

# Reaction of silazirconacyclopentene formed from zirconium–silene complex and alkyne with isocyanide

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## Abstract

The reaction of silazirconacyclopentene (**3**), which was formed from zirconium–silene complex **1** and diarylacetylene (**5**), with *tert*-butyl isocyanide afforded iminosilazirconacyclohexene (**7**). Treatment of iminosilazirconacyclohexene (**7**) with HCl–Et<sub>2</sub>O gave the imino-zirconium complex **6**, whose structure was confirmed by X-ray crystallography. The reaction was monitored by <sup>1</sup>H-NMR spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Silene; Zirconium–silene complex; Iminosilazirconacyclohexene; Isocyanide; Silazirconacyclopentene

## 1. Introduction

During the course of our study [1] of complexes having silicon–zirconium bonds [2], we found that the zirconium–silene complex **1** is formed from Cp<sub>2</sub>ZrCl<sub>2</sub> and Me<sub>2</sub>PhSiLi (two equivalents to Cp<sub>2</sub>ZrCl<sub>2</sub>) [3]. Silenes are very reactive organosilicon species and their formation has been confirmed by trapping reactions [4]. The insertion of diarylacetylene into the silicon–zirconium bond of **1** gave silazirconacyclopentene (**3**), while 3-hexyne was inserted into the carbon–zirconium bond of **1** to give silazirconacyclopentene (**4**) (R = Et) (Scheme 1).

Here we report the formation and reactivity of silazirconacyclohexene (**7**), which was prepared by insertion of isocyanide [5] into silazirconacyclopentene (**3**), synthesized from zirconium–silene complex **1** and diarylalkyne **5**.

## 2. Results and discussion

### 2.1. Synthesis of imino-zirconium complexes **6a–d**

To a THF solution of Cp<sub>2</sub>ZrCl<sub>2</sub> (1.5 equivalents) and

diphenylacetylene (**5a**) (one equivalent) was added Me<sub>2</sub>PhSiLi (three equivalents) at –78°C, and the solution was stirred at the same temperature for 1 h and then at room temperature (r.t.) for 3 h. To this solution was added *tert*-butyl isocyanide (2.1 equivalents), and the solution was stirred at r.t. overnight. Surprisingly, treatment with HCl–Et<sub>2</sub>O gave the imino-zirconium complex **6a**, but neither **8a** nor **9a**, in 57% yield based on alkyne **5a**. When the reaction mixture was quenched with 20% DCl–D<sub>2</sub>O, **6a-D** was obtained in 68% yield (D content: quant.). The intermediate was iminosilazirconacyclohexene **7a**, and the carbon–zirconium bond remained unchanged due to the strong coordination of nitrogen in **6a** to zirconium (Scheme 2).

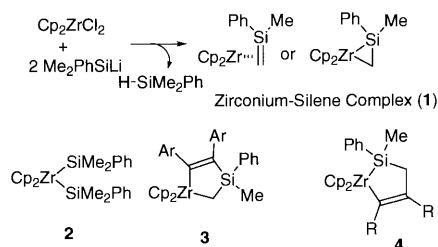
Various imino-zirconium complexes **6** were synthesized. The corresponding imino-zirconium complexes **6** were obtained from Cp<sub>2</sub>ZrCl<sub>2</sub> (1.5 equivalents), Me<sub>2</sub>PhSiLi (three equivalents), and various diarylacetylenes **5** (one equivalent) by a one-pot reaction in good to moderate yields (Table 1). In this reaction, the electron-donating group on the aromatic ring gave good results.

### 2.2. Confirmation of the structure of **6**

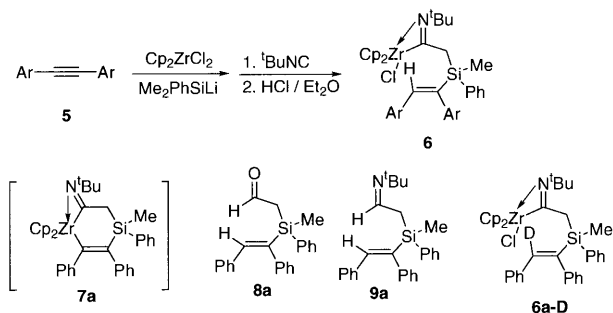
Since compound **6d** was crystallized, it was confirmed by X-ray crystallography (Fig. 1, see Section 4).

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Scheme 1.



Scheme 2.

Table 1  
Synthesis of imino-zirconium complex

Run	Ar	Alkyne	Product	Yield (%)
1	Ph	<b>5a</b>	<b>6a</b>	57
2	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>5b</b>	<b>6b</b>	62
3	4-MeC <sub>6</sub> H <sub>4</sub>	<b>5c</b>	<b>6c</b>	68
4	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>5d</b>	<b>6d</b>	27

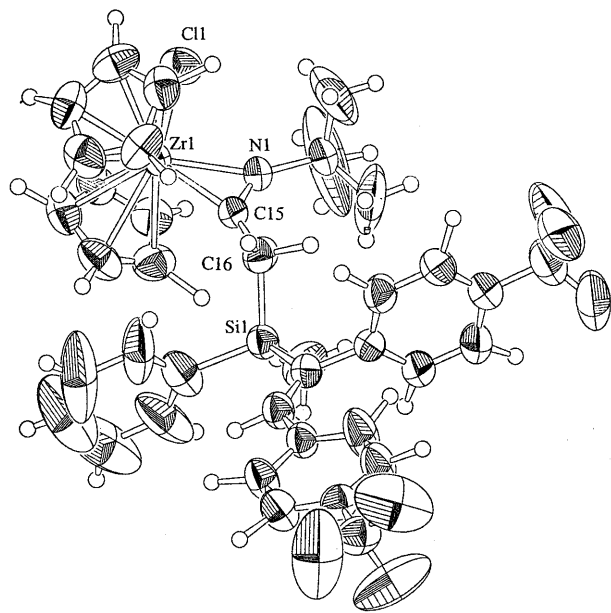


Fig. 1. X-ray crystallography of **6d**. Selected bond lengths (Å) and angles (°): Zr1–C15, 2.219(5); Zr1–N1, 2.216(4); N1–C15, 1.281(7); Zr1–N1–C15, 73.4(3); Zr1–C15–N1, 73.1(3); N1–Zr1–C15, 33.6(2).

The bond length of the zirconium–carbon and zirconium–nitrogen bonds are almost equal (2.219 and 2.216 Å, respectively). It indicates that the imino-nitrogen of **6d** strongly coordinates to zirconium metal, and complex **6d** would be stabilized.

To confirm the formation of iminosilazirconacyclohexene (**7**), the reaction was monitored by <sup>1</sup>H-NMR spectra, and the spectra of **7b** are shown in Fig. 2 (Table 2).

To a solution of Cp<sub>2</sub>ZrCl<sub>2</sub> (15.9 mg, 54.4 μmol) and di-4-methoxyphenylacetylene (**5b**) (8.5 mg, 35.7 μmol) in THF-*d*<sub>8</sub> (0.8 ml) was added Me<sub>2</sub>PhSiLi (0.72 M in THF, 0.15 ml, 108 μmol) in an NMR tube under argon atmosphere, whereupon the solution was allowed to stand at –78°C. The solution was then monitored at room temperature by <sup>1</sup>H-NMR spectroscopy. With the passage of time, the Cp peaks of silazirconacyclopentene **3b** at δ 6.17 and 6.30 were enhanced (Fig. 2(I)) [3]. After 3.5 h, *tert*-butyl isocyanide (10.0 μl, 88.4 μmol) was added. The new Cp and methylene peaks appeared at δ 5.49, 5.51 and 2.67 (d, *J* = 12.4 Hz, 1H) and δ 3.27 (d, *J* = 12.4 Hz, 1H), respectively (Fig. 2(II)). When HCl–Et<sub>2</sub>O was added to this solution, Cp protons were changed to δ 5.75 and 5.54, whose peaks agreed with those of imino-zirconium complex **6b** (Fig. 2(III)). The Cp protons at δ 5.49 and 5.51 (10H), and methylene protons at δ 2.67 (d, *J* = 12.4 Hz, 1H) and 3.27 (d, *J* = 12.4 Hz, 1H) as an AB quartet on Fig. 2(II) indicate that iminosilazirconacyclohexene **7b** is formed.

We investigated the synthesis of the zirconium–silene complex **1**, which was prepared from Cp<sub>2</sub>ZrCl<sub>2</sub> and Me<sub>2</sub>PhSiLi. It was interesting that iminosilazirconacyclohexene **7** could be synthesized from silazirconacyclopentene **3**, which was prepared from zirconium–silene complex **1** and diarylacetylene **5**, and *tert*-butyl isocyanide, and it gave air stable imino-zirconium complex **6** by treatment with HCl–Et<sub>2</sub>O in a one-pot reaction.

### 3. Experimental

<sup>1</sup>H- (270 MHz), <sup>13</sup>C-NMR (125 MHz) spectra were recorded on JEOL EX-270 and Bruker ARX-500 spectrometers. <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to internal Me<sub>4</sub>Si or internal CHCl<sub>3</sub>. Mass spectra were measured on a JEOL JMS 700TZ mass spectrometer. X-ray crystallography was carried out on a Rigaku AFC7R diffractometer. Column chromatography was performed by using Merck aluminum oxide 90 active neutral (activity stage I, 70–230 mesh ASTM). THF was distilled under argon from sodium–benzophenone.

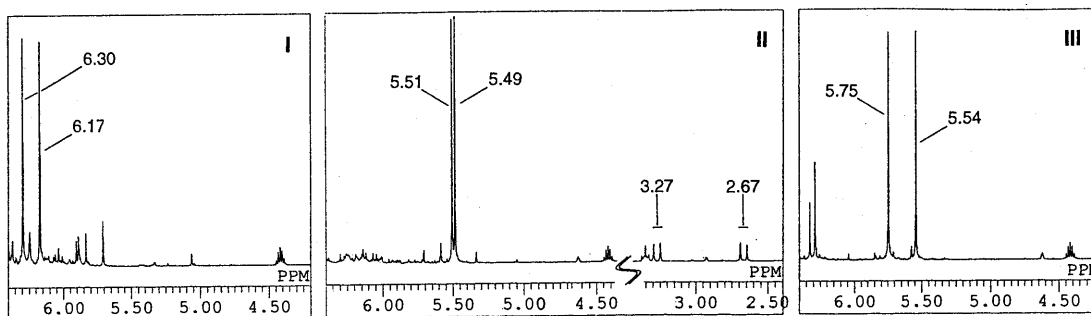


Fig. 2. NMR spectra of **7b**. (I) To a solution of  $\text{Cp}_2\text{ZrCl}_2$  and **5b** in  $\text{THF-}d_8$  was added  $\text{Me}_2\text{PhSiLi}$ , and the solution was stirred at room temperature for 3 h. (II) *tert*-Butyl isocyanide was added. (III) To this solution was added  $\text{HCl-Et}_2\text{O}$ .

### 3.1. A typical procedure for the synthesis of imino-zirconium complex **6b**

To a solution of  $\text{Cp}_2\text{ZrCl}_2$  (148.3 mg, 0.507 mmol) and di-4-methoxyphenylacetylene (**5b**) (80.6 mg, 0.338 mmol) in THF (3.4 ml) was added  $\text{Me}_2\text{PhSiLi}$  (0.78 M in THF, 1.3 ml, 1.01 mmol). The solution was stirred at  $-78^\circ\text{C}$  for 1 h and then at r.t. for 3 h. To this solution was added *tert*-butyl isocyanide (80  $\mu\text{l}$ , 0.707 mmol), and the resulting solution was stirred at r.t. overnight. Anhydrous HCl (1.0 M in  $\text{Et}_2\text{O}$ , 0.340 ml, 0.34 mmol) was added at  $0^\circ\text{C}$ , and the solution was stirred at r.t. and then concentrated. The residue was purified by column chromatography on aluminum oxide (10:1 hexane–AcOEt) to give imino-zirconium complex **6b** (62% yield).

### 3.2. Spectral data for imino-zirconium complex **6a–d**

**6a**.  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.59 (s, 3H), 1.30 (s, 9H), 3.31 (d,  $J = 11.7$  Hz, 1H), 3.39 (d,  $J = 11.7$  Hz, 1H), 5.51 (s, 5H), 5.74 (s, 5H), 6.90 (s, 1H), 6.93–6.99 (m, 4H), 7.07–7.11 (m, 3H), 7.24–7.34 (m, 3H), 7.49–7.51 (m, 3H), 7.72–7.76 (m, 2H).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.11, 27.38, 29.93, 62.40, 108.89, 109.00, 126.46, 127.77, 127.81, 128.04, 128.34, 128.93, 129.59, 130.22, 134.51, 134.99, 136.52, 141.15, 141.18, 142.54, 228.77. MS:  $m/z$  594 [ $\text{M}^+ - \text{Bu}$ ], 299, 255. HRMS Calc. for  $\text{C}_{33}\text{H}_{31}\text{ClNSi}^{90}\text{Zr}$ : 594.0961 [ $\text{M}^+ - \text{Bu}$ ]. Found: 594.0952.

**6b**.  $^1\text{H-NMR}$  (270 MHz,  $\text{THF-}d_8$ ):  $\delta$  0.58 (s, 3H), 1.35 (s, 9H), 3.44 (d,  $J = 11.7$  Hz, 1H), 3.51 (d,  $J = 11.7$  Hz, 1H), 3.68 (s, 3H), 3.76 (s, 3H), 5.54 (s, 5H), 5.74 (s, 5H), 6.64 (br, d,  $J = 8.9$  Hz, 2H), 6.85–6.98 (m, 7H), 7.46–7.50 (m, 3H), 7.79–7.82 (m, 2H).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.12, 27.52, 29.89, 55.05, 55.14, 62.32, 108.82, 108.92, 113.42, 114.43, 128.20, 128.96, 129.40, 129.99, 130.96, 133.27, 134.40, 135.41, 139.10, 140.71, 158.15, 159.00, 228.83. MS:  $m/z$  654 [ $\text{M}^+ - \text{Bu}$ ], 399, 359, 255. HRMS Calc. for  $\text{C}_{35}\text{H}_{35}\text{ClNO}_2\text{-Si}^{90}\text{Zr}$ : 654.1172 [ $\text{M}^+ - \text{Bu}$ ]. Found: 654.1166.

**6c**.  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.56 (s, 3H), 1.31 (s, 9H), 2.23 (s, 3H), 2.34 (s, 3H), 3.30 (d,  $J = 11.6$  Hz, 1H), 3.39 (d,  $J = 11.6$  Hz, 1H), 5.52 (s, 5H), 5.74 (s, 5H), 6.84–6.93 (m, 7H), 7.11 (d,  $J = 7.9$  Hz, 2H), 7.47–7.49 (m, 3H), 7.70–7.74 (m, 2H).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.09, 21.10, 21.11, 27.47, 29.90, 62.33, 108.85, 108.95, 127.67, 128.23, 128.73, 129.51, 129.58, 130.04, 133.84, 134.45, 135.33, 135.87, 137.64, 138.09, 140.99, 141.14, 228.84. MS:  $m/z$  622 [ $\text{M}^+ - \text{Bu}$ ], 367, 327, 255. HRMS Calc. for  $\text{C}_{35}\text{H}_{35}\text{ClNSi}^{90}\text{Zr}$ : 622.1274 [ $\text{M}^+ - \text{Bu}$ ]. Found: 622.1279.

**6d**.  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.62 (s, 3H), 1.30 (s, 9H), 3.30 (d,  $J = 11.6$  Hz, 1H), 3.37 (d,  $J = 11.6$  Hz, 1H), 5.49 (s, 5H), 5.73 (s, 5H), 6.95 (s, 1H), 7.00 (d,  $J = 8.3$  Hz, 2H), 7.04 (d,  $J = 8.3$  Hz, 2H), 7.37 (d,  $J = 8.3$  Hz, 2H), 7.52–7.55 (m, 3H), 7.58 (d,  $J = 8.3$  Hz, 2H), 7.72–7.76 (m, 2H).

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141337 for compound **6d**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road,

Table 2  
Crystal data

Empirical formula	$\text{C}_{39}\text{H}_{38}\text{F}_6\text{NSiClZr}$
Formula weight	789.48
Space group	$P2_1/c$
Unit cell dimensions	
$a$ ( $\text{\AA}$ )	18.863(2)
$b$ ( $\text{\AA}$ )	10.016(2)
$c$ ( $\text{\AA}$ )	20.358(2)
$\beta$ ( $^\circ$ )	95.867(8)
$V$ ( $\text{\AA}^3$ )	3825(1)
$Z$	4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.370
$R$	0.050
$R_w$	0.072
Unique reflections	8988

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