

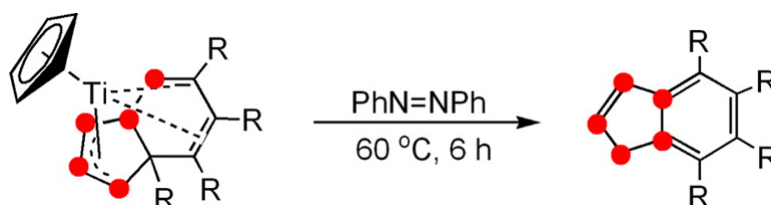
Communication

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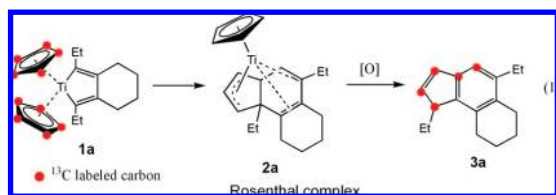
Once Cleaved C–C Bond Was Reformed: Reversible C–C Bond Cleavage of Dihydroindenyltitanium Complexes

Tamotsu Takahashi,^{*,†} Zhiyi Song,[†] Yi-Fang Hsieh,[†] Kiyohiko Nakajima,[‡] and Ken-ichiro Kanno[†]

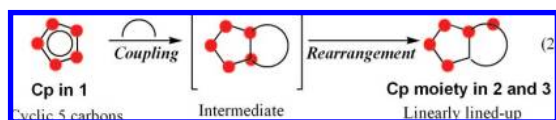
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Carbon–carbon bond cleavage of organic molecules has been a challenging target in organic chemistry.^{1–4} Rosenthal et al. have reported that **1a** was converted into **2a** by coupling of a Cp moiety and a diene moiety of **1a**.² Recently we have converted **2a** into Et group migrated compound **3a** by oxidation and proved that the carbon–carbon bond of the original Cp moiety was cleaved in **3a** by ¹³C labeled experiment as shown in eq 1.^{3a} It was unusual that cyclic



five carbons of the cyclopentadienyl ligand of **1a** were converted into linearly aligned five carbons in **2a** and **3a**. It is reasonable to assume that there is an intermediate obtained by coupling of a Cp ligand and a diene moiety without carbon–carbon bond cleavage and then its rearrangement proceeds by the carbon–carbon bond cleavage as shown in eq 2. Rosenthal et al. demonstrated that a titanacyclopentadiene

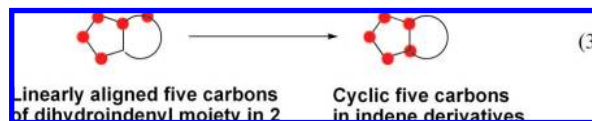


prepared from a pyridyl group-substituted alkyne afforded a dihydroindenyl titanium complex without C–C bond cleavage of the Cp moiety. It is due to the stabilization of the intermediate-type complex by coordination of the pyridyl group to titanium metal center.⁵

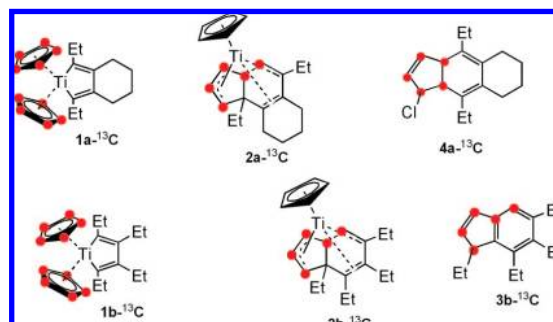
Very recently we observed the existence of the intermediate from the same starting material **1a**. Chlorodihydroindene derivative without carbon–carbon bond cleavage of the Cp moiety **4a** was obtained by the reaction of **1a** with TiCl₄.⁶ ¹³C labeled experiment showed the five carbons from a Cp ligand of **1a**-¹³C were in the cyclic five-membered ring in **4a**-¹³C. However, it is still unusual for the mechanism for the formation of the linearly aligned five carbons in **2** or **3** from the cyclic five carbons of the intermediate.

In this paper, we would like to report that the once cleaved carbon–carbon bond of the Cp moiety in **2** was reformed in the indene products as shown eq 3 and also propose a novel mechanism for the cleavage of the carbon–carbon bond of the Cp moiety.

First we carried out verification of the linearly aligned five carbons in **2a** and **2b** by ¹³C labeling experiments.^{6,3b} The complexes **2a**-¹³C and **2b**-¹³C were prepared from **1a**-¹³C and **1b**-

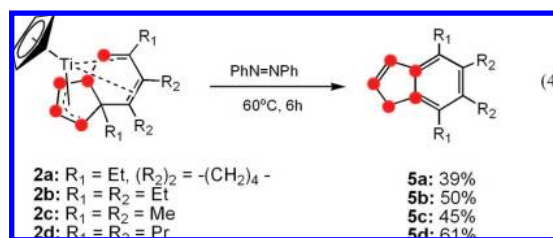


¹³C, respectively. ¹³C NMR spectra clearly showed the original five Cp carbons were linearly lined-up in the dihydroindenyl moiety of **2a**-¹³C and **2b**-¹³C.



When the complex **2b**-¹³C was treated with azobenzene at 60 °C for 6 h, surprisingly, 4,5,6,7-tetraethylindene **5b**-¹³C was obtained in 50% yield along with the formation of **3b**-¹³C as a byproduct in 40% yield. ¹³C NMR study revealed that five carbons originally from a Cp ligand were recombined as a cycle in **5b**-¹³C.

At lower temperature such as 25 °C, the ethyl group transfer compound **3b** was the major product. With increase the temperature, the yield of **5b** increased to 50%. Rosenthal complex **2a** was also converted into 4,7-diethyl-5,6-tetramethyleneindene **5a** in 39% yield as shown in eq 4. Compounds **5c,d** were obtained in 45–61% yields.

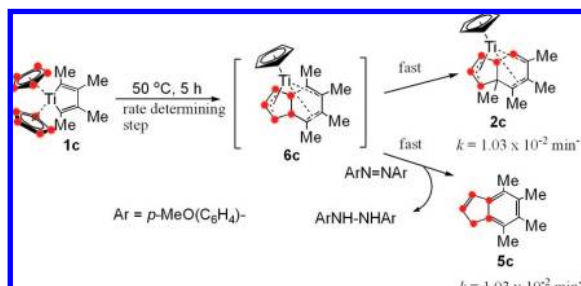


It is interesting to note that direct treatment of **1a–d** with azobenzene also gave **5a–d** in 72–95% yields at 50 °C for 8 h. The formation of alkyl transferred product **3a–d** was not observed in these cases. First, the yields of **5a–d** were much higher than the reaction from **2a–d**. Second, alkyl transferred byproduct **3a–d** were not formed. Therefore, the formation of **5a–d** from **1a–d** did not go through the complexes **2a–d**.

Investigation of the reaction rates from **1c** to **2c** and from **1c** to **5c** revealed very interesting result (Scheme 1). Both reactions were found to exhibit first order kinetic behavior and the both rates were

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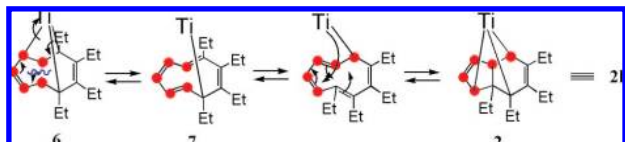
Scheme 1. Reaction Path from **1c** to **2c** and **5c**

(1.03 ± 0.04) $\times 10^{-2} \text{ min}^{-1}$ and (1.03 ± 0.09) $\times 10^{-2} \text{ min}^{-1}$ at 50 °C, respectively. Even at the different temperatures such as 60 and 70 °C, the reaction rates for both reactions were almost the same, for example, at 60 °C, (3.01 ± 0.10) $\times 10^{-2}$ and (3.02 ± 0.16) $\times 10^{-2} \text{ min}^{-1}$ and at 70 °C, (8.16 ± 0.24) $\times 10^{-2}$ and (8.73 ± 0.43) $\times 10^{-2} \text{ min}^{-1}$, respectively. Activation energy values for both reactions were $95.2 \pm 7.2 \text{ kJ/mol}$ and $99.3 \pm 8.8 \text{ kJ/mol}$, respectively. In the case of the reaction from **2c** to **5c**, the reaction also obeyed the first order rule but the reaction rate was (2.96 ± 0.46) $\times 10^{-2} \text{ min}^{-1}$ at 50 °C. The reaction from **2c** to **5c** was faster than that from **1c** to **5c**.

This result suggests that the reaction from **1c** to **2c** and that from **1c** to **5c** have the same intermediate **6**, and the path from **1c** to the intermediate **6c** is the rate determining step.

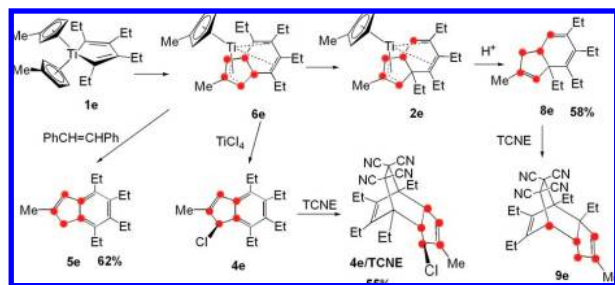
This result strongly suggests that the complexes **2** and intermediate **6** are in equilibrium. Higher stability of **2** over **6** may be due to the number of substituents of diene moiety which coordinates to Ti. Hydrogen transfer from **6** to azobenzene and aromatization afford indene **5**.

At the beginning, we believed that the formation of nine-membered cyclic ligand **7** is reasonable to explain the transformation from the intermediate **6** to **2** as shown in Scheme 2. A complex

Scheme 2. Mechanism for Reversible Path for **2** and **6** via Cyclononatetraenyl Moiety

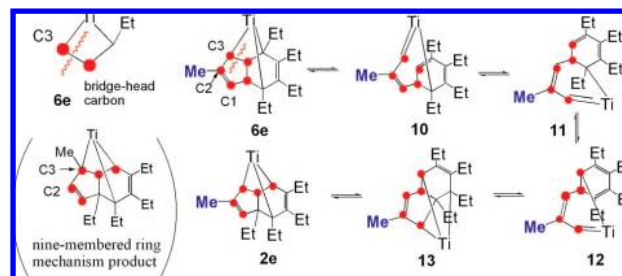
with cyclic nine-membered ring has been known and a nine-membered cyclic ligand can be formed via cleavage of the bridge-head carbon–carbon bond of dihydroindene moiety.^{7,8}

To confirm the possibility of this mechanism, we carried out the reaction using methyl-substituted cyclopentadienyltitanacyclopentadiene **1e**. As shown in Scheme 3, first, **1e** was treated with azobenzene and

Scheme 3. Transformation of Me-Substituted Titanacyclopentadiene **1e**

2-methylindene **5e** was obtained. In addition, **1e** was also treated with TiCl_4 and the corresponding chlorodihydroindene **4e** was obtained. The position of the Me group in **4e** was verified by X-ray analysis

after converting to Diels–Alder product with TCNE. This clearly shows that in the intermediate **6e**, the methyl group occupied C2 position of the dihydroindene moiety. After heating, **1e** was converted into **2e**. The position of Me group was checked after hydrolysis. X-ray analysis of Diels–Alder reaction product **9e** of the hydrolysis product **8e** with TCNE revealed that the methyl group occupied the C2 position of dihydroindene **2e** and **8e**. According to the nine-membered ring mechanism shown in Scheme 2, the methyl substituent should occupy C3 position as shown in parentheses in Scheme 4. However, the methyl

Scheme 4. Mechanism for Transformation between **2e** and **6e** via Metathesis

group occupied C2 position in **2e**. This clearly shows that the mechanism via the cyclic nine-membered ring is not consistent.

Me group occupied at the second carbon of linearly aligned five carbons in **2e**. This indicates that the carbon–carbon bond of the bridge-head carbon and C3 carbon in **6e** should be cleaved as shown in Scheme 4. This bond is a part of the titanacyclobutane moiety which can be converted into the titanium carbene moiety and the olefin moiety by metathesis. The metathesis cleavage of the bond provides **10** containing titanium carbene moiety. The complex **11** is the same as **10**. Pentadienyl migration of titanium on six-membered ring gives **12**. The titanium carbene and one olefin coupling affords again titanacyclobutane moiety in **13**. Changing the position of Ti in **13** gives **2e**. This mechanism via metathesis can explain all the results we obtained. Therefore, we propose a novel reversible mechanism via metathesis of titanacyclobutane moiety of **6e** and **2e** as shown in Scheme 4.

Supporting Information Available: Experimental details and spectra data for all new compounds (PDF), X-ray analysis data for **9e**, and Diels–Alder products of **4e** with TCNE. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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