# Formation of Silazirconacyclopentenes from Zirconium−Silene Complex and Alkynes and Their Reactivities

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**Abstract:** During the course of our study on the formation of a complex having a zirconium−silicon bond, we found that zirconium−silene complex **7** was formed from $Cp_2ZrCl_2$ and $Me_2PhSiLi$. In the presence of alkyne, diarylalkyne reacted with silene coordinated with zirconium to give silazirconacyclopentene **8**. On the other hand, dialkylalkyne inserted into a zirconium−silene complex gave silazirconacyclopentene **9**. Hydrolysis of **8** or **9** afforded vinylsilane **13** or allylsilane **16**. Transmetalation of zirconacycle **8** into copper in the presence of allyl halide gave a bis-allylated compound in high yield, indicating that alkylation occurred on the alkyne carbon and the methyl group of silicon. From bis-allylated compounds, eight-membered ring compounds having silicon were obtained in high yield using olefin metathesis.

## Introduction

Reactivity between metal−metal bonds is very interesting because it is expected that the insertion of unsaturated compounds into these metal−metal bonds would form the new carbon−metal bonds, which would be converted into the various carbon−carbon bonds. Thus, a new methodology in synthetic organic chemistry would be obtained.

We have been interested in the zirconium−silicon bonds (Scheme 1).

There have not been many reports on the synthesis of complex having a zirconium−silicon bond and the reactivity of such a complex. Lappert reported the synthesis of complex **1a** from $Cp_2ZrCl_2$ and $Ph_3SiLi$.[1a] Later Tilley reported the synthesis of complex **1b** from $Cp_2ZrCl_2$ and $Al(SiMe_3)_3 \cdot OEt_2$.[2a] Takahashi[3] and Buchwald[4] independently reported the formation of zirconium−silicon complexes **1c** and **1d** by hydrosilylation of alkene coordinated to zirconium metal. Berry[5] and Xue[6] reported the synthesis of complex **1e** and **1f** (Figure 1).



**Figure 1.** Complexes having a Zr−Si bond.

**Scheme 1.** Silylzirconation of Alkynes and Alkenes



Little is known the reactivity of complexes having a zirconium−silicon bond. Reaction of **1a** with hydrogen chloride afforded triphenylsilane.[1a] The insertion of carbon monoxide or isocyanide into a zirconium−silicon bond gave acylzirconium complex **2** or iminosilylzirconium complex **3**.[2b,c] As for carbon−carbon multiple bonds, it is known that ethylene can be inserted into a zirconium−silicon bond of **1h**,[2g] but other multiple bonds such as alkene and alkyne could not be inserted into a zirconium−silicon bond[2b,c] (Scheme 2).

We have been very interested in complexes having a zirconium−silicon bond, and we have studied the reactivities of such complexes.[7] Complex **1i** prepared from $Cp_2ZrCl_2$ and $^tBuPh_2SiLi$ was treated with phenylisocyanide to give air-stable iminosilaacylzirconium complex **3c**, which was treated with $LiEt_3BH$ in the presence of alkyne to afford azazirconacyclopentene **5** via azazirconacyclopropane **4**. From this complex **5**, various organic compounds could be synthesized[7c,d] (Scheme 3).

In the present study, we tried to insert alkene or alkyne into a zirconium−silicon bond and to produce complexes having carbon−zirconium and silicon−carbon bonds (Scheme 1).

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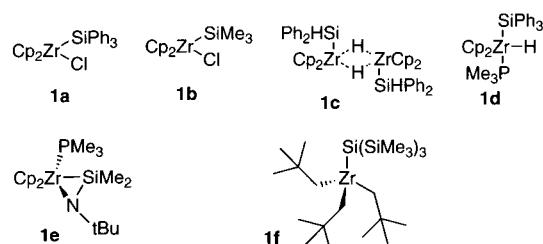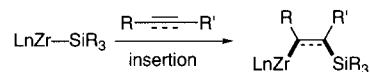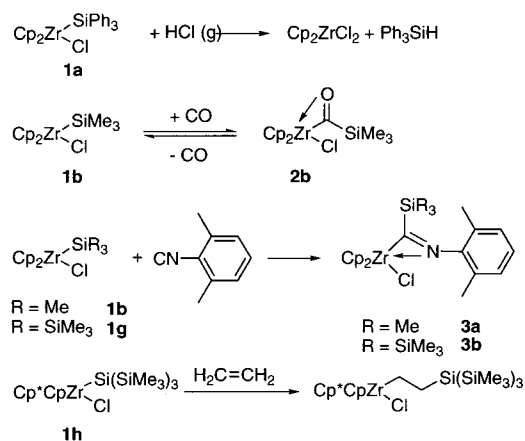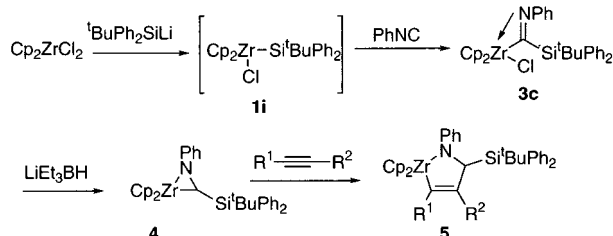
(7) (a) Honda, T.; Satoh, S.; Mori, M. *Organometallics* **1995**, *14*, 1548. (b) Honda, T.; Mori, M. *Organometallics* **1996**, *15*, 5464. (c) Honda, T.; Mori, M. *J. Org. Chem.* **1996**, *61*, 1196. (d) Dekura, F.; Honda, T.; Mori, M. *Chem. Lett.* **1997**, 825.

**Scheme 2.** Reactivity of Cp$_2$Zr(SiR$_3$)Cl



**Scheme 3.** Reaction of a Complex Having Zr–Si Bond with Isocyanide



During the course of our study on the formation of complex **6** having a zirconium–silicon bond, we found that zirconium–silene complex **7** or **7′** was formed from Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi. In the presence of alkyne, the insertion of alkyne into the zirconium–silicon bond or the zirconium–carbon bond of silazirconacyclopropane **7′** gave silazirconacyclopentene **8** or **9**[14a] (Figure 2).

Silenes are usually reactive organosilicon species whose formation has been confirmed by trapping reactions.[8–10] Recently, Tilley reported the first stable ruthenium–silene complexes **10c–e**,[11] and iridium- **10f** [12] and tungsten–silene com-
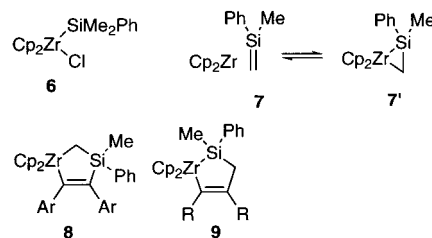


**Figure 2.**
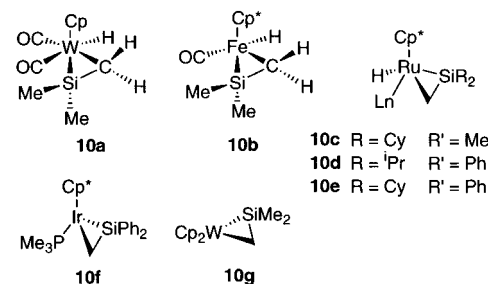


**Figure 3.** Transition metal–silene complexes.

plexes **10g**[13] have subsequently been synthesized. Although Berry reported the reaction of tungsten–silene complex with MeOH, H$_2$, and Me$_3$SiH, little is known about the reactivity of a complex coordinated by silene[13] (Figure 3).

We tried to confirm the structure of zirconium–silene complex **7** by ^{1}H NMR spectra, and we investigated the reactivity of zirconium–silene complex **7**. It was found that silazirconacyclopentene **8** was formed from zirconium–silene complex **7** and diaryl alkyne **11** and that silazirconacyclopentene **9** was synthesized from zirconium–silene complex **7** and dialkyl alkyne **16**. The reactivity of silazirconacyclopentene **8** was also investigated.

## Results and Discussion

**Formation of Zirconium–Silene Complex.** It was thought that the reaction of Cp$_2$ZrCl$_2$ with R$_3$SiLi or (Me$_3$Si)$_3$Al·Et$_2$O gave a complex having a zirconium–silicon bond. When a THF solution of Me$_2$PhSiLi **12** (1 equiv) was added to a THF solution of Cp$_2$ZrCl$_2$ (1 equiv) and diphenylacetylene **11a** (1 equiv) at −78 °C and the solution was stirred at room temperature for 3 h, a reddish brown solution was obtained. After hydrolysis of the reaction mixture with H$_2$O, vinylsilane **13a** was obtained in 36% yield along with **11a** in 40% yield. In this reaction, when the reaction mixture was treated with D$_2$O, compound **13a–D$_2$** having two deuteriums was obtained. One deuterium was introduced as the vinylic proton, and the other deuterium was incorporated into the methyl proton on the silicon (39% yield, each D-content; quant.). Although vinylsilane **13a** was an expected product from the insertion of alkyne **11a** into the zirconium–silicon bond of **6**, we cannot at this stage explain the formation of compound **13a–D$_2$** having two deuteriums (Scheme 4).

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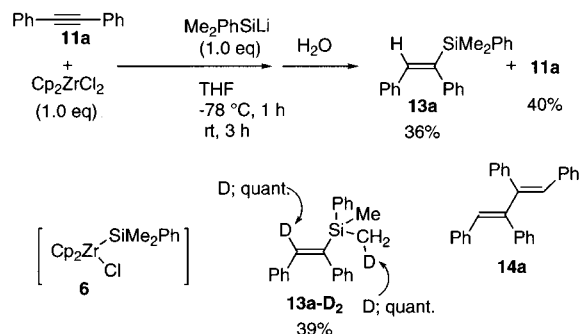
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**Scheme 4.** Reaction of Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi in the Presence of **11a**



**Table 1.** Reaction of Cp$_2$ZrCl$_2$, Me$_2$PhSiLi **12** and **11a**[a]

| run | Cp$_2$ZrCo$_2$ (equiv) | Me$_2$PhSiLi (equiv) | °C | yield of **13a** (%) |
|-----|-----|-----|-----|-----|
| 1 | 1 | 1 | rt | 36[b] |
| 2 | 1 | 2 | rt | 68 |
| 3 | 2 | 2 | rt | 59 |
| 4 | 1.5 | 3 | rt | 76 |
| 5 | 1.5 | 3 | rt | 78[c] |
| 6 | 1.5 | 3 | 40 | 74 |
| 7 | 2 | 4 | rt | 82 |
| 8 | 1.5 | 3 | 0 | 66 |
| 9 | 1.5 | 3 | 0 | 74[d] |
| 10 | 1.5 | 3 | rt | 79[e] |

[a] To a THF solution of Cp$_2$ZrCl$_2$ and **11a** was added in **12** in THF at −78 °C, and the solution was stirred at −78 °C for 1 h, and then the solution was stirred at the ambient temperature for 3 h. [b] **11a** was recovered in 40% yield. [c] D$_2$O was added to the reaction mixture and **13a-D$_2$** was obtained. [d] Reaction time; 6 h. [e] Toluene was used as the solvent and a THF solution of **12** was added.

**Scheme 5.** Synthesis of Various Vinyl Silanes **13**
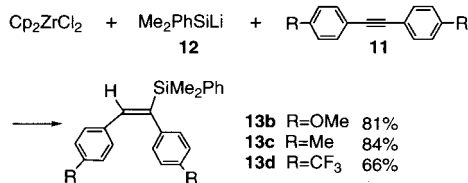


The reaction was carried out under various conditions to estimate the reaction mechanism (Table 1). When 2 equiv of Me$_2$PhSiLi to Cp$_2$ZrCl$_2$ was used for this reaction, the yield of **13a** increased to 68% along with dimeric compound **14a** in 6% yield (run 2), but a 1 to 1 molar ratio of Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi did not affect the yield of **13a** (run 3). The yield improved to 76% when 1.5 equiv of Cp$_2$ZrCl$_2$ and 3 equiv of Me$_2$PhSiLi were used (run 4). After deuteriolysis, the same product **13a−D$_2$** was also obtained in the reaction of a 1 to 2 molar ratio of Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi (run 5). The yield of **13a** increased to 82% when excess amounts of Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi **12** were used (run 7). The reaction proceeded even at 0 °C (run 8), although the yield was slightly lower, but a longer reaction time improved the yield of **13a** (run 9). Toluene can be used for this reaction (run 10). In all cases, a small amount (less than 8%) of dimeric compound **14a** was produced.

Various alkynes **11** were used for this reaction. In each case, the desired vinylsilane **13** was obtained in high yield (Scheme 5). The electron-donating group on the aromatic ring caused a slight increase in the yield of desired vinylsilane **13**.

On the other hand, when 3-hexyne **15a** was used as the alkyne for this reaction, surprisingly, allylsilane **16a** was obtained in 15% yield. In this reaction, the reaction mixture was treated with D$_2$O, and two deuteriums were also incorporated, one at

**Table 2.** Synthesis of Allylsilane[a]

| run | R | temp. (°C) | yield (%) |
|-----|-----|-----|-----|
| 1 | Et **15a** | rt | **16a** 15 |
| 2 | Et **15a** | 40 | **16a** 41 |
| 3 | Et **15b** | 40 | **16b** 29[b] |
| 4 | Pr **15b** | 40 | **16b** 25 |
| 5 | Pr **15b** | 70 | **16b** 35 |

[a] To a THF solution of Cp$_2$ZrCl$_2$ and **15** was added **12** in THF at −78 °C, and the solution was stirred at −78 °C for 1 h, and then the solution was stirred for 3 h. [b] PPh3 (1.0 eq.) was added.

**Scheme 6.** Reaction with Alkyne Having Alkyl Group
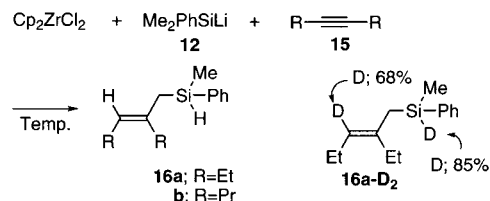


**Scheme 7.** Reaction of Zirconium−Silene Complex and Enyne
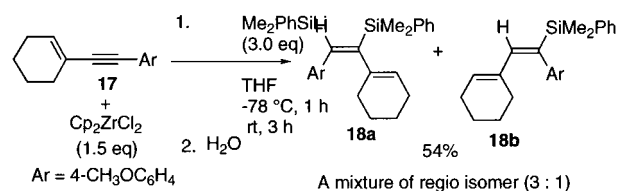


the vinylic proton and one at the proton on the silicon of **16a−D$_2$**. (D-contents: 68% and 85%, respectively). The higher reaction temperature increased the yield of the desired compound **16a** (Table 2, run 2), but the addition of PPh$_3$ as a ligand did not give a good result (run 3). Allylsilane **16b** was also obtained when 4-octyne was used for this reaction (run 4), and in this case, the yield of **16b** increased when the reaction was carried out at 70 °C (run 5) (Scheme 6).

Furthermore, as the alkyne, enyne **17** was used in this reaction to afford two inseparable regioisomers of vinylsilanes **18** in 54% yield in a ratio of 3 to 1 (Scheme 7).

**Possible Reaction Course**

On the basis of these results, we considered the possible reaction course (Scheme 8). At first, complex **6** would be formed from Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi, and then it would be converted into disilylzirconocene **19**. It is known that dibutylzirconocene, prepared from Cp$_2$ZrCl$_2$ and 2 equiv of BuLi, gives zirconocene coordinated by a butene ligand (Negishi's reagent, eq 1).[15]
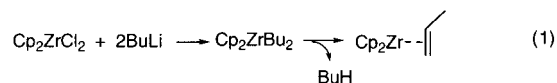


Therefore, **19** would be converted into zirconium−silene complex **7** or silazirconacyclopropane **7′**. The insertion of alkyne **11a** into the zirconium−silicon bond of **7′** gives silazirconacyclopentene **8a**. On the other hand, the insertion of dialkyl alkyne **15a** into the carbon−zirconium bond of **7′** gives silazirconacyclopentene **9a**.

Deuteriolysis of silazirconacyclopentene **8a** or **9a** gives **13a−D$_2$** or **16a−D$_2$**, respectively. In the case of enyne **17**, the olefin part would have the same role as that of the aromatic ring on alkyne **11**, and the insertion of the alkyne part of **17** into the zirconium−silicon bond occurs to give silazirconacy-

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**Scheme 8.** Possible Reaction Course
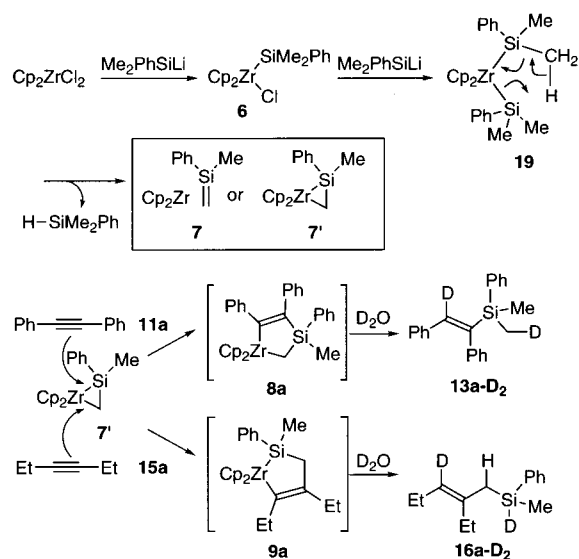


clopentene and hydrolysis of it gives **18**. The reasons why the alkyne having the aryl group or the vinyl group inserts into the zirconium−silicon bond of **7′** and the alkyne having the alkyl group inserts into the carbon−zirconium bond of **7′** are still not clear. Presumably, the electronic factor of alkyne is important for the insertion reaction.

It is known that silene is a very unstable and reactive organosilicon species. In this case, it is very interesting that silene is generated from disilylzirconocene **19** and coordinates to zirconium to give zirconium−silene complex **7**.

**Confirmation of the Reaction Mechanism.** To confirm this reaction mechanism, the reaction of $Cp_2ZrCl_2$ and $Me_2PhSiLi$ (**12**) with bis-4-methoxyphenylacetylene **11b** was monitored by the $^1H$ NMR spectra. As the first experiment, we monitored the formation of silazirconacyclopentene **8b** under the standard reaction conditions for the formation of vinyl silane **13b** by the $^1H$ NMR spectra. At first, the NMR spectrum of a THF-$d_8$ solution of $Cp_2ZrCl_2$ (Cp; $\delta$ 6.48) and **11b** was measured. Then a THF solution of $Me_2PhSiLi$ was added to this solution at −78 °C, and then the $^1H$ NMR spectrum was measured at room temperature. The Cp-protons appeared at $\delta$ 5.07, and a Si−H proton of $Me_2PhSiH$ was clearly shown at $\delta$ 4.42, whose $\delta$ value was confirmed by authentic $Me_2PhSiH$ in THF-$d_8$ (0 min). Then the solution was allowed to stand at room temperature and was monitored by the $^1H$ NMR spectrum each time. After 7 min, new peaks appeared at $\delta$ 6.30 and 6.17 (Figure 4, Chart 1). With the passage of time, the peak at $\delta$ 5.07 decreased, and the peaks at $\delta$ 6.30 and 6.17 increased (Figure 4, Chart 2), and after 4.3 h, the peak at $\delta$ 5.07 disappeared (Figure 4,Chart 3). When $HCl$-$Et_2O$ was added to the reaction mixture, a single peak of $Cp_2ZrCl_2$ appeared at $\delta$ 6.50. From the reaction mixture in the NMR tube, **13b** was obtained in 69% yield. It means that the Cp-protons of $\delta$ 6.30 and 6.17 in Chart 3 are those of silazirconacyclopentene **8b**.

Subsequently, the reaction of $Cp_2ZrCl_2$ and $Me_2PhSiLi$ in the absence of alkyne **13b** was monitored by $^1H$ NMR spectra. The results are shown in Figure 5, Charts 4−6. After addition of $Me_2PhSiLi$ to the solution of $Cp_2ZrCl_2$ in THF-$d_8$, the $^1H$ NMR-spectrum was immediately measured. The Cp-protons appeared at $\delta$ 6.11, 6.01 and 5.06 (Figure 5, Chart 4). After 3.5 min, there was no change in the spectrum (Figure 5, Chart 5). However, after 1.5 h, many peaks appeared on the NMR spectrum (Figure 5, Chart 6).
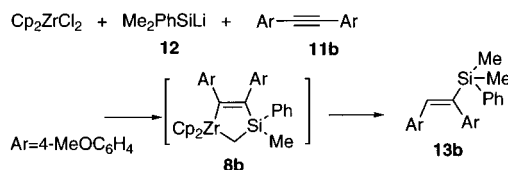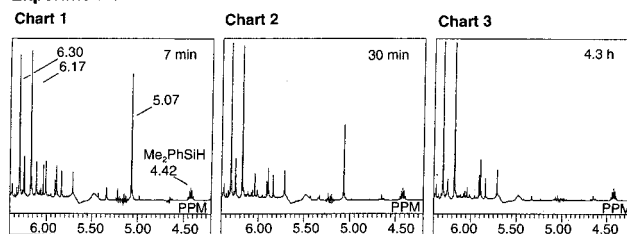


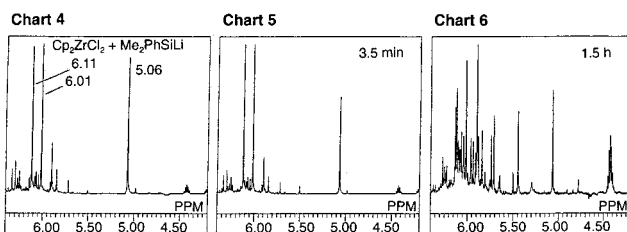**Figure 4.** $^1H$ NMR spectra of the reaction of $Cp_2ZrCl_2$ and **12** in the presence of **11b**.



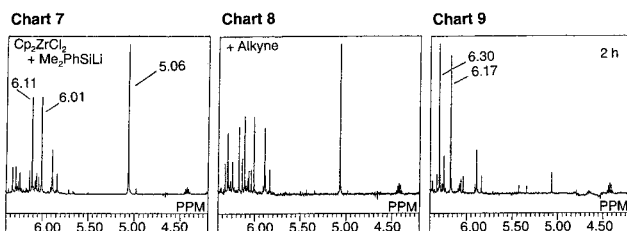**Figure 5.** $^1H$ NMR spectra of the reaction of $Cp_2ZrCl_2$ and **12**.



**Figure 6.** $^1H$ NMR spectra of the reaction of $Cp_2ZrCl_2$ and **12** and then the addition of **11b**.

Next, after a THF solution of **12** was added to $Cp_2ZrCl_2$ in THF-$d_8$, $^1H$ NMR spectrum was measured (Figure 6, Chart 7, the same conditions as that of Chart 4). Then alkyne **11b** was at once added in the NMR tube. New peaks appeared at $\delta$ 6.30 and 6.17 (Figure 6, Chart 8). After 2 h, the peaks of $\delta$ 5.06, 6.01, and 6.11 disappeared (Figure 6, Chart 9), whose chart was almost the same as Chart 3. From this reaction mixture, we obtained **13b** in 33% yield.

The $\delta$-values of the typical Cp-signals of zirconacycles and zirconocenes in the literature are shown in Figure 7.[2a,c,15−17]

From these data (Figure 7), the results of our $^1H$ NMR experiments suggested the following. Although the chemical shift of the Cp peak of zirconium−silene complex [Zr(II)] or silazirconacyclopropane is not known, it is already reported that the Cp protons of zirconacyclopropane **21** ($\delta$ 5.25)[16] or zirconocene **22** [Zr(II), $\delta$ 5.50][17] coordinated by the ethylene ligand show the values of the higher chemical shift compared with those of Cps of Zr(IV) complexes. Thus, the peak of $\delta$ 5.06 appearing at a higher chemical shift should be that of the Cp peak of Zr(II), and it would be the Cp signal of the zirconium(II)−silene complex **7**. This is supported by the fact

(16) Takahashi, T.; Swanson, D. R.; Negishi, E.; *Chem. Lett.* **1987**, 623.

(17) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579.
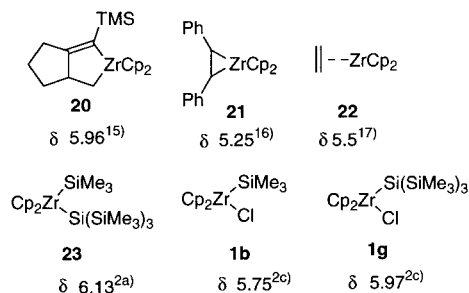
**Figure 7.** The $\delta$ values of Cp signal.

that the peak of $\delta$ 5.06 decreased when alkyne **11b** was added to the $d_8$-THF solution, and the new peaks appeared at $\delta$ 6.30 and 6.17 (Charts 8 and 9). It indicates that zirconium–silene complex **7** or **7′** converted into silazirconacyclopentene **8b** in the presence of alkyne, and we could obtain vinyl silane **13b** from the reaction mixture in the NMR tube (Experiments I and III). Therefore, the Cp peaks at $\delta$ 6.30 and 6.17 in Charts 3 and 9 are those of zirconacyclopentene **8b** because the chemical schift of Cp peaks of zirconacyclopentene **20** was known to be $\delta$ 5.96.[15] Silene is thought to be very unstable, and it decomposed after 1.5 h in the absence of alkyne (Chart 6). The Cp peaks of $\delta$ 6.11 and 6.01 (Chart 4) are thought to be those of disilylzirconocene or chlorosilylzirconocene by comparison with that of disilylzirconocene **23** ($\delta$ 6.13), [2a] and those of chlorosilylzirconocenes, **1b** or **1g** ($\delta$ 5.75[2c] or 5.97[2c]). These results strongly suggested that silene is formed from $Cp_2ZrCl_2$ and 2 equiv of $Me_2PhSiLi$, and it reacted with **11b** to give silazirconacyclopentene **8b**, which afforded vinyl silane **13b** after hydrolysis.

**The Reactivity of Silazirconacyclopentene. Insertion of Carbon Monoxide.** The results of the insertion of isocyanide into silazirconacyclopentene **8** has been already reported.[14b] In this reaction, the formation of iminosilazirconacyclohexene **24b** (Ar = $4\text{-MeOC}_6H_4$) was monitored by ^{1}H NMR spectra, and the structure of the product **25d** (Ar = $4\text{-CF}_3C_6H_4$) was confirmed by X-ray crystallography (Scheme 9).
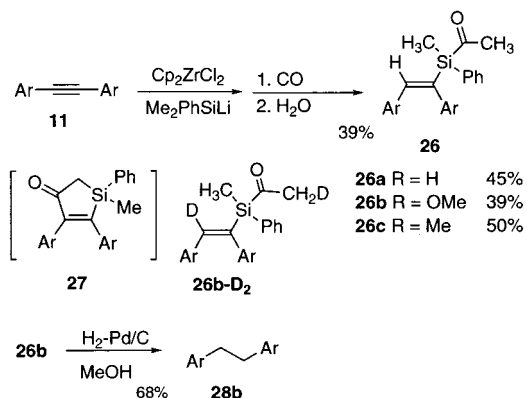
**Scheme 9.** Reaction of Silazirconacyclopentene with Isocyanide
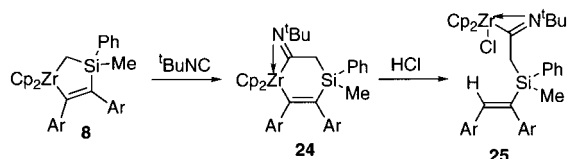


Thus, we next attempt to insert of carbon monoxide into silazirconacyclopentene **8b**. A THF solution of silazirconacyclopentene **8b**, which was prepared from alkyne **11b**, $Cp_2ZrCl_2$, and $Me_2PhSiLi$ in THF, was stirred under carbon monoxide at room temperature overnight. After hydrolysis of the reaction mixture, the carbonylation product was obtained. However, from the ^{1}H NMR, mass, and IR spectra, it was clear that the desired carbonylation product **27b** was not formed. To estimate the structure of the product, when the reaction mixture was quenched with $D_2O$, two deuteriums were incorporated at the vinyl carbon and at the acetyl methyl carbon of the product. Hydrogenation of **26b** afforded bibenzyl **28b**. On the basis of these results, the structure of the product was determined to be methyl silyl ketone **26b**. Treatment of alkynes **11a** and **11c** in a similar manner gave the corresponding methyl silyl ketones **26a** and **26c** in moderate yields (Scheme 10).

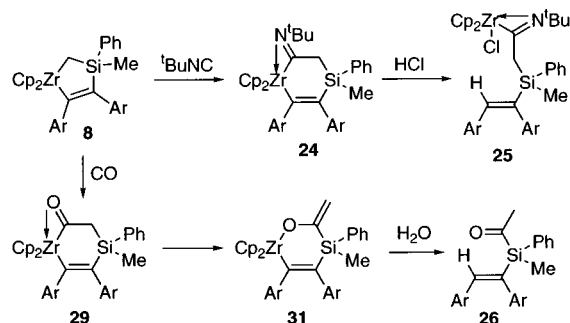The possible reaction mechanism for the formation of **26** was shown in Scheme 11.

**Scheme 10.** Reaction of Silazirconacyclopentene with Carbon Monoxide



|  |  |  |
|---|---|---|
| **26a** R = H | 45% |
| **26b** R = OMe | 39% |
| **26c** R = Me | 50% |

**Scheme 11.** Possible Reaction Mechanism
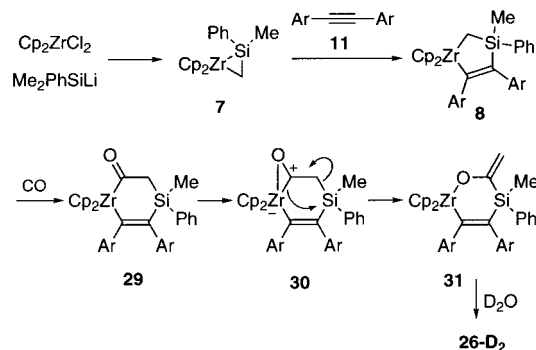


**Scheme 12.** Difference in Reaction Course



Insertion of carbon monoxide into the carbon–zirconium bond in silazirconacyclopentene **8** gave silazirconacyclohexenone **29**, whose carbonyl oxygen would coordinate to zirconium metal. Then the zirconium carbon bond migrates to silicon to afford oxazirconacyclohexene **31** via **30**.[18] Hydrolysis of **31** with $D_2O$ would afford **26-D₂**.

It was quite interesting that hydrolysis of iminosilacylcyclohexene **24** gave iminozirconium complex **25**, while silazirconacyclohexenone **29** converted into oxazirconacycle **31**, which was treated with $H_2O$ and gave methyl silyl ketone **26**. The differences in the reactivity between iminosilazirconacyclohexene **24** and silazirconacyclohexenone **27** would be due to the strong coordination of the carbonyl oxygen in **27** to zirconium metal compared with that of the imino nitrogen in **24** to zirconium metal (Scheme 12).

These substituents were introduced on the methyl group on the silicon moiety via silazirconacyclopentene **8**.

(18) (a)Lappert, M. F.; Raston, C. L.; Engelhardt, L. M.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 521. (b) Petersen, J. L.; Egan, J. W., Jr. *Organometallics* **1987**, *6*, 2007.

**Transmetalation of Zirconium to Copper of Silazircona-
cyclopentene.** It is already known that transmetalation from
zirconium to copper is a useful tool for the formation of a new
carbon−carbon bond. Schwarts reported the first transmetalation
from zirconium to copper.[19] Then Lipschuts[20] and Takahashi[21]
independently reported the transmetalation of zirconium to
copper. If this transmetalation were used for our zirconacycle
**8**, new carbon−carbon bonds would be formed on the vinyl
carbon and on the methyl carbon of the silicon center. To a
THF solution of CuCl (2 equiv to Cp$_2$ZrCl$_2$) and allyl chloride
was added a THF solution of silazirconacyclopentene **8a**,
generated from Cp$_2$ZrCl$_2$, alkyne **11a**, and Me$_2$PhSiLi **12**, and
the solution was stirred at room temperature for 18 h. After the
usual work up, bis-allylated compound **33a** was obtained in 76%
yield (Scheme 13).

**Scheme 13.** Transmetalation of Zr on
Silazirconacyclopentene with CuCl
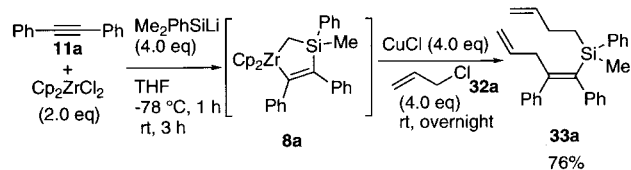


The results indicated that two allyl groups were introduced
on the alkyne carbon and on the methyl group on the silicon
moiety. As the results, two different substituents were introduced
on the alkyne carbons, respectively, by a one-pot reaction. One
is the allyl group, and the other is the butenylmethylphenyl silyl
group (Figure 8). Transmetalations of various zirconacycles **8**
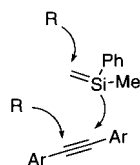to copper were carried out in the presence of allyl halide **32**,



**Figure 8.**

(19) Yoshifuji, M.; Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1977**,
1303.

(20) (a) Lipshutz, B. H.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*,
7440. (b) Lipshutz, B. H.; Kato, K. *Tetrahedron Lett.* **1991**, *32*, 5647. (c)
Lipshutz, B. H.; Fatheree, P.; Hagen, W.; Stevens, K. L. *Tetrahedron Lett.*
**1992**, *33*, 1041. (d) Venanzi, L. M.; Lehmann, R.; Keil, R.; Lipshutz, B.
H. *Tetrahedron Lett.* **1992**, *33*, 5857. (e) Lipshutz, B. H.; Keil, R. *J. Am.
Chem. Soc.* **1992**, *114*, 7919. (f) Lipshutz, B. H.; Wood, M. R. *J. Am. Chem.
Soc.* **1993**, *115*, 12625. (g) Lipshutz, B. H.; Segi, M. *Tetrahedron* **1995**,
*51*, 4407. (h) Lipshutz, B. H. *Acc. Chem. Res.* **1997**, *30*, 277.

(21) (a) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Tetrahedron
Lett.* **1994**, *35*, 5685. (b) Kasai, K.; Kotora, M.; Suzuki, N.; Takahashi, T.
*J. Chem. Soc., Chem. Commun.* **1995**, 109. (c) Takahashi, T.; Kotora, M.;
Kasai, K.; Suzuki, N.; Nakajima, K. *Organometallics* **1994**, *13*, 4183. (d)
Takahashi, T.; Kotora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**,
1503. (e) Takahashi, T.; Xi, Z.; Kotora, M.; Xi, C.; Nakajima, K.
*Tetrahedron Lett.* **1996**, *37*, 7521. (f) Takahashi, T.; Kotora, M.; Xi, Z. *J.
Chem. Soc., Chem. Commun.* **1995**, 361. (g) Takahashi, T.; Hara, R.;
Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (h) Xi, C.;
Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*,
4099. (i) Hara, R.; Liu, Y.; Sun, W.-H.; Takahashi, T. *Tetrahedron Lett.*
**1997**, *38*, 4103. (j) Takahashi, T.; Nishihara, Y.; Hara, R.; Huo, S.; Kotora,
M. *Chem. Commun.* **1997**, 1599. (k) Kotora, M.; Xi, Z.; Takahashi, T. *J.
Synth. Org. Chem., Jpn.* **1997**, *55*, 958. (l) Kotora, M.; Umeda, C.; Ishida,
T.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 8355. (m) Ubayama, H.; Sun,
W.-H.; Xi, Z.; Takahashi, T. *Chem. Commun.* **1998**, 1931. (n) Takahashi,
T.; Sun, W.-H.; Liu, Y.; Kotora, M. *Organometallics* **1998**,
*17*, 3841. (o) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.;
Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672. (p) Liu, Y.; Shen, B.; Kotora,
M.; Takahashi, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 949.

**Table 3.** Transmetalation of **8** to Copper

| run | Ar | R | product | yield (%) |
|-----|-----|-----|---------|-----------|
| 1 | Ph | H (**32a**) | **33a** | 76 |
| 2 | 4-CH$_3$OC$_6$H$_4$ | H (**32a**) | **33b** | 72 |
| 3 | 4-CH$_3$OC$_6$H$_4$ | H (**32a**) | **33c** | 76 |
| 4 | Ph | Me (**32b**) | **33d** | 66 |

**Scheme 14.** Transmetalation of Zr on
Silazirconacyclopentene with Cu
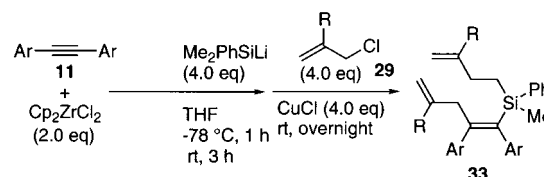


and the results are shown in Table 3. In each case, bisallylated
compound **33** was obtained in high yield (Scheme 14).

**Synthesis of Eight-Membered Ring Componds Containing
Silicon.** Little has been reported about the synthesis of eight-
membered ring compounds containing silicon.[22] It was ex-
pected that eight-membered ring compounds containing sili-
con could be synthesized from compounds **33** using ruthen-
ium-catalyzed olefin metathesis.[23] When a CH$_2$Cl$_2$ solution of
diene **33a** was stirred at room temperature in the presence of
10 mol % of ruthenium carbene complex **34** overnight, the
desired eight-membered ring compound **35a** was obtained in
quantitative yield. The structure of **35a** was confirmed by $^1$H
NMR, $^{13}$C NMR, COSY, and mass spectra. Various dienes **33**
were treated in a similar manner, and eight-membered ring
compounds **35** were obtained in high yields (Scheme 15 and
Table 4).

**Scheme 15.** Synthesis of Eight-Membered Ring Compounds
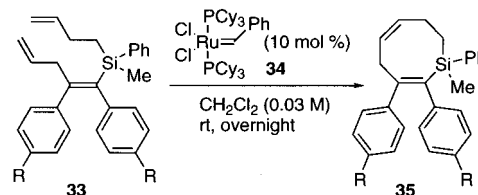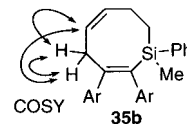Using Olefin Metathesis



**Table 4.** Synthesis of Eight-Membered Ring Compounds



| run | R | product | yield (%) |
|-----|-----|---------|-----------|
| 1 | H | **35a** | quant. |
| 2 | OCH$_3$ | **35b** | 97 |
| 3 | CH$_3$ | **35c** | 99 |

The synthesis of eight-membered ring compounds having
silicon was quite interesting, and in this case, they could be
obtained from alkyne by a two-step synthesis.

In conclusion, zirconium−silene complex **7** or **7′** can be
formed from disilylzirconocene **19** generated from Cp$_2$ZrCl$_2$ and

(22) Kagoshima, H.; Hayashi, M.; Hashimoto, Y.; Saigo, K. *Organo-
metallics* **1996**, *15*, 5439.

(23) (a) Fu, G.; Grubbs, R. H. *J. Am. Chem. Soc.,* **1992**, *114*, 5426. (b)
Furstner, A. *Topics in Organometallic Chemistry*; Springer-Verlag: Berlin
Heidelberg, 1998; Vol 1. (c) Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs,
R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108.

2 equiv of Me$_2$PhSiLi **12**. The insertion of alkyne **11**, **17**, or **15** into the zirconium−silicon bond or zirconium−carbon bond of zirconium−silene complex **7′** gives silazirconacyclopentenes **8** or **9**. As a result, novel carbon−silicon or carbon−carbon bond formation occurs on the alkyne carbons. It is quite interesting that the methyl group on the silicon can react with various electrophiles such as protons, deuteriums, isocyanide, carbon monoxide, and allyl halides.

## Experimental Section

**General.** All manipulations were performed under an argon atmosphere unless otherwise mentioned. All solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70−230 mesh), and flash chromatography was performed silica gel 60 (Merck, 230−400 mesh) using the indicated solvent. $^1$H and $^{13}$C NMR spectra were recorded at 270 or 500 MHz and at 67.5, 100, 125 MHz, respectively. Infrared spectra were recorded on a Perkin-Elmer FTIR 1605 spectrometer. Mass spectra were measured on JEOL DX-303 and JEOL JMS-700TZ, JEOL JMS-PABmate, and Perkin-Elmer Q-mass910 mass spectrometers.

**Typical Procedure for the Synthesis of (*E*)-α-Phenylsilyl− Stilbene 13a.** To a solution of Cp$_2$ZrCl$_2$ (204.6 mg, 0.700 mmol) and diphenyl acetylene **11a** (62.5 mg, 0.351 mmol) in THF (3.8 mL) was added Me$_2$PhSiLi (0.70 M THF solution, 2.0 mL, 1.40 mmol) at −78 °C and the solution was stirred at −78 Å °C for 1 h and then at room temperature for 3 h. Water was added at 0 °C, and the color of the solution was changed from reddish brown to colorless. The aqueous layer was extracted with Et$_2$O. The organic layer was washed with brine, dried over Na$_2$SO$_4$, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give a colorless oil of **13a** (90.9 mg, 0.289 mmol, 82%). IR (neat) *ν* 3066, 2956, 1598, 1570, 1494, 1446, 1428, 1112, 954 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 0.43 (s, 6H), 6.87 (s, 1H), 6.93 (m, 2H), 6.98 (m, 2H), 7.07−7.12 (m, 3H), 7.20 (m, 1H), 7.26 (m, 2H), 7.35−7.42 (m, 3H), 7.58 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ −3.1 (CH$_3$), 125.7 (CH), 127.2 (CH), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.5 (CH), 129.1 (CH), 129.5 (CH), 134.2 (CH), 137.2 (C), 137.6 (C), 139.2 (CH), 142.3 (C), 145.0 (C); MS (EI) *m/z* (%) 314 (M$^+$, 47.99), 299 (27.64), 236 (10.02), 221 (38.47), 178 (10.87), 136 (17.00); HRMS (EI) calcd for C$_{22}$H$_{22}$Si: 314.1492, found: 314.1508.

**(*E*)-3-Methylphenylsilylmethyl-3-hexene (16).** IR (neat) δ 3068, 2962, 2120, 1458, 1428, 1250, 1114, 880 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 0.34 (d, *J* = 3.6 Hz, 3 H), 0.91 (t, *J* = 7.5 Hz, 3 H), 0.96 (t, *J* = 7.5 Hz, 3 H), 1.72 (dd, *J* = 14.0, 4.3 Hz, 1 H), 1.80 (dd, *J* = 14.0, 2.5 Hz, 1 H), 1.95−2.02 (m, 4H), 4.39 (m, 1 H), 4.99 (t, *J* = 7.2 Hz, 1H), 7.33−7.40 (m, 3 H), 7.53−7.55 (m, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ −5.7 (CH$_3$), 13.1 (CH$_3$), 14.9 (CH$_3$), 21.1 (CH$_2$), 23.2 (CH$_2$), 24.8 (CH$_2$), 125.7 (CH), 127.7 (CH), 129.2 (CH), 134.4 (CH), 136.6 (C), 136.8 (C); MS (EI) *m/z* (%) 218 (M$^+$, 9.80), 189 (2.63), 162 (19.49), 148 (15.68), 135 (10.12), 121 (100.00), 105 (12.42), 43 (17.15); HRMS (EI) calcd for C$_{14}$H$_{22}$Si: 218.1492, found: 218.1492.

**Typical Procedure for Carbonylation of Silazirconacyclopentene 8b. (4*E*)-4,5-Bis(4-methoxyphenyl)-3-methyl-3-phenyl-3-silapent-4-en-2-one (26b).** A THF solution of silazirconacyclopentene **2b**, which was prepared from Cp$_2$ZrCl$_2$ (154.9 mg, 0.530 mmol), **11b** (84.0 mg, 0.353 mmol) in THF (3.5 mL), and Me$_2$PhSiLi (0.70 M THF sol. 1.5 mL, 1.05 mmol), was stirred under carbon monoxide (1 atm) at room-temperature overnight. Water was added at 0 °C, and the solution was stirred until the color of the solution was changed from red−black to colorless. The aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexanes− ethyl acetate, 5:1) to give a colorless oil of **26b** (55.2 mg, 39%). IR *ν* (neat) 2958, 1642, 1604, 1508 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 0.56 (s, 3H), 2.21 (s, 3H), 3.71 (s, 3H), 3.78 (s, 3H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.37−7.43 (m, 3H), 7.62 (bd, *J* = 7.5

Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ −5.45, 37.16, 55.11, 113.35, 144.38, 128.10, 129.02, 129.54, 129.98, 131.16, 132.81, 133.33, 135.02, 136.02, 142.17, 158.07, 159.01, 243.86; MS *m/z* 402 (M$^+$), 387, 359, 281, 266, 121; HRMS calcd for C$_{25}$H$_{26}$O$_3$Si: 402.1651, found: 402.1632.

**Typical Procedure for Transmetalation. 6-Methyl-4,5,6-tri-phenyl-6-sila-1,4,9-decatriene (33a).** To a solution of Cp$_2$ZrCl$_2$ (203.8 mg, 0.697 mmol) and **11a** (62.2 mg, 0.349 mmol) in THF (7.0 mL) was added Me$_2$PhSiLi (0.77 M THF solution, 1.8 mL, 1.39 mmol), and the solution was stirred overnight to afford a solution of **8a**. To the solution of CuCl (138.2 mg, 1.40 mmol) and allyl chloride (0.11 mL, 1.35 mmol) in THF (1.0 mL) was added a solution of **8a**, and then the solution was stirred at room-temperature overnight. Water was added and the aqueous layer was extracted with Et$_2$O and the organic layer was washed with water, dried over Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel (hexane) to give a colorless oil of **33a** (105 mg, 0.266 mmol, 76%). IR (neat) *ν* 3068, 1638, 1596, 1586, 1486, 1440, 1428, 1252, 1108, 1026, 994, 910 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 0.31 (s, 3H), 0.94 (t, *J* = 8.5 Hz, 2H), 1.92−2.06 (m, 2H), 3.25 (d, *J* = 6.5 Hz, 2H), 4.69 (d, *J* = 17.4 Hz, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.91 (d, *J* = 17.3 Hz, 1H), 5.46 (m, 1H), 5.81 (m, 1H), 6.86 (m, 2H), 6.93 (m, 2H), 6.95−7.00 (m, 2H), 7.04−7.08 (m, 4H), 7.41−7.43 (m, 3H), 7.68−7.71 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) d 2.1 (CH$_3$), 15.1 (CH$_2$), 27.9 (CH$_2$), 42.8 (CH$_2$), 112.8 (CH$_2$), 116.3 (CH$_2$), 124.7 (CH), 125.8 (CH), 127.2 (CH), 127.4 (CH), 128.0 (CH), 128.9 (CH), 129.0 (CH), 129.2 (CH), 134.0 (CH), 135.1 (CH), 138.7 (C), 141.4 (CH), 142.3 (C), 144.0 (C), 153.5 (C); MS (EI) *m/z* (%) 394 (M$^+$, 2.95), 339 (74.92), 316 (3.10), 261 (31.07), 197 (43.53), 121 (100.00), 97 (31.60).; HRMS (EI) calcd for C$_{28}$H$_{30}$Si: 394.2118, found: 394.2117.

**Typical Procedure for Synthesis of Eight-Membered Ring Compound. (2*E*,5*Z*)-1-Methyl-1,2,3-triphenyl-1-silacycloocta-2,5-diene (35a).** A solution of ruthenium carbene complex **31** (14.9 mg, 18.1 μmol) and **33a** (65.3 mg, 0.165 mmol) in CH$_2$Cl$_2$ (6 mL) was stirred at room temperature overnight. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (hexane/Et$_2$O, 100/1) to give a colorless oil of **35a** (60.4 mg, 0.165 mmol, quant).

IR (neat) *ν* 3018, 2862, 1596, 1486, 1426, 1252, 1106 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ -0.07 (s, 3H), 1.13 (ddd, *J* = 14.9, 12.4, 2.4 Hz, 1H), 1.47 (ddd, *J* = 14.9, 8.8, 1.4 Hz, 1H), 2.35 (m, 1H), 2.51 (m, 1H), 2.88 (dd, *J* = 12.7, 5.3 Hz, 1H), 3.60 (dd, *J* = 12.7, 9.5 Hz, 1H), 5.75−5.83 (m, 2H), 6.81−6.83 (m, 2H), 6.92 (m, 1H), 7.00− 7.06 (m, 5H), 7.09−7.12 (m, 2H), 7.41−7.44 (m, 3H), 7.72−7.74 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ −0.2, 16.3, 21.8, 38.0, 124.6, 126.0, 127.3, 127.5, 128.1, 128.4, 129.0, 129.1, 130.1, 130.9, 134.2, 138.0, 138.2, 143.9, 144.11, 156.2; MS *m/z* 366 (M$^+$), 351, 288, 275, 245, 121; HRMS calcd for C$_{26}$H$_{26}$Si: 366.1804, found: 366.1801.

**$^1$H NMR Experiment.** The reaction was performed in an NMR tube under argon atmosphere. To a solution of Cp$_2$ZrCl$_2$ (16.5 mg, 56.4 μmol) and bis-4-methoxyphenylacetylene **11b** (8.8 mg, 36.9 μmol) in THF-*d$_8$* (0.8 mL) was added Me$_2$PhSiLi (0.7 M in THF, 0.16 mL, 112 μmol), and the mixture was stirred at −78 °C. Then the mixture was monitored at room temperature by the $^1$H NMR spectrum. After 4.5 h, anhydrous HCl (1.0 M in Et$_2$O) was added. To the mixture was added H$_2$O, and the aqueous layer was extracted with Et$_2$O, and the organic layer was washed with brine, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 50/1) to give vinylsilane **13b** (69% yield).

**Reaction of Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi.** When to the solution of Cp$_2$ZrCl$_2$ (1.0 equiv) was added Me$_2$PhSiLi (2 equiv) in THF-*d$_8$* and the $^1$H NMR was monitored, the peak of δ 5.06 (s) was shown instantly. However, this peak gradually disappeared. After 1.5 h, many peaks were shown with a small peak of δ 5.06.

**Reaction of Cp$_2$ZrCl$_2$ and Me$_2$PhSiLi and Then the Addition of Alkyne 11b.** When to the solution of Cp$_2$ZrCl$_2$ (1.5 equiv) was added Me$_2$PhSiLi (3 equiv) in the absence of ligand in THF-*d$_8$* and the $^1$H NMR was monitored after the peak of δ 5.06 was recognized on $^1$H NMR chart, **11b** (1 equiv) was added at once. The new peaks was

shown at $\delta$ 6.30 and 6.17 with the peak of $\delta$ 5.06. The peak at $\delta$ 5.06 disappeared after 6 h, and **13b** was obtained in 33% yield along with **11b** in 40% yield after the usual work up.

**Supporting Information Available:** The spectral data of **13a$-$D$_2$**, **13b$-$d**, **14b**, **16a$-$D$_2$**, **18a**, **18b**, **26a**, **26c**, **33b$-$d**, and **35b$-$c** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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