

Formation of Silazirconacyclopentene via Zirconium–Silene Complex and Alkyne

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Silenes are usually reactive organosilicone species whose formation has been confirmed by trapping reactions.^{1,2} Recently, Tilley reported the first stable ruthenium–silene complexes,^{3a,b} and iridium–^{3c} and tungsten–silene complexes have subsequently been synthesized.^{4,5} Although Berry reported the reaction of tungsten–silene complex with MeOH, H₂, and Me₃SiH,⁴ little is known about the reactivity of the complex coordinated by silene. During the course of our study on the preparation and reactivity of zirconium–silyl complex **2**,⁶ we found that zirconium–silene complex **1** would be formed from disilylzirconocene **3** (Figure 1). Here, we report the formation of silazirconacyclopentene from zirconium–silene complex **1**, generated from Cp₂ZrCl₂ and Me₂-PhSiLi **4**, and alkyne.

When a THF solution of Me₂PhSiLi **4** (1 equiv) was added to a THF solution of Cp₂ZrCl₂ (1 equiv) and diphenylacetylene **5a** (1 equiv) at –78 °C and the solution was stirred at room temperature for 3 h, a reddish brown solution was obtained. After hydrolysis with H₂O, vinylsilane **6a** was obtained in 36% yield along with **5a** in 40% yield (Table 1, run 1). In this reaction, when the reaction mixture was treated with D₂O, the vinylic proton and the methyl proton on the silyl group were deuterated to give vinylsilane **6a-D₂** (39% yield, each D-content; quant) (Scheme 1). Although vinylsilane **6a** was an expected product by the insertion of alkyne **5a** into the zirconium–silyl bond of **2a**, we cannot explain the formation of **6a-D₂** at this stage.

The reaction was carried out under various conditions (Table 1). When 2 equiv of Me₂PhSiLi **4** to Cp₂ZrCl₂ were used for this reaction, the yield of **6a** increased to 68% along with dimeric compound **7a** in 6% yield (run 2). The same product **6a-D₂** was also obtained in the reaction of a 1 to 2 molar ratio of Cp₂ZrCl₂ and Me₂PhSiLi **4** (run 5). The yield of **6a** increased to 82% when excess amounts of Cp₂ZrCl₂ and Me₂PhSiLi **4** were used (run 7). The reaction proceeded even at 0 °C (run 8). When a THF solution

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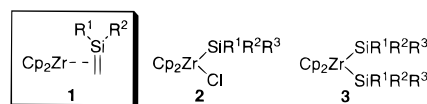


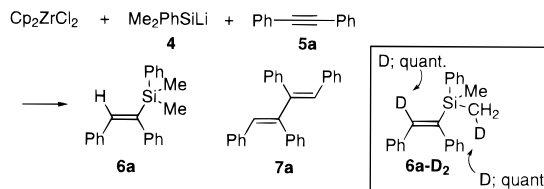
Figure 1. Silyl-zirconium complex.

Table 1. Reaction of Cp₂ZrCl₂, Me₂PhSiLi **4** and **5a**^a

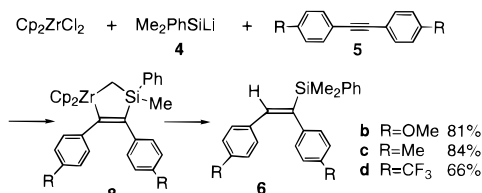
run	Cp ₂ ZrCl ₂ (equiv)	Me ₂ PhSiLi (equiv)	temp (°C)	yield of 6a (%)
1	1	1	rt	36 ^b
2	1	2	rt	68
3	2	2	rt	59
4	1.5	3	rt	76
5	1.5	3	rt	78 ^c
6	1.5	3	40	74
7	2	4	rt	82
8	1.5	3	0	74 ^d
9	1.5	3	rt	35 ^e
10	1.5	3	rt	79 ^f

^a To a THF solution of Cp₂ZrCl₂ and **5a** was added **4** 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 **5a** was recovered in 40% yield. ^c D₂O was added to the reaction mixture, and **6a-D₂** was obtained. ^d Reaction time; 6 h. ^e The solution of Cp₂ZrCl₂ and **4** was stirred at –78 °C for 1 h, **5a** was added at –78 °C, and the solution was stirred at rt for 3 h. ^f Toluene was used as the solvent, and a THF solution of **4** was added.

Scheme 1



Scheme 2

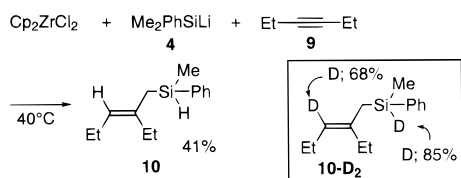


of Cp₂ZrCl₂ and Me₂PhSiLi **4** was stirred at –78 °C for 1 h and then alkyne **5a** was added and the solution was stirred at room temperature for 3 h, the desired product **6a** was obtained, although the yield decreased to 35% (run 9). In all cases, a small amount (less than 8%) of dimeric compound **7a** was produced. Various alkynes **5** were used for this reaction. In each case, the desired vinylsilane **6** was obtained in high yield (Scheme 2).

On the other hand, when 3-hexyne **9** was used for this reaction as alkyne, we surprisingly obtained allylsilane **10** in 41% yield. When the reaction mixture was treated with D₂O, two deuteriums were also incorporated, at the vinylic proton and at the proton on the silyl center of **10-D₂** (D-contents: 68 and 85%, respectively) (Scheme 3).

On the basis of these results, we considered the possible reaction course as shown in Scheme 4. At first, silylzirconium complex **2a** is formed, and it is then converted into disilylzirconocene **3a**. It is known that dibutylzirconocene gives zirconocene coordinated by butene ligand (Negishi's reagent).⁷ Therefore, **3a** would convert into zirconium–silene complex **1a** or **1a'**. The insertion of alkyne **5a** into the zirconium–silyl bond

Scheme 3



Scheme 4

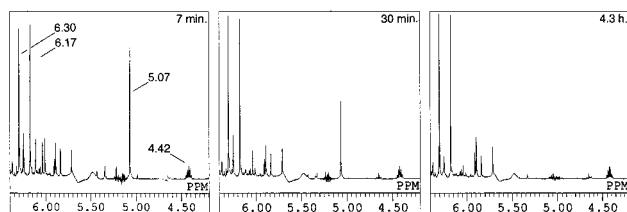
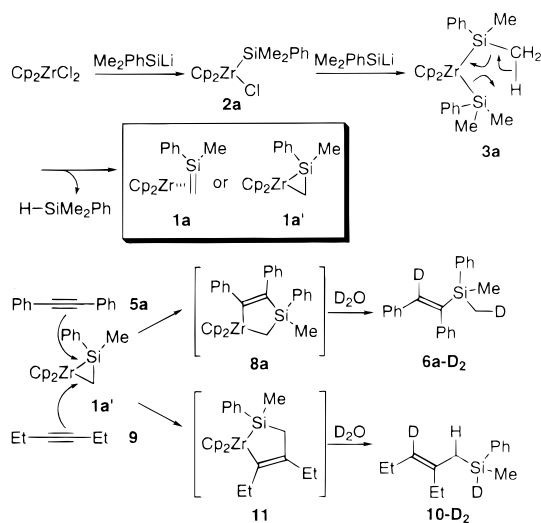


Figure 2.

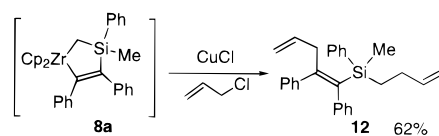
of **1a'** gives silazirconacyclopentene **8a**. On the other hand, the insertion of dialkyl alkyne **9** into the zirconium–carbon bond of **1a'** gave silazirconacyclopentene **11**. Deuteration of silazirconacyclopentene **8a** or **11** gave **6a-D₂** or **10-D₂**, respectively. The reason the alkyne having a phenyl group inserts into the zirconium–silyl bond and the alkyne having an alkyl group inserts into the zirconium–carbon bond is still not clear. Presumably, the electronic factor of alkyne is important for the insertion reaction.

To confirm this reaction mechanism, the reaction of Cp_2ZrCl_2 and Me_2PhSiLi **4** with di-*p*-methoxyphenylacetylene **5b** was monitored by the ^1H NMR spectrum⁸ (see Figure 2). When a THF solution of Me_2PhSiLi **4** was added to a THF-*d*₈ solution of Cp_2ZrCl_2 and **5b**, the Cp-protons appeared at δ 5.07, and a Si–H proton of Me_2PhSiH was clearly shown at δ 4.42. After 7 min, new peaks appeared at δ 6.30 and 6.17. With the passage of time, the peak at δ 5.07 decreased and the peaks at δ 6.30 and 6.17 increased, and after 4.3 h, the peak at δ 5.07 disappeared. When $\text{HCl-Et}_2\text{O}$ was added to the reaction mixture, a single peak of

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(8) The reaction was performed in an NMR tube under argon atmosphere. To a solution of Cp_2ZrCl_2 (16.5 mg, 56.4 μmol) and di-*p*-methoxyphenylacetylene **5b** (8.8 mg, 36.9 μmol) in THF-*d*₈ (0.8 mL) was added Me_2PhSiLi **4** (0.7 M in THF, 0.16 mL, 112 μmol), and the mixture was stirred at -78°C . The mixture was monitored at room temperature by the ^1H NMR spectrum. After 4.5 h, anhydrous HCl (1.0 M in Et_2O) was added. To the mixture was added H_2O . The aqueous layer was extracted with Et_2O , and the organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. The residue was purified by flash column chromatography on silicagel (hexane/AcOEt = 50/1) to give vinylsilane **6b** (69% yield).

Scheme 5



Cp_2ZrCl_2 appeared at δ 6.50. From the reaction mixture in the NMR tube, **6b** was obtained in 69% yield. These results indicate that the former Cp-signal at δ 5.07 would be that of silene complex **1a**,⁹ and the latter peaks at δ 6.30 and 6.17 should be those of silazirconacyclopentene **8b**.¹⁰

It is already known that transmetalation from zirconium to copper is a useful tool for new carbon–carbon bond formations.¹¹ If this transmetalation proceeds, new carbon–carbon bond would be formed on the methyl carbon of the silyl center. When CuCl (2 equiv to Cp_2ZrCl_2) and allyl chloride were added to a THF solution of silazirconacyclopentene **8a**, generated from Cp_2ZrCl_2 , alkyne **5a** and Me_2PhSiLi **4**, and the solution was stirred at room temperature for 18 h, diallylated compound **12** was obtained in 62% yield (Scheme 5).

In conclusion, zirconium–silene complex **1a** or **1a'** would be formed from disilylzirconocene **3a** generated from Cp_2ZrCl_2 and 2 equiv of Me_2PhSiLi **4**. The insertion of alkyne **5** and **9** into the silyl–zirconium bond or zirconium–carbon bond of silazirconacyclopentene **1a'** gave silazirconacyclopentenes **8** and **11**. As a result, the methyl group on the silyl center could react with electrophiles such as proton, deuterium, and allyl halide.

Further studies are in progress.

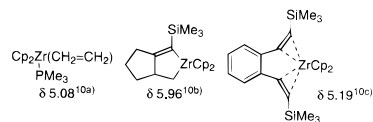
Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, “The Chemistry of Inter-element Linkage” (No. 09239203) from Ministry of Education, Science, Sports and Culture, Japan. We thank the Japan Society for the Promotion of Science (JSPS) Research Fellowships for Young Scientists (to K.S.).

Supporting Information Available: Experimental details and ^1H spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(9) We carried out the other three ^1H NMR experiments. When the reaction of Cp_2ZrCl_2 (1.5 equiv) and Me_2PhSiLi (3 equiv) in the presence of PMe_3 (1.5 equiv) in THF-*d*₈ was monitored by ^1H NMR, the peaks of δ 5.27 (d, $J = 1.4$ Hz), 5.02 (d, $J = 1.4$ Hz), and 5.06 (s) were shown. Then the peaks of δ 5.27 and 5.02 gradually increased and the peak of δ 5.06 decreased. After 4.5 h, alkyne **5b** (1 equiv) was added. The new peaks of δ 6.30 and 6.17 appeared and the peaks of δ 5.27, 5.02, and 5.06 disappeared. After the usual work up, the desired vinyl silane **6b** was obtained in 28% yield along with **5b** (54% yield). The second experiment is the reaction of Cp_2ZrCl_2 (1 equiv) and Me_2PhSiLi (2 equiv). The third one: after the same reaction as the second one was carried out and the peak of δ 5.06 was confirmed, **5b** was added at once, and **6b** was obtained in 33% yield. These reactions were monitored by ^1H NMR, and the spectral data are shown in Supporting Information.

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