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Communication

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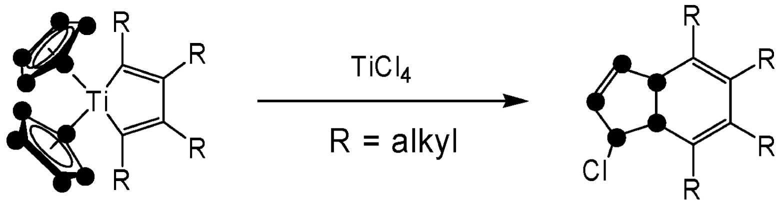

1 **8**

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COMMUNICATIONS

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

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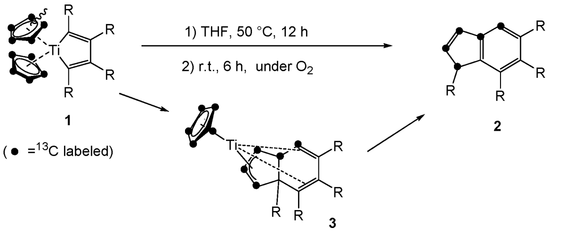
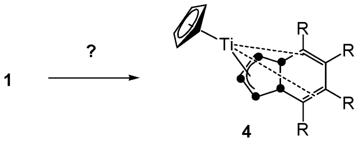
Recently, we have reported the formation of unusual indene derivatives **2** with alkyl group migration via carbon−carbon bond cleavage from bis(cyclopentadienyl)titanacyclopentadienes **1**, which were prepared from alkyl-substituted alkynes (eq 1).[1]



(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 **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.



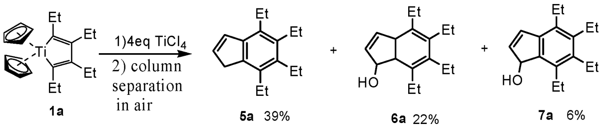
(2)

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 TiCl$_4$, where the five-membered ring moiety of the chlorodihydroindene came from a Cp ligand[9] 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 TiCl$_4$ at room temperature for 1 h gave indene **5a**, dihydroindenol **6a**, and indenol **7a** in 39, 22, and 6% yield, respectively.



(3)

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 TiCl$_4$. When the amount of TiCl$_4$ increased to 8 equiv, the yield was remarkably improved to 99%. With CuCl$_2$, a small amount of **8a** (11% yield) was obtained. However, other metal chlorides, such as ZnCl$_2$, ZrCl$_4$, and TaCl$_5$, did not give the compound **8a** at all. Use of TiBr$_4$ instead of TiCl$_4$ 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 TiCl$_4$ are summarized in Table 2. The reactions of monocyclic titanacyclopentadienes **1b** and **1c** with TiCl$_4$ 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 indenes **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 ^{13}C-enriched titanacyclopentadiene **1a-^{13}C** of which a preparative method was reported previously.[3a] The product was converted to **5a-^{13}C**, and the ^{13}C content of the five-membered ring carbons of **5a** was checked.

As shown in eq 4, comparison of ^{13}C NMR spectra of **5a** and **5a-^{13}C** revealed that the ^{13}C-enriched carbons of Cp in **1a-^{13}C** were located at five-membered ring carbons in **5a-^{13}C**. Furthermore, a deuterium-labeled experiment was also carried out as shown in eq 5. The reaction of titanacyclopentadiene **1a-*d*$_{10}$** deuterated on the Cp ligands with TiCl$_4$ produced indene **5a-*d*$_4$** deuterated at 1-, 1-, 2-, and 3-positions. This result is consistent with that of the ^{13}C-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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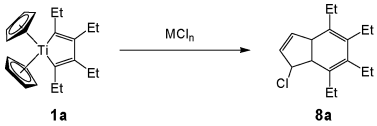
Table 1. Reaction of Titanacyclopentadienes **1a** with Metal Halides Affording **8a**



1a **8a**

entry	metal chloride	*n* 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.

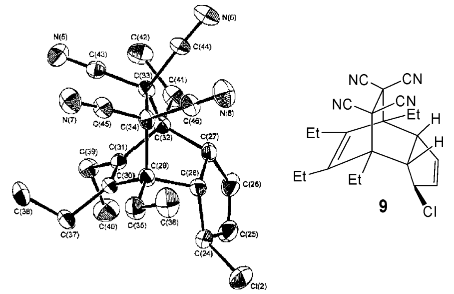
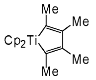
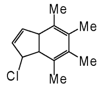
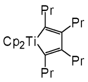
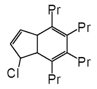
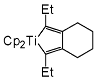
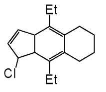
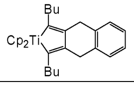
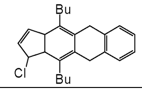


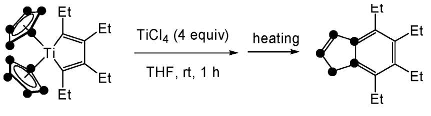
Figure 1. X-ray crystal structure of **9**.

Table 2. Formation of 1-Chloro-4,5,6,7-tetrasubstituted Dihydroindene Derivatives **8** from Titanacyclopentadienes **1**

entry	titanacyclopentadienes	1- chlorodihydroindene	yields[a]
1	 **1b**	 **8b**	84
2	 **1c**	 **8c**	95
3	 **1d**	 **8d**	96
4	 **1e**	 **8e**	99

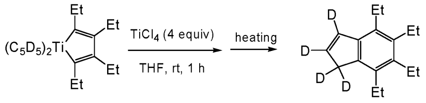
[a] NMR yields.

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.



(4)

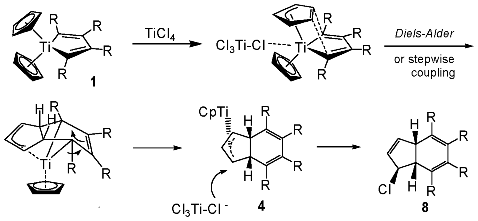
1a-^{13}C (● =^{13}C enriched) **5a-^{13}C** (78%)



(5)

1a-*d*$_{10}$ **5a-*d*$_4$** (83%)

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 $TiCl_4$. Diels−Alder reaction or stepwise coupling between the slipped Cp ring and butadienyl moiety of the titanacycle occurs to produce the corresponding dihydroindenyl 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 $TiCl_4$ 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*$_4$**, **5a-^{13}C**, **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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(9) For reaction of Cp ligand, see: (a) Ref 7. (b) Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc.* **1996**, *118*, 5508−5509. (c) Gleiter, R.; Wittwer, W. *Chem. Ber.* **1994**, *127*, 1797. (d) Giolando, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 6455.

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