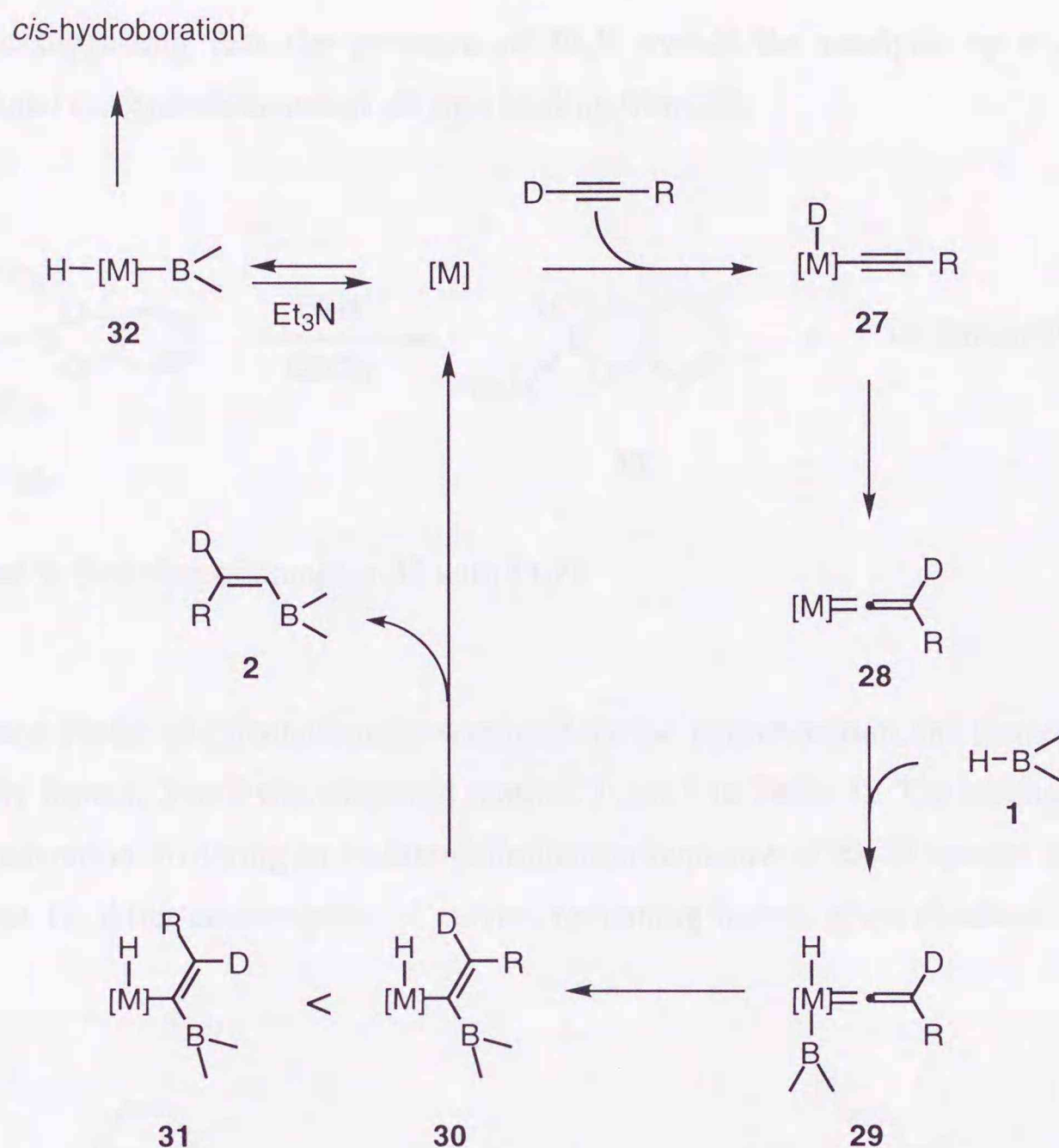
Mechanism B (Ojima-Crabtree Mechanism)



Mechanism C (Lewis Acid Mechanism)



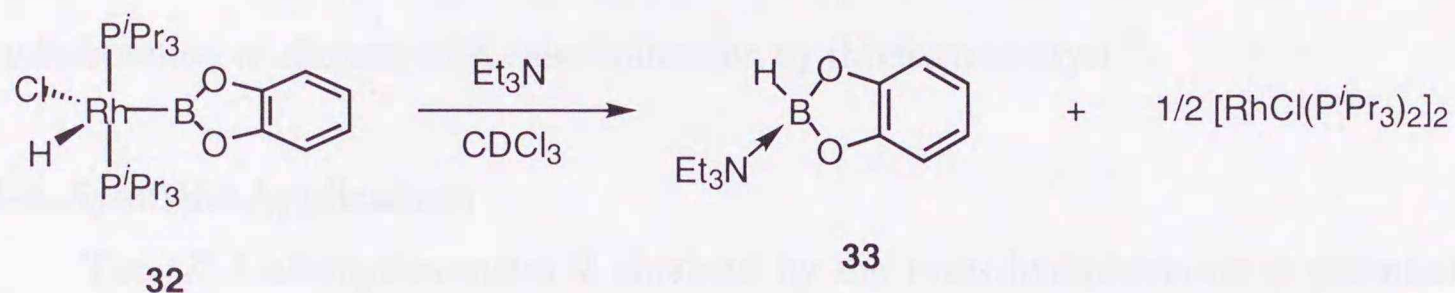
Scheme 7. Previously Proposed Mechanism for Metal-Catalyzed *trans*-Hydrometalation (Y = SiR₃, SnR₃)



Scheme 8. Proposed Catalytic Cycle for *trans*-Hydroboration (M = RhCl, IrCl)

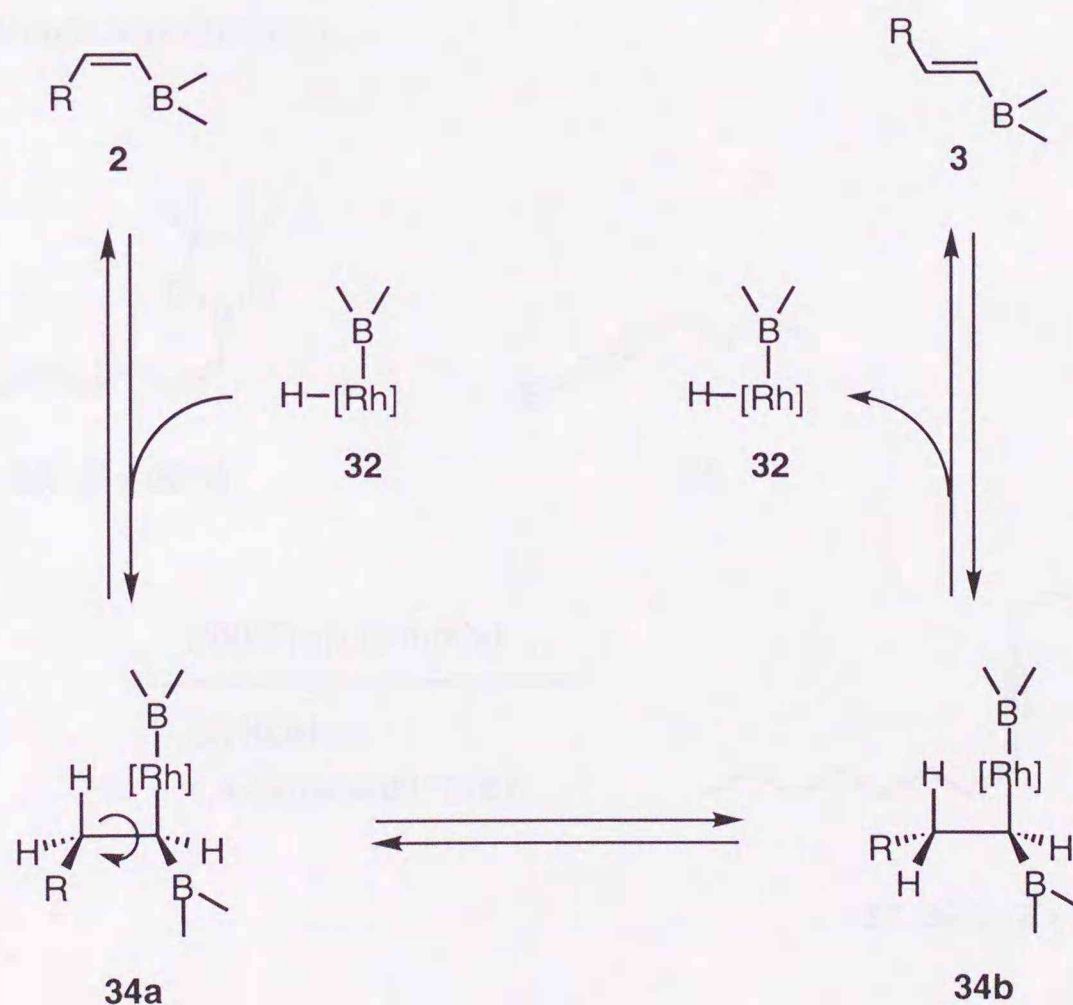
The high electron-donating property of P^iPr_3 favoring the oxidative addition of the terminal C–H bond and stabilizing the vinylidene complex ($27 \rightarrow 28$) in the presence of an amine base has been amply demonstrated in the rhodium,¹⁷ ruthenium,²⁴ and iridium^{17b} complexes and in the catalytic reactions induced by those metal complexes. This process will be followed by oxidative addition of borane and the 1,2-migration of the boryl group to the α -carbon.²⁵ The key step leading to the *cis*-product can be derived from the stereospecific formation of **30** which is observed in the related migratory insertion of an alkynyl^{24a,26} or a phenyl²⁷ group into the vinylidene complexes. The treatment of the key intermediate for *cis*-hydroboration $[\text{RhH}(\text{Cl})(\text{Bcat})(\text{P}^i\text{Pr}_3)_2]$ (**32**)²⁸ with Et_3N led to the complete reductive elimination of **1a**/ Et_3N complex **33** (Scheme

9),²⁹ thus suggesting that the presence of Et₃N avoids the catalytic cycle for the conventional *cis*-hydroboration of alkynes starting from **32**.



Scheme 9. Reaction of complex **32** with Et₃N

When excess of catecholborane was used for the hydroboration, the isomerization of initially formed **2** to **3** was observed (entries 2 and 3 in Table 3). The mechanism of this isomerization involving an addition/elimination sequence of Rh–H species is shown in Scheme 10. After consumption of alkyne, remaining borane gives rhodium–hydride

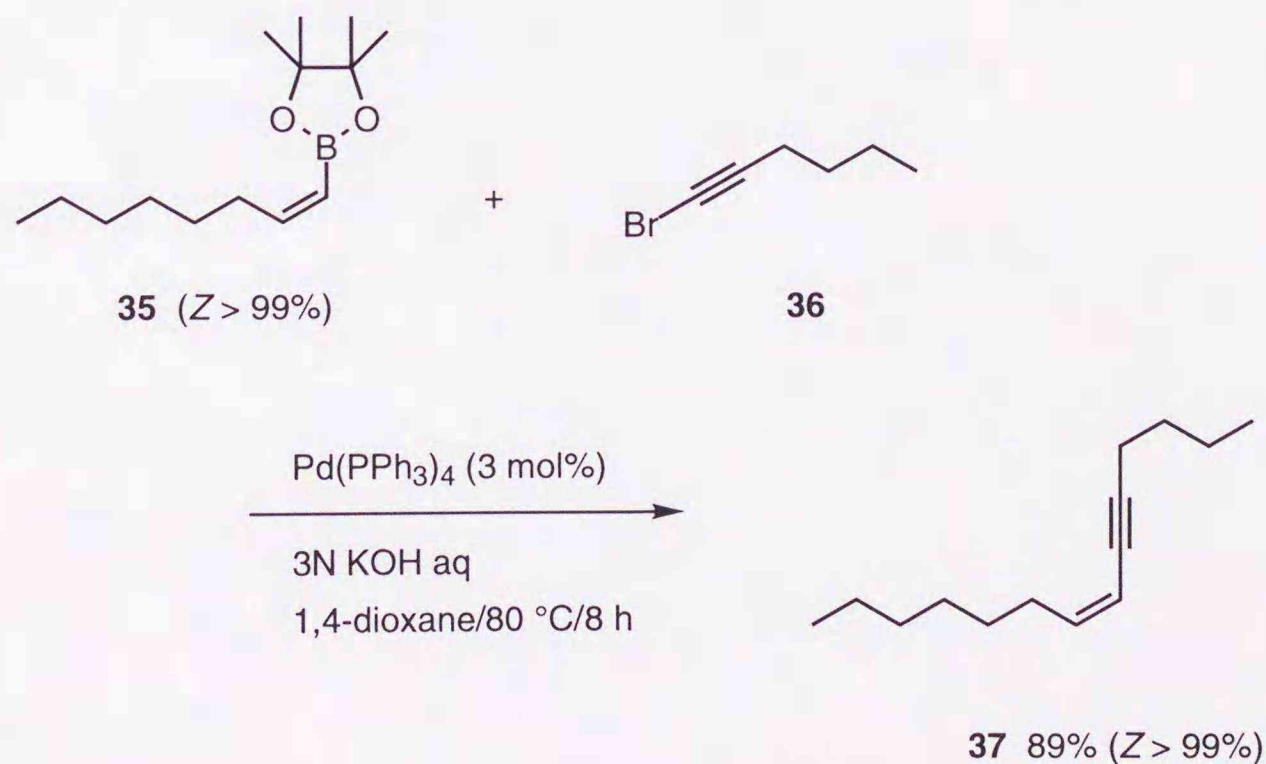


Scheme 10. Isomerization between **2** and **3**

complex **32**. An addition of Rh–H bond to **2** affords alkyl rhodium complex **34a** which rotates to more favorable configuration **34b**. Finally, β -hydride elimination from **34b** affords **3** and **32**. The reversibility of alkene insertion to Rh–H bond and β -hydride elimination from resulting alkyl rhodium complex has been demonstrated in the hydroboration of alkenes with catecholborane by rhodium catalyst.³⁰

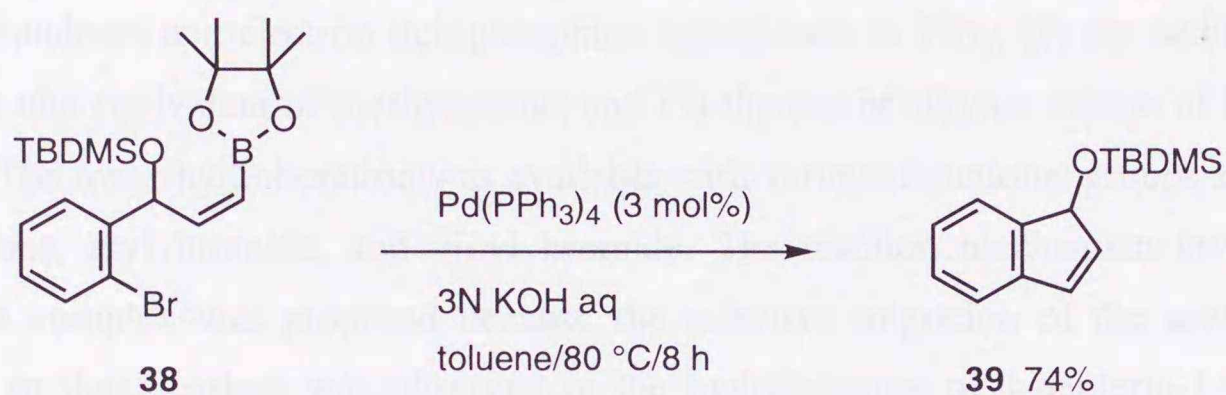
2–4. Synthetic Applications

The (Z)-1-alkenylboronates **2** obtained by the *trans*-hydroboration is potentially useful starting materials for palladium-catalyzed cross-coupling reaction. Although a great deal of attention has been focused on the cross-coupling of alkenylboron compounds with organic halides and triflates,² the examples using (Z)-1-alkenylboranes is still limited because of the difficulty of their stereoselective preparation.³¹ Since now a number of (Z)-1-alkenylboranes were in hand by the *trans*-hydroboration of terminal alkynes, cross-coupling reaction was then investigated. The cross-coupling of (Z)-1-octenylboronates **35** with 1-bromo-1-hexyne **36** proceeded smoothly in the presence of a $\text{Pd}(\text{PPh}_3)_4$ catalyst and an aqueous potassium hydroxide to give (Z)-7-tetradecen-5-yne **37** in 89% yield (Scheme 11). The geometry of resulting enyne retained completely and a pure (Z)-isomer was obtained.



Scheme 11. Pd-Catalyzed Cross-Coupling of (Z)-1-Alkenylboronates with 1-Alkynyl Halides

Further advantage of the *trans*-hydroboration was demonstrated in the intramolecular cross-coupling reaction. The reaction of bromoalkenylboronate **38**, directly synthesized by *trans*-hydroboration of bromoalkyne **16**, gave indenol derivative **39** in 74% yield (Scheme 12). The combination of *trans*-hydroboration and intramolecular cross-coupling would provide a useful method for a synthesis of cyclic compounds having endocyclic double bond.



Scheme 12. Pd-Catalyzed Intramolecular Cross-Coupling

3. Conclusion

Rhodium and iridium catalyzed *trans*-hydroboration of terminal alkynes with catecholborane and pinacolborane was demonstrated for the synthesis of (Z)-1-alkenylboronates. The complex *in situ* generated from $[M(\text{cod})\text{Cl}]_2$ ($M = \text{Rh}$ or Ir) and P^iPr_3 exhibited an excellent catalyst activity to give (Z)-1-alkenylboronates with high yields and high regio- and stereoselectivity for various terminal alkynes. Important factors for achieving high yields and Z-selectivity are as follows: (1) the use of sterically hindered and electron rich phosphine ligand such as P^iPr_3 , (2) the addition of more than one equivalent of triethylamine, and (3) the use of alkynes excess of borane reagents. The *trans*-hydroboration was available with various functional groups such as ester, ketone, aryl bromide, and vinyl bromide. The reaction mechanism involving vinylidene complex was proposed because the selective migration of the acetylenic hydrogen to the β -carbon was observed in the hydroboration of 1-deuterio-1-octyne with catecholborane. To best of our knowledge, we presented a first example for the catalytic hydrometalation of alkynes proceeding through a vinylidene intermediate.

4. Experimental Section

General.

^1H NMR spectra were recorded by a JEOL JNM-A400II (400 MHz) spectrometer using CDCl_3 as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra in CDCl_3 were taken on JEOL JNM-A400II (100 MHz) spectrometer. Chemical shifts in ^{13}C NMR spectra were measured relative to CDCl_3 and converted to $\delta_{\text{Me}_4\text{Si}}$ values by using δ_{CDCl_3} 77.0 ppm. ^{11}B NMR spectra was recorded with a Bruker MSL-400 (128 MHz) in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as an external standard. IR spectra were determined on a HITACHI 260-10 spectrometer. Mass spectra were obtained on a Finnigan MAT GCQTM apparatus. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-FABmate or a JMS-700TZ apparatus in the Instrumental Analysis Center of the Graduate School of Pharmaceutical Sciences, Hokkaido University.

All the experiments were carried out under argon atmosphere.

Solvents and Amines

Cyclohexane and hexane were distilled over lithium aluminum hydride. Benzene and toluene was distilled over sodium. Dichloromethane, and all amines were distilled over calcium hydride. Anhydrous THF was purchased from KANTO CHEMICAL CO., INC.

Catalysts and Ligands.

$[\text{Rh}(\text{cod})\text{Cl}]_2$,³² $[\text{Rh}(\text{coe})_2\text{Cl}]_2$,³³ $\text{Rh}(\text{coe})_2(\text{acac})$,³⁴ $[\text{Rh}(\text{cod})_2]\text{BF}_4$,³⁵ $[\text{Ir}(\text{cod})\text{Cl}]_2$,³⁶ $\text{RuHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$,³⁷ $[\text{RuCl}_2(p\text{-cymene})]_2$,³⁸ $\text{Pd}(\text{dba})_2$,³⁹ $\text{Pd}(\text{PPh}_3)_4$,⁴⁰ and $\text{Pt}(\text{dba})_2$ ⁴¹ were prepared by the literature method. All trialkylphosphines were commercially and purified by distillation if necessary.

Boranes.

Catecholborane (**1a**)⁴² and pinacolborane (**1b**)⁴ were prepared from borane-methyl sulfide complex by the methods reported in the literature.

Alkynes.

1-Octyne and 1-decyne were prepared from sodium acetylide and hexylbromide or

octylbromide in liquid ammonia by the reported procedure.⁴³ 3,3-Dimethyl-1-butyne (**12**) and phenylacetylene (**14**) were commercially available. Trimethylsilylacetylene (**13**) was synthesized by the reaction of ethynylmagnesium bromide with trimethylchlorosilane by the literature method.⁴⁴ TBDMSO(CH₂)₃C≡CH (**8**), TBDMSOCH₂C≡CH (**9**), CH₃(TBDMSO)CHC≡CH (**10**), and ⁱPr(TBDMSO)CHC≡CH (**11**) were synthesized by the silylation of corresponding alkynols with *tert*-butylchlorodimethylsilane and imidazole in DMF. AcO(CH₂)₃C≡CH (**6**) was prepared by the reaction of HO(CH₂)₃C≡CH⁴⁵ with Ac₂O in the presence of Et₃N. 4,4-Dimethyl-1-hepten-6-one (**15**) was synthesized by two step method from isophorone.⁴⁶ 3-(2-bromophenyl)-3-(*tert*-butyldimethylsilyloxy)-1-propyne (**16**) was prepared by the reaction of ethynylmagnesium bromide with 2-bromobenzaldehyde followed by silylation of hydroxyl group. 2-Bromo-4,4-dimethoxycarbonyl-1-hepten-6-yne (**17**) was synthesized by the reaction of sodium malonate with propargyl bromide and 2,3-dibromopropene. 1-Deuterio-1-octyne was synthesized by the reaction of 1-octynylmagnesiumbromide with D₂O. 1-bromo-1-hexyne (**36**) was prepared by the reaction of 1-hexyne with N-bromosuccinimide in the presence of catalytic amount of silver nitrate.⁴⁷

Reaction Conditions: General procedure for the Catalytic Hydroboration of 1-Octyne with Catecholborane (1a) (Table 1–5).

A 25-ml two-neck flask, equipped with a magnetic stirrer bar and a rubber septum cap, was charged with catalyst precursor (0.015 mmol for a dimer complex such as [Rh(cod)Cl]₂ or 0.03 mmol for monomer complex) and then flushed with argon. A solvent (3 ml), phosphine ligand (0.03 mmol–0.09 mmol), amine (0.03 mmol–5.0 mmol), and **1a** (0.120 g, 1.0 mmol) were successively added. After being stirred for 30 min, 1-octyne (0.85–1.2 mmol) was added in one portion and the mixture was stirred at room temperature for 0.25–1h. Cyclohexane (1 ml) solution of pinacol (0.177 g, 1.5 mmol) was added and resulting mixture was stirred at room temperature for 12 h to convert the catechol ester to the pinacol ester. After evaporation of volatile materials, the crude products were analyzed by ¹H NMR to determine the ratio of **2/3/4** and by GC to obtain a yield (anisole as an internal standard).

General procedure for the Catalytic Hydroboration of 1-Octyne with

Pinacolborane (1b) (Table 6).

A 25-ml two-neck flask, equipped with a magnetic stirrer bar and a rubber septum cap, was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ or $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.015 mmol) and then flushed with argon. Cyclohexane (3 ml), P^iPr_3 (0.06 mmol), Et_3N (0.14 ml, 1 mmol), and **1b** (1.0 mmol) were successively added. After being stirred for 30 min, 1-octyne (1.2 mmol) was added in one portion and the mixture was stirred at room temperature for 1 h. The borane remained was quenched with MeOH (0.5 ml), then volatile materials were evaporated from the reaction mixture. The resulting crude products were analyzed by ^1H NMR to determine the ratio of **2/3/4** and by GC to obtain a yield (anisole as an internal standard).

General Procedure for the Rhodium-Catalyzed Hydroboration of Terminal Alkynes with Catecholborane (1a) (entries 1, 3–7, 9, 11, 14, 16, and 18–20 in Table 7).

A 25-ml two-neck flask, equipped with a magnetic stirrer bar and a rubber septum cap, was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.007 g, 0.015 mmol) and then flushed with argon. Cyclohexane (3 ml), P^iPr_3 (0.06 mmol), Et_3N (0.14 ml, 1.0 mmol), and **1a** (0.120 g, 1.0 mmol) were successively added. After being stirred for 30 min, an alkyne (1.2 mmol) was added in one portion and the mixture was stirred at room temperature for 1–4 h. Cyclohexane (1 ml) solution of pinacol (0.177 g, 1.5 mmol) was added and resulting mixture was stirred at room temperature for 12 h to convert the catechol ester to the pinacol ester. The chromatography over silica gel afforded the product.

General Procedure for the Rhodium-Catalyzed Hydroboration of Terminal Alkynes with Pinacolborane (1b) (entries 2, 8, 10, 12, 15, and 17 in Table 7).

A 25-ml two-neck flask, equipped with a magnetic stirrer bar and a rubber septum cap, was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.007 g, 0.015 mmol) and then flushed with argon. Cyclohexane (3 ml), P^iPr_3 (0.06 mmol), Et_3N (0.7 ml, 5.0 mmol), and **1b** (0.128 g, 1.0 mmol) were successively added. After being stirred for 30 min, an alkyne (2.0 mmol) was added in one portion and the mixture was stirred at room temperature for 1–4 h. The borane remained was quenched with MeOH (0.5 ml), then the product was isolated by chromatography over silica gel.

The Iridium-Catalyzed Hydroboration of 3,3-Dimethyl-1-butyne (12) with Pinacolborane (1b) (entry 13 in Table 7).

A 25-ml two-neck flask, equipped with a magnetic stirrer bar and a rubber septum cap, was charged with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.010 g, 0.015 mmol) and then flushed with argon. Cyclohexane (3 ml), P^iPr_3 (0.06 mmol), Et_3N (0.7 ml, 5.0 mmol), and **1b** (0.128 g, 1.0 mmol) were successively added. After being stirred for 30 min, **12** (2.0 mmol) was added in one portion and the mixture was stirred at room temperature for 2 h. The borane remained was quenched with MeOH (0.5 ml), the product was then isolated by chromatography over silica gel.

2-[(Z)-1-Octenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $\text{CH}_3(\text{CH}_2)_5$, **Table 1–6**]: ^1H NMR (400 MHz, CDCl_3): δ 6.43 (dt, J = 13.4, 7.3 Hz, 1H), 5.32 (d, J = 13.4 Hz, 1H), 2.39 (dt, J = 7.3, 7.2 Hz, 2H), 1.28–1.39 (m, 8H), 1.27 (s, 12H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.3, 82.7, 32.2, 31.6, 29.4, 28.7, 24.8, 22.6, 14.1. ^{11}B NMR (128 MHz, CDCl_3): δ 29.83. IR (neat): 2990, 2965, 2930, 2870, 1630, 1425, 1375, 1320, 1260, 1150, 975, 850, 765 cm^{-1} . MS (EI): m/z 238 (M^+ , 5), 223 (23), 194 (42), 181 (33), 153 (100), 137 (22), 125 (39), 109 (57), 95 (53), 81 (59), 67 (68), 55 (31). HRMS (EI) calcd for $\text{C}_{14}\text{H}_{27}\text{BO}_2$ 238.2104, found 238.2104.

2-[(Z)-1-Decenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $\text{CH}_3(\text{CH}_2)_7$, **entries 1 and 2 in Table 7**]: ^1H NMR (400 MHz, CDCl_3): δ 6.43 (dt, J = 13.4, 7.3 Hz, 1H), 5.32 (d, J = 13.4 Hz, 1H), 2.39 (q, J = 7.3 Hz, 2H), 1.27 (s, 12H), 1.25–1.39 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.3, 82.8, 32.2, 31.9, 29.5, 29.4, 29.3, 29.1, 24.8, 22.7, 14.1. ^{11}B NMR (128 MHz, CDCl_3): δ 29.84. IR (neat): 2980, 2925, 2850, 1630, 1420, 1370, 1315, 1260, 1145, 970, 850, 765 cm^{-1} . MS (EI): m/z 266 (M^+ , 21), 251 (31), 222 (48), 209 (59), 181 (58), 153 (100), 138 (51), 125 (80), 109 (90), 95 (96), 81 (90), 67 (93). HRMS (EI) calcd for $\text{C}_{16}\text{H}_{31}\text{BO}_2$ 266.2417, found 266.2426.

2-[(Z)-5-Acetoxy-1-pentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $\text{AcO}(\text{CH}_2)_3$, **entry 3 in Table 7**]: ^1H NMR (400 MHz, CDCl_3): δ 6.42 (dt, J = 13.4, 7.6 Hz, 1H), 5.38 (d, J = 13.4 Hz, 1H), 4.07 (t, J = 6.8 Hz, 2H), 2.47 (q, J = 7.6 Hz, 2H), 2.05 (s, 3H), 1.73 (tt, J = 7.6, 6.8 Hz, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 153.3, 82.9, 64.1, 28.6, 28.4, 24.8, 21.0. IR (neat): 2970, 1740, 1625, 1412, 1365, 1313, 1250, 1235, 1135, 1035, 965, 875, 840, 755. MS (EI): m/z 254 (M^+ , 24),

194 (15), 179 (11), 153 (92), 152 (32), 136 (100), 135 (29), 108 (39), 101 (34), 100 (24), 93 (27), 67 (33). HRMS (EI) calcd for $C_{13}H_{23}BO_4$ 254.1689, found 254.1707.

2-[(Z)-6-Methoxycarbonyl-1-hentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $MeO_2C(CH_2)_4$, entry 4 in Table 7]: 1H NMR (400 MHz, $CDCl_3$): δ 6.41 (dt, $J = 13.4, 7.3$ Hz, 1H), 5.35 (d, $J = 13.4$ Hz, 1H), 3.66 (s, 3H), 2.42 (q, $J = 7.3$ Hz, 2H), 2.34 (t, $J = 7.3$ Hz, 2H), 1.61–1.69 (m, 2H), 1.43 (quintet, $J = 7.3$ Hz, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 154.3, 82.8, 51.4, 33.8, 31.6, 28.8, 24.8, 24.2. IR (neat): 2980, 2940, 2860, 1740, 1630, 1435, 1420, 1370, 1320, 1255, 1140, 970, 875, 845 cm^{-1} . MS (EI): m/z 268 (M^+ , 1), 237 (9), 210 (9), 181 (18), 168 (61), 139 (100), 127 (22), 101 (21), 83 (22), 67 (20). HRMS (EI) calcd for $C_{14}H_{25}BO_4$ 268.1846, found 268.1853.

2-[(Z)-5-(*tert*-Butyldimethylsilyloxy)-1-pentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $TBDMSO(CH_2)_3$, entry 5 in Table 7]: 1H NMR (400 MHz, $CDCl_3$): δ 6.44 (dt, $J = 13.4, 7.6$ Hz, 1H), 5.33 (dt, $J = 13.4, 1.2$ Hz, 1H), 3.63 (t, $J = 6.8$ Hz, 2H), 2.44 (dq, $J = 7.6, 1.2$ Hz, 2H), 1.61 (tt, $J = 7.6, 6.8$ Hz, 2H), 1.26 (s, 12H), 0.90 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 82.8, 63.0, 32.8, 28.9, 26.0, 24.8, 18.4, -5.3. ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.77. IR (neat): 2985, 2960, 2935, 2860, 1630, 1420, 1375, 1320, 1255, 1140, 1105, 970, 835, 775 cm^{-1} . MS (EI): m/z 326 (M^+ , 1), 269 (2), 187 (11), 169 (100), 168 (27), 151 (10), 127 (38), 109 (13). HRMS (EI) calcd for $C_{13}H_{26}BO_3Si$ ($M^+ - tert-C_4H_9$) 269.1744, found 269.1742.

2-[(Z)-3-(*tert*-Butyldimethylsilyloxy)-1-propenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $TBDMSOCH_2$, entry 6 in Table 7]: 1H NMR (400 MHz, $CDCl_3$): δ 6.51 (dt, $J = 13.7, 6.1$ Hz, 1H), 5.39 (dt, $J = 13.7, 1.7$ Hz, 1H), 4.50 (dd, $J = 6.1, 1.7$ Hz, 1H), 1.26 (s, 12H), 0.91 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 83.1, 63.3, 26.0, 24.8, 18.4, -5.0. ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.47. IR (neat): 2960, 2930, 2855, 1635, 1415, 1375, 1317, 1255, 1145, 1085, 970, 835, 775 cm^{-1} . MS (EI): m/z 283 ($M^+ - CH_3$, 1), 241 ($M^+ - tert-C_4H_9$, 20), 141 (100), 125 (14), 99 (28), 83 (41), 75 (19), 73 (30), 57 (11), 41 (20). HRMS (EI) calcd for $C_{11}H_{22}BO_3Si$ ($M^+ - tert-C_4H_9$) 241.1431, found 241.1422.

2-[(Z)-3-(*tert*-Butyldimethylsilyloxy)-1-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $CH_3(TBDMSO)CH$, entries 7 and 8 in Table 7]: 1H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, $J = 13.7, 8.5$ Hz, 1H), 5.25 (d, $J = 13.7$ Hz, 1H), 5.01 (dq, $J = 8.5, 6.1$ Hz, 1H), 1.26 (s, 12H), 1.18 (d, $J = 6.1$ Hz, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.04

(s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.8, 83.0, 68.3, 26.0, 24.9, 24.8, 24.6, 18.3, -4.5, -4.7. ^{11}B NMR (128 MHz, CDCl_3): δ 29.49. IR (neat): 2990, 2970, 2940, 2860, 1635, 1420, 1373, 1330, 1260, 1145, 1070, 990, 835, 775 cm^{-1} . MS (EI): m/z 312 (M^+ , 26), 297 (24), 255 (28), 181 (27), 173 (23), 155 (100), 154 (28), 139 (27), 137 (22), 127 (23), 119 (64), 113 (58), 83 (59). HRMS (EI) calcd for $\text{C}_{12}\text{H}_{24}\text{BO}_3\text{Si}$ ($\text{M}^+ - \text{tert-C}_4\text{H}_9$) 255.1588, found 255.1610.

2-[(Z)-3-(tert-Butyldimethylsilyloxy)-4-methyl-1-pentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $\text{Pr}(\text{TBDMSO})\text{CH}$, entries 9 and 10 in Table 7]: ^1H NMR (400 MHz, CDCl_3): δ 6.28 (dd, $J = 13.7, 9.0$ Hz, 1H), 5.37 (d, $J = 13.7$ Hz, 1H), 4.56 (dd, $J = 9.0, 6.3$ Hz, 1H), 1.55–1.65 (m, 1H), 1.25 (s, 12H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.87 (s, 9H), 0.82 (d, $J = 6.8$ Hz, 3H), 0.05 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.5, 82.9, 76.3, 34.6, 25.9, 24.8 (2C), 18.2, 18.0, -4.2, -4.9. ^{11}B NMR (128 MHz, CDCl_3): δ 29.53. IR (neat): 2960, 2930, 2850, 1635, 1415, 1375, 1315, 1255, 1140, 1060, 835, 770 cm^{-1} . MS (EI): m/z 340 (M^+ , 7), 325 (12), 298 (25), 297 (98), 296 (23), 283 (37), 209 (32), 183 (67), 141 (100), 121 (21), 83 (73), 81 (56), 75 (22). HRMS (EI) calcd for $\text{C}_{18}\text{H}_{37}\text{BO}_3\text{Si}$ 340.2605, found 340.2611.

2-[(Z)-2-tert-Butylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = *tert*-Bu, entries 11–13 in Table 7]: ^1H NMR (400 MHz, CDCl_3): δ 6.26 (d, $J = 15.1$ Hz, 1H), 5.18 (d, $J = 15.1$ Hz, 1H), 1.28 (s, 12H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.7, 83.3, 35.1, 29.9, 24.8. ^{11}B NMR (128 MHz, CDCl_3): δ 30.59. IR (neat): 2990, 2960, 2875, 1630, 1420, 1370, 1300, 1255, 1145, 970, 780 cm^{-1} . MS (EI): m/z 210 (M^+ , 31), 195 (22), 153 (100), 152 (34), 111 (27), 110 (22), 109 (52), 95 (20). HRMS (EI) calcd for $\text{C}_{12}\text{H}_{23}\text{BO}_2$ 210.1791, found 210.1802.

2-[(Z)-2-Trimethylsilylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = Me_3Si , entries 14 and 15 in Table 7]: ^1H NMR (400 MHz, CDCl_3): δ 6.87 (d, $J = 18.8$ Hz, 1H), 6.41 (d, $J = 18.8$ Hz, 1H), 1.27 (s, 12H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.0, 83.3, 24.9, -0.2. ^{11}B NMR (128 MHz, CDCl_3): δ 29.24. IR (neat): 2990, 1590, 1385, 1327, 1255, 1145, 970, 845, 770 cm^{-1} . MS (EI): m/z 226 (M^+ , 3), 212 (17), 211 (100), 210 (27), 169 (44), 129 (42), 83 (28), 55 (16). HRMS (EI) calcd for $\text{C}_{10}\text{H}_{20}\text{BO}_2\text{Si}$ ($\text{M}^+ - \text{CH}_3$) 211.1326, found 211.1342.

2-[(Z)-2-Phenylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = Ph, entries 16 and 17 in Table 7]: ^1H NMR (400 MHz, CDCl_3): δ 7.53 (d, $J = 7.1$ Hz, 2H), 7.26–7.33 (m, 3H), 7.22 (d, $J = 14.9$ Hz, 1H), 5.59 (d, $J = 14.9$ Hz, 1H), 1.29 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.1, 138.4, 128.6, 128.0, 127.9, 83.5, 24.8. ^{11}B NMR (128 MHz, CDCl_3): δ 30.33. IR (neat): 2990, 1623, 1425, 1375, 1318, 1260, 1145, 970, 855, 780, 695 cm^{-1} . MS (EI): m/z 230 (M^+ , 30), 145 (27), 144 (100), 131 (21), 130 (40), 129 (86). HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{BO}_2$ 230.1478, found 230.1484.

2-[(Z)-4,4-Dimethyl-6-oxo-1-heptenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $\text{H}_3\text{CC}(\text{O})\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$, entry 18 in Table 7]: ^1H NMR (400 MHz, CDCl_3): δ 6.46 (dt, J = 13.4, 8.1 Hz, 1H), 5.47 (dt, J = 13.4, 1.2 Hz, 1H), 2.43 (dd, J = 8.1, 1.2 Hz, 2H), 2.35 (s, 2H), 2.13 (s, 3H), 1.27 (s, 12H), 1.02 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 208.9, 150.5, 82.9, 53.9, 44.4, 34.0, 32.5, 26.9, 24.8. IR (neat): 2975, 1710, 1625, 1415, 1360, 1320, 1255, 1210, 1140, 1320, 1255, 1210, 1140, 970, 880, 845, 730 cm^{-1} . MS (EI): m/z 266 (M^+ , 11), 251 (43), 208 (71), 165 (94), 164 (48), 151 (35), 123 (37), 122 (44), 121 (30), 111 (61), 110 (42), 109 (44), 108 (85), 107 (100), 101 (97). HRMS (EI) calcd for $\text{C}_{15}\text{H}_{27}\text{BO}_3$ 266.2053, found 266.2029.

2-[(Z)-3-(*tert*-Butyldimethylsilyloxy)-3-(*o*-bromophenyl)-1-pentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = (*o*-BrPh)(TBDMSO)CH, entry 19 in Table 7]: ^1H NMR (400 MHz, CDCl_3): δ 7.66 (dd, J = 7.8, 1.7 Hz, 1H), 7.47 (dd, J = 8.1, 1.2 Hz, 1H), 7.32 (dt, J = 7.6, 1.2 Hz, 1H), 7.08 (dt, J = 7.8, 1.7 Hz, 1H), 6.22 (dd, J = 12.9, 9.5 Hz, 1H), 6.12 (d, J = 9.5 Hz, 1H), 5.39 (d, J = 12.9 Hz, 1H), 1.32 (s, 6H), 1.31 (s, 6H), 0.89 (s, 9H), 0.11 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.9, 143.3, 132.6, 128.7, 128.5, 127.5, 121.8, 83.3, 72.4, 25.9, 25.1, 25.0, 18.2, -4.3, -4.8. IR (neat): 2950, 2925, 1632, 1460, 1407, 1365, 1320, 1250, 1135, 1065, 875, 835, 770, 745 cm^{-1} . MS (EI): m/z 397 (36), 395 (M^+ -*tert*- C_4H_9 , 34), 297 (60), 295 (57), 255 (95), 253 (100), 215 (39), 201 (28), 142 (36), 115 (47), 83 (43), 75 (63), 73 (51), 57 (44). HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{BBrO}_3\text{Si}$ (M^+ -*tert*- C_4H_9) 395.0849, found 395.0858.

2-[(Z)-6-Bromo-4-dimeethoxycarbonyl-1,6-heptadienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [**R** = $\text{H}_2\text{C}=\text{C}(\text{Br})\text{CH}_2\text{C}(\text{CO}_2\text{CH}_3)_2\text{CH}_2$, entry 20 in Table 7]: ^1H NMR (400 MHz, CDCl_3): δ 6.26 (dt, J = 13.4, 7.3 Hz, 1H), 5.68 (s, 1H), 5.57 (d, J = 1.7 Hz, 1H), 5.49 (dt, J = 13.4, 1.5 Hz, 1H), 3.73 (s, 6H), 3.16 (s, 2H), 3.13 (dd, J = 7.3, 1.5 Hz, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.6, 146.8, 126.9, 122.0, 83.1, 56.8, 52.6, 43.8, 34.8, 24.8. MS (EI): m/z 387 (10), 385 (M^+ - OCH_3 , 10), 337 (M^+ -Br, 100), 302 (47), 300 (48), 237 (62), 197 (50), 179 (36), 177 (34), 153 (56), 151 (46), 119 (64), 91 (55), 83 (53), 59 (49). HRMS (EI) calcd for $\text{C}_{17}\text{H}_{26}\text{BBrO}_6$ 416.1005, found 416.1021.

Deuterium-Labeling Experiment: Rhodium-Catalyzed Hydroboration of 1-Deuterio-1-octyne with Catecholborane (**1a**) (Scheme 6)

A 25-ml two-neck flask, equipped with a magnetic stirrer bar and a rubber septum cap, was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.007 g, 0.015 mmol) and then flushed with argon. Cyclohexane (3 ml), P^iPr_3 (0.06 mmol), Et_3N (0.14 ml, 1.0 mmol), and **1a** (0.120 g, 1.0 mmol) were successively added. After being stirred for 30 min, 1-deuterio-1-octyne (2.0 mmol) was added in one portion and the mixture was stirred at room temperature for 1 h. Cyclohexane (1 ml) solution of pinacol (0.177 g, 1.5 mmol) was added and resulting mixture was stirred at room temperature for 12 h to convert the catechol ester to the pinacol ester. The chromatography over silica gel (hexane:ether = 40:1) afforded the (Z)- $\text{CH}_3(\text{CH}_2)_5\text{CD}=\text{CHB}(\text{OCMe}_2\text{CMe}_2\text{O})$ **21** (0.184 g, 0.77 mmol, 75%): ^1H NMR (400 MHz, CDCl_3): δ 5.32 (s, 1H), 2.38 (t, $J = 7.3$ Hz, 2H), 1.23–1.39 (m, 8H), 1.27 (s, 12H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 82.7, 32.0, 31.6, 29.4, 28.7, 24.8, 22.6, 14.1. ^{11}B NMR (128 MHz, CDCl_3): δ 29.85. IR (neat): 2980, 2960, 2925, 2850, 1615, 1460, 1368, 1320, 1240, 1140, 975, 865, 700 cm^{-1} . MS (EI): m/z 239 (M^+ , 10), 224 (23), 195 (45), 182 (37), 154 (100), 138 (28), 124 (42), 110 (70), 96 (70), 82 (51), 68 (65), 55 (35). HRMS (EI) calcd for $\text{C}_{14}\text{H}_{26}\text{DBO}_2$ 239.2166, found 239.2151.

The cross-coupling reaction of (Z)-1-octenylboronates **35** with 1-bromo-1-hexyne **36** (Scheme 11)

To a 1,4-dioxane (3 ml) solution of $\text{Pd}(\text{PPh}_3)_4$ (0.017 g, 0.015 mmol) was successively added 2-[(Z)-1-octenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **35** (0.138 g, 0.58 mmol), 1-bromo-1-hexyne **36** (0.074 g, 0.46 mmol), and aqueous 3M solution of potassium hydroxide (0.5 ml, 1.5 mmol). The mixture was stirred at 80 °C for 4 h. The reaction mixture was extracted with ether, washed with water, and dried with magnesium sulfate. After evaporation of volatile materials, the product was purified by silica gel column chromatography (hexane) to give (Z)-7-tetradecen-5-yne **37** (0.079 g, 0.41 mmol, 89%): ^1H NMR (400 MHz, CDCl_3): δ 5.81 (dt, $J = 10.7, 7.3$ Hz, 1H), 5.43 (d, $J = 10.7$ Hz, 1H), 2.34 (dt, $J = 6.8, 2.0$ Hz, 2H), 2.28 (q, $J = 7.3$ Hz, 2H), 1.29–1.57 (m, 12H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.6, 109.3, 94.4, 77.4, 31.7, 31.0, 30.0, 28.9 (2C), 22.6, 21.9, 19.2, 14.1, 13.6. MS (EI): m/z 192 (M^+ , 42), 135 (14), 121 (16), 107 (29), 93 (76), 91 (55), 86 (34),

84 (68), 79 (100), 77 (33). HRMS (EI) calcd for $C_{14}H_{24}$ 192.1878, found 192.1865.

Synthesis of indenol derivative 39 by the intramolecular cross-coupling of bromoalkenylboronate 38 (Scheme 12)

To a toluene solution (10 ml) of $Pd(PPh_3)_4$ (0.034 g, 0.03 mmol) was successively added 2-[(*Z*)-6-Bromo-4-dimethoxycarbonyl-1,6-heptadienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **38** (0.440 g, 0.97 mmol) and aqueous 3M solution of potassium hydroxide (1.0 ml, 3.0 mmol). The mixture was stirred at 80 °C for 8 h. The reaction mixture was extracted with ether, washed with water, and dried with magnesium sulfate. After evaporation of volatile materials, the product was purified by silica gel column chromatography (hexane:benzene = 3:1) to give 1-(*tert*-butyldimethylsilyloxy)-indene **39** (0.178 g, 0.72 mmol, 74%): 1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.1 Hz, 1H), 7.17–7.26 (m, 3H), 6.70 (dd, J = 5.6, 0.7 Hz, 1H), 6.35 (dd, J = 5.6, 1.7 Hz, 1H), 5.25 (s, 1H), 0.95 (s, 9H), 0.17 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 142.1, 138.1, 131.8, 128.0, 125.8, 123.3, 121.3, 78.1, 25.9, 18.3, -4.2. IR (neat): 2960, 2940, 2860, 1465, 1360, 1330, 1250, 1170, 1120, 1090, 980, 870, 835, 775, 760 cm^{-1} . MS (EI): m/z 246 (M^+ , 24), 191 (16), 190 (59), 189 (93), 115 (100), 75 (19). HRMS (EI) calcd for $C_{15}H_{22}OSi$ 246.1440, found 246.1436.

Abbreviations

acac	acetylacetonate
cod	1,5-cyclooctadiene
coe	cyclooctene
dba	dibenzylideneacetone
Ac	acetyl
Cy	cyclohexyl
TBDMS	<i>tert</i> -butyldimethylsilyl
ttmpp	tris(2,4,6-trimethoxyphenyl)phosphine
dppm	bis(diphenylphosphino)methane, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$
dppe	1,2-bis(diphenylphosphino)ethane, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$
dppp	1,3-bis(diphenylphosphino)propane, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$
dppb	1,4-bis(diphenylphosphino)butane, $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$
dppf	1,1'-bis(diphenylphosphino)ferrocene
THF	tetrahydrofuran

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List of Publications

1. A Stereoselective Isomerization of Allyl Silyl Ethers to (*E*)- or (*Z*)-Silyl Enol Ethers by the Cationic Iridium Complexes
Ohmura, T.; Shirai, Y.; Yamamoto, Y.; Miyaura, N.
Chem. Commun. **1998**, 1337-1338
2. Synthesis of Chiral Esters of (*E*)-3-(Silyloxy)-2-propenylboronic Acid via the Iridium-Catalyzed Isomerization of the Double Bond
Yamamoto, Y.; Miyairi, T.; Ohmura, T.; Miyaura, N.
J. Org. Chem. **1999**, 64, 296-298
3. Stereoselective Synthesis of Silyl Enol Ethers via the Iridium-Catalyzed Isomerization of Allyl Silyl Ethers
Ohmura, T.; Yamamoto, Y.; Miyaura, N.
Organometallics **1999**, 18, 413-416
4. Iridium-Catalyzed Dimerization of Terminal Alkynes to (*E*)-Enynes, (*Z*)-Enynes, or 1,2,3-Butatrienes
Ohmura, T.; Yorozyu, S.-i.; Yamamoto, Y.; Miyaura, N.
Organometallics **2000**, 19, 365-367
5. Rhodium- or Iridium-Catalyzed *trans*-Hydroboration of Terminal Alkynes, Giving (*Z*)-1-Alkenylboron Compounds
Ohmura, T.; Yamamoto, Y.; Miyaura, N.
J. Am. Chem. Soc. **2000**, 122, 4990-4991

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