Formation of Zirconacyclohexadienes from Zirconacyclopentadienes and $LiCHClSiR_3$

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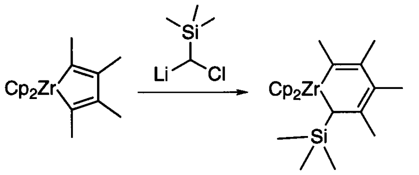
Six-membered zirconacyclohexadienes were formed by insertion of $LiCHClSiR_3$ into zirconacyclopentadienes.

Five-membered zirconacycles have been conveniently prepared by coupling of two unsaturated compounds such as alkynes, alkenes, nitriles, ketones and so on.[1] On the other hand, zirconacyclohexadienes are very rare,[2,3] due to lack of preparative methods. We have recently reported the first example of 1-zirconacyclohexa-2,4-diene derivatives.[4] These zirconacyclohexadiene derivatives, which were fused with a silacyclobutene ring, were formed *via* intramolecular C-C triple bond insertion into zirconacyclopentadienes followed by a novel intramolecular skeletal rearrangement.[4] However, the preparative method of these zirconacyclohexadiene derivatives is very limited. In order to develop more general methods for the preparation of simple zirconacyclohexadienes from readily available zirconacyclopentadienes,[5] we investigated intermolecular attack of 1-metallo-1-halo reagents to zirconacyclopentadienes.[6-8] In this paper, we would like to report that zirconacyclopentadienes were expanded to zirconacyclohexadienes *via* one carbon insertion of a 1-halo-1-lithio compound (Eq. 1).



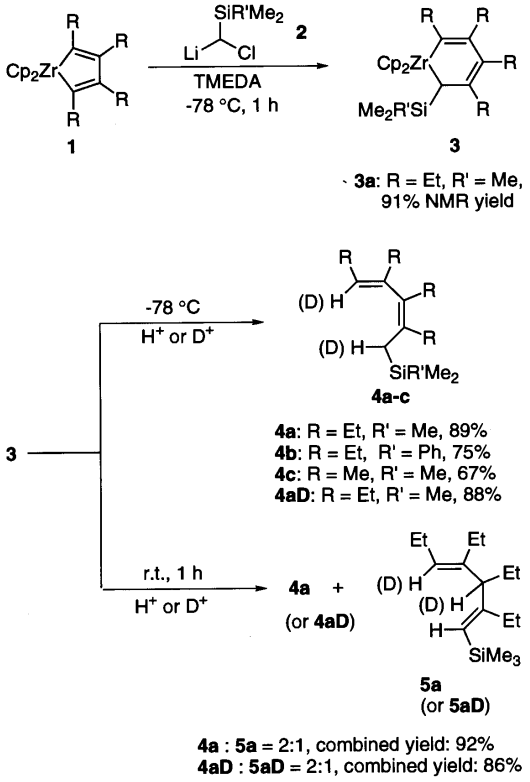
(1)

Zirconacyclopentadiene **1a**[9] reacted with 1-halo-1-lithio compound $LiCHClSiMe_3$ **2** at -78 °C for 1h (Scheme 1).[10] Hydrolysis of the reaction mixture at -78°C gave **4a** in 89% yield. Deuterolysis instead of hydrolysis at -78 °C afforded compound **4aD** in 88% yield. This result clearly indicates the formation of zirconacyclohexadiene **3a**. The reaction mixture of **1a** with **2** was monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum showed a clean formation of **3a** in 91% yield. ^1H and ^{13}C NMR spectra of **3a**[11] were obtained in C_6D_6 at room temperature after removing THF and all volatile compounds, although the complex **3a** gradually decomposed at room temperature. Cp protons appeared at 5.57 and 5.81 ppm as two singlet peaks. Three methyl protons on Si were observed at 0.34 ppm as a singlet. A singlet proton at 0.58 ppm was assigned to methine proton of Zr-CH-Si. This is consistent with the high field shift as observed for alkylsilanes and alkylzirconocene. The corresponding methine carbon was observed at 63.71 ppm in the ^{13}C NMR spectrum of **3a**. High field shift of -C*H* in ^1H NMR spectrum and a low field shift of -*C*H in ^{13}C NMR spectrum is characteristic for a -CH group attached to zirconocene.

Four quaternary carbons were observed at 112.61, 138.62, 138.87 and 195.61 ppm. The signal at 195.61 was assigned to the carbon attached to zirconium. All NMR spectrum data were consistent with the structure of **3a** as described above.

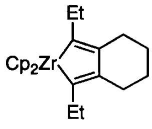
Attempts of isolation of **3a** failed due to its instability. This compound was stable at -78°C in solution. But at higher temperature it easily isomerized. Hydrolysis of the reaction mixture of **1a** with **2** at room temperature gave a mixture of **4a** and **5a** which is a double bond positional isomer of **4a**. It is interesting to note that deuterolysis of the mixture at room temperature instead of hydrolysis gave **5aD** which revealed the allylic rearrangement of **3a.**

A similar reaction of bicyclic zirconacyclopentadiene **1c**[9] with **2** was observed. In this case, the allylic rearrangement took place even at -78 °C. Allylic rearrangement product **6** was isolated (67% yield) as the major compound after hydrolysis of the reaction mixture at room temperature.

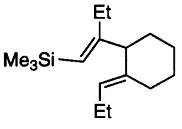


Scheme 1.

When 2.5 equiv of **2** (R' = Me) was used, the reaction with **1a** at room temperature resulted in a mixture of two major



1c



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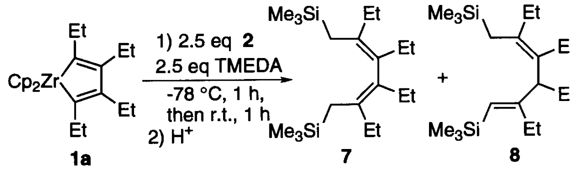
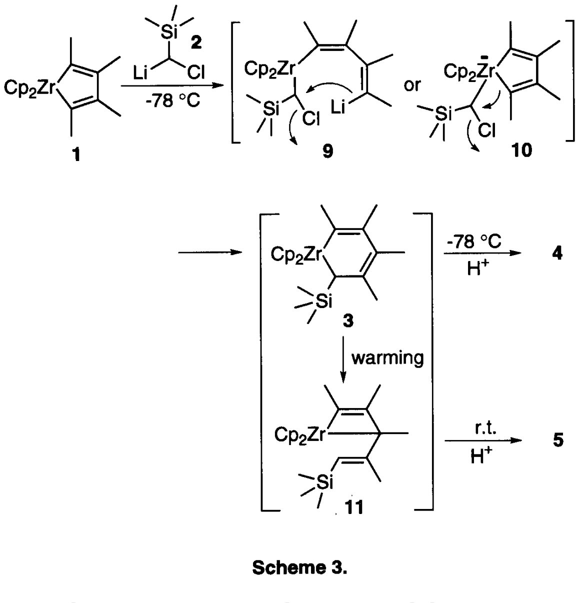
products (**7** and **8**) in a ratio of 4:1 in 71% combined yield after hydrolysis (Scheme 2). Compound **7** is a double insertion product and **8** is the allylic rearrangement product.



Scheme 2.

One possible mechanism of the reaction of **1a** with **2** forming **4** or **5** is shown in Scheme 3. Attack of **2** at **1** forms ate-complex **10** and lithiated compound **9**, which are in equilibrium.[6-8] Both **9** and **10** transform to **3**, which is relatively stable at -78 °C. Hydrolysis of **3** at - 78 °C gives **4**. At higher temperature, **3** might undergo an allylic rearrangement to form intermediate **11**,[7] which affords **5** after hydrolysis at room temperature. Actually, the ^{1}H NMR spectrum of **3a** showed the gradual decomposition at room temperature.



Scheme 3.

Further investigation on the scope and the reaction mechanism is currently in progress. A part of this work was supported by the Ministry of Education, Science, Sport and Culture, Japan (09440212). Z. Xi thanks National Natural Science Foundation of China and President Fund of Peking University for partial support of this work.

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10 A typical procedure: To a THF (5 mL) solution of $ClCH_2SiMe_3$ (1.2 mmol) at -78 °C were added *sec*-BuLi (1.2 mmol) and TMEDA (1.2 mmol). The above mixture was stirred at -78 °C for 1 h to give $LiCHClSiMe_3$ (**2**) And then, to the mixture at -78 °C was added zirconacyclopentadiene **1a** (1.0 mmol). After stirring the reaction mixture at -78 °C for 1 h, hydrolysis with 3M HCl at -78 °C afforded the product **4a**. Alternatively, the reaction mixture was warmed to room temperature instead of hydrolysis at -78 °C and stirred at room temperature for 1 h. Hydrolysis of this mixture with 3 N HCl gave a mixture of two products (**4a** and **5a**) in 2:1 ratio. NMR data for **4a**: ^{1}H NMR ($CDCl_3$, $SiMe_4$) δ 0.02 (s, 9H), 0.88-1.01 (m, 12H), 1.61 (s, 2H), 1.99-2.12 (m, 8H), 4.95 (t, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, $SiMe_4$) δ -0.14 ($SiMe_3$), 12.87, 13.32, 13.77, 14.79, 20.98, 23.18, 23.71, 25.78, 28.17, 129.11, 133.17, 135.67, 141.07. HRMS found 252.2283, calcd for $C_{16}H_{32}Si$ 252.2272.

11 NMR data for **3a**: ^{1}H NMR (C_6D_6, $SiMe_4$) δ 0.34 (s, 9H), 0.58 (s, 1H), 0.86 (t, J = 7.6 Hz, 3H), 1.02 (t, J = 7.6 Hz, 3H), 1.13 (t, J = 7.5 Hz, 3H), 1.25 (t, J = 7.4 Hz, 3H), 1.82-1.89 (m, 2H), 2.26-2.41 (m, 4H), 2.83-2.87 (m, 1H), 2.58-2.63 (m, 1H), 5.57 (s, 5H, Cp), 5.81 (s, 5H, Cp). ^{13}C NMR (C_6D_6, $SiMe_4$) δ 4.67 ($SiMe_3$), 12.55, 13.81, 14.08, 15.95, 25.14, 25.60, 30.04, 32.05, 63.71, 104.74 (Cp), 108.08 (Cp), 112.61, 138.62, 138.87, 195.61.

12 Data for **7**: ^{13}C NMR ($CDCl_3$, $SiMe_4$) δ 0.01, 13.15, 14.44, 22.14, 25.19, 25.68, 133.08, 134.48. HRMS found 338.2828, calcd for $C_{20}H_{42}Si_2$ 338.2823.