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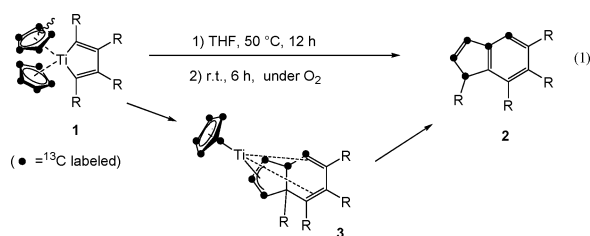
1-Chloro-4,5,6,7-tetraalkyldihydroindene Formation by Reaction of Bis(cyclopentadienyl)titanacyclopentadienes with Titanium Chloride

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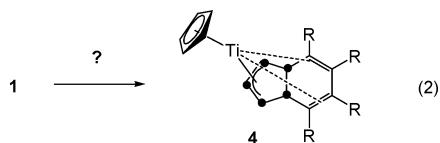
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Recently, we have reported the formation of unusual indene derivatives **2** with alkyl group migration via carbon–carbon bond cleavage from bis(cyclopentadienyl)titanacyclopentadienes **1**, which were prepared from alkyl-substituted alkynes (eq 1).¹



We also found this transformation proceeded via Rosenthal-type reaction of complex **3**² with an alkyl group at a bridgehead carbon. We could rationalize that the alkyl group of the bridgehead of **3** transferred to give **2** by oxidation of the titanium metal center. However, the formation of **3** from **1** is still mysterious since the formation of complex **3** involves the carbon–carbon bond cleavage of the Cp ligand.^{3–5}

It is interesting to know if complex **4** can be formed without the carbon–carbon bond cleavage of the Cp ligand by either intramolecular Diels–Alder-type reaction of one olefin moiety of one Cp ligand with the metallacyclopentadienyl moiety in **1** or stepwise C–C bond formation of one Cp ligand with metallacyclopentadienyl moiety in **1** (eq 2).⁶ First we focused on the possibility for the formation of **4** from **1** prepared from alkyl-substituted alkynes.

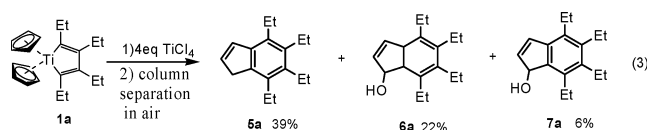


Rosenthal's pioneering work revealed that a dihydroindene titanium species similar to **4** was obtained when **4** had pyridyl substituents instead of alkyl substituents. In this case, the pyridyl group stabilized complex **4** by coordination.⁷ However, unfortunately, there is no report for the formation of **2** with the pyridyl substituents.

This prompted us to investigate evidence for the formation of dihydroindene titanium complexes **4** with usual alkyl substituents which can provide complex **2**.

In this paper, we would like to report the formation of 1-chloro-4,5,6,7-tetraalkyldihydroindenes by the reaction of titanacyclopentadienes **1**⁸ with TiCl₄, where the five-membered ring moiety of the chlorodihydroindene came from a Cp ligand⁹ without the C–C bond cleavage.

Column separation of the reaction products with silica gel in air after the reaction of **1a** with 4 equiv of TiCl₄ at room temperature for 1 h gave indene **5a**, dihydroindene **6a**, and indenol **7a** in 39, 22, and 6% yield, respectively.



It was found that before treatment with silica gel in air 1-chloro-4,5,6,7-tetraethyldihydroindene **8a** was formed in high yield.

As shown in Table 1, the yield of **8a** was dependent on the amount of TiCl₄. When the amount of TiCl₄ increased to 8 equiv, the yield was remarkably improved to 99%. With CuCl₂, a small amount of **8a** (11% yield) was obtained. However, other metal chlorides, such as ZnCl₂, ZrCl₄, and TaCl₅, did not give the compound **8a** at all. Use of TiBr₄ instead of TiCl₄ afforded **5a** in less than 10% yield.

In order to verify the structure of **8a**, Diels–Alder reaction of **8a** with TCNE was carried out to obtain compound **9**. The structure of **9** was determined by X-ray analysis. The structure is shown in Figure 1.

It clearly shows that four Et groups are in the six-membered ring moiety but not at the bridgehead carbon of **8a**. It also reveals that the Cl atom attached to the five-membered ring with exo-configuration.

The results for the reaction of **1b–e** with 8 equiv of TiCl₄ are summarized in Table 2. The reactions of monocyclic titanacyclopentadienes **1b** and **1c** with TiCl₄ produced the corresponding **8b** and **8c** in high yields (entries 1 and 2). The reactions with bicyclic titanacyclopentadiene **1d** and tricyclic titanacyclopentadiene **1e** also gave the corresponding indenenes **8d** and **8e** in high yields, respectively.

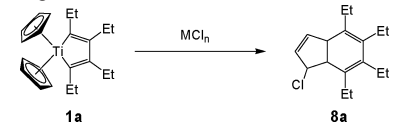
The products **8a–e** were converted into indene derivatives **5a–e** after reflux in toluene for 2 h in 50–65% isolated yields.

It is important to know if the five-membered ring of **8** came from the Cp ligand of **1** with or without C–C bond cleavage of the Cp ligand. Therefore, we used ¹³C-enriched titanacyclopentadiene **1a-¹³C** of which a preparative method was reported previously.^{3a} The product was converted to **5a-¹³C**, and the ¹³C content of the five-membered ring carbons of **5a** was checked.

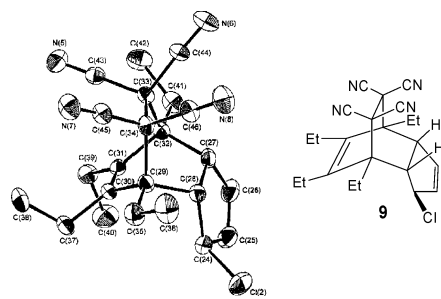
As shown in eq 4, comparison of ¹³C NMR spectra of **5a** and **5a-¹³C** revealed that the ¹³C-enriched carbons of Cp in **1a-¹³C** were located at five-membered ring carbons in **5a-¹³C**. Furthermore, a deuterium-labeled experiment was also carried out as shown in eq 5. The reaction of titanacyclopentadiene **1a-d₁₀** deuterated on the Cp ligands with TiCl₄ produced indene **5a-d₄** deuterated at 1-, 1-, 2-, and 3-positions. This result is consistent with that of the ¹³C-labeled experiment. The existence of two deuterium atoms on the C-1 carbon indicates the migration of one deuterium atom during

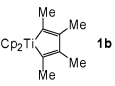
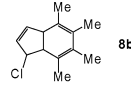
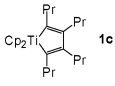
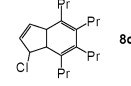
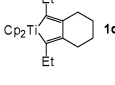
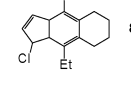
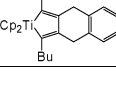
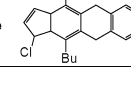
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Table 1. Reaction of Titanacyclopentadienes **1a** with Metal Halides Affording **8a**


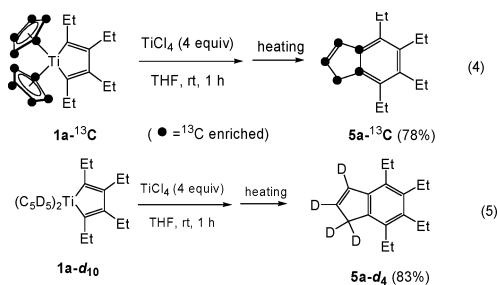
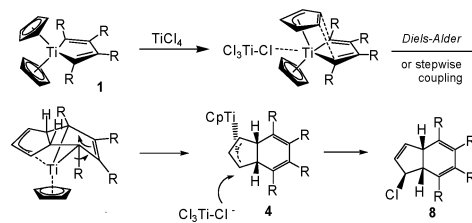
entry	metal chloride	<i>n</i> equiv	yield ^a /%
1	TiCl ₄	1	5
2	TiCl ₄	4	70
3	TiCl ₄	8	99
4	CuCl ₂	4	11
5	ZnCl ₂	4	0
6	ZrCl ₄	4	0
7	TaCl ₅	4	0

^a NMR yield. Conditions: 0 °C, 1 h.**Figure 1.** X-ray crystal structure of **9**.**Table 2.** Formation of 1-Chloro-4,5,6,7-tetrasubstituted Dihydroindene Derivatives **8** from Titanacyclopentadienes **1**

entry	titanacyclopentadienes	1-chlorodihydroindene	yields ^a
1			84
2			95
3			96
4			99

^a NMR yields.

the formation of the indene. These results clearly showed that, during the coupling reaction of Cp ligand of **1** with titanacyclopentadiene moiety giving dihydroindene complex, the carbon–carbon bond of the Cp ligand was not cleaved.

**Scheme 1.** Possible Reaction Mechanism for the Formation of **8** from **1**

This is a strong evidence of the formation of complex **4** without carbon–carbon bond cleavage from titanacyclopentadiene **1** with usual alkyl substituents in addition to all previously described products on the basis of complex **3** with carbon–carbon bond cleavage.^{1,4a}

Scheme 1 shows a plausible mechanism of the indene formation reaction. At first, coordination mode of the Cp ring is changed from η^5 - to η^3 -fashion, caused by coordination of the Cl atom of TiCl₄. Diels–Alder reaction or stepwise coupling between the slipped Cp ring and butadienyl moiety of the titanacycle occurs to produce the corresponding dihydroindene complex **4**. It is known that the titanium metal center in the type **4** complex occupied the endo-position as an allyltitanium species having an interaction with the diene moiety. This means that the Cl anion attacks from the back side of the π -allyltitanium of the five-membered ring giving **8**. This is also consistent with the configuration of the Cl atom shown in X-ray structure of **9**.

In conclusion, titanacyclopentadienes reacted with TiCl₄ to give 1-chlorotetraalkyldihydroindene derivatives **8** without carbon–carbon bond cleavage of the Cp ligand. This is in sharp contrast to the reaction using the same starting complexes, which affords **2** with carbon–carbon bond cleavage of the Cp ligand.

We must await further investigation to elucidate how the carbon–carbon bond is cleaved in the coupling reaction of a Cp ligand and the diene moiety of titanacyclopentadienes **1**.

Supporting Information Available: Experimental procedure, spectra data and NMR spectra for **5a–e**, **5a-d**, **5a-¹³C**, **6a**, **7a**, **8a–e**, and **9**. Crystallographic data for **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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