Communication

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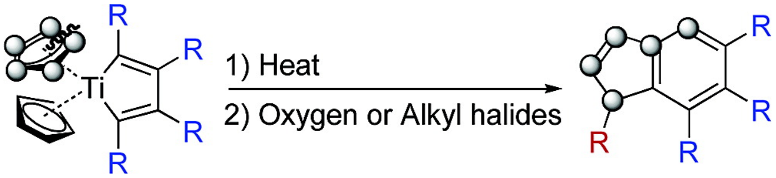

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Formation of Indene Derivatives from Bis(cyclopentadienyl)titanacyclopentadienes with Alkyl Group Migration via Carbon−Carbon Bond Cleavage

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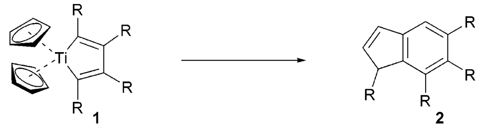
Carbon−carbon bond cleavage is a challenging target in organic chemistry.[1] A cyclopentadienyl ligand usually acts as an inert ligand toward the C−C bond cleavage on transition-metal complexes. Recently, four examples of the C−C bond cleavage of the cyclopentadienyl ligand have been reported by Rosenthal,[2] Crowe,[3] Stryker,[4] and our group.[5]

In our reaction, two carbon−carbon bonds of a cyclopentadienyl ligand of titanacyclopentadienes **1** were cleaved into a two-carbon unit and a three-carbon unit, which were converted into a benzene derivative and a pyridine derivative, respectively, when the complexes **1** were treated with nitriles.[5]

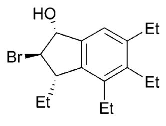
During our further study on this reaction, we found a novel type of migration of an alkyl group in the formation of indene derivatives from titanacyclopentadienes. We would like to report here the formation of the indene derivatives **2** from titanacyclopentadienes with unusual migration of an alkyl group to the five-membered ring of the indene derivatives as shown in eq 1.



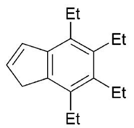
(1)

Heating of 2 mmol of **1a** (R = Et)[6] without nitriles at 50 °C in THF for 24 h under nitrogen and the column separation of the products under air surprisingly afforded **2a** in 31% isolated yield. When the reaction scale was increased to 10 mmol of **1a** for the same reaction, unfortunately, the yield of **2a** was very low. This result prompted us to stir the reaction mixture for 12 h under air after heating. The yield of **2a** was improved to 35% yield.

To verify the structure of **2a**, bromination of **2a** and treatment of the brominated product with silica gel were carried out. Bromoindanol **3a** was obtained as crystals. X-ray analysis of **3a** clearly showed that one of ethyl groups was attached to the five-membered ring, and that there were only three ethyl groups in the six-membered ring of the indane derivative **3a**. The usual indene **4a** was not obtained in this reaction.[7]



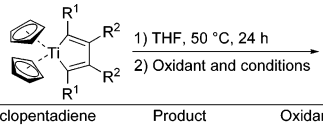
3a



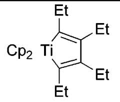
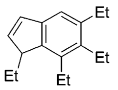
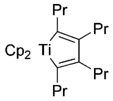
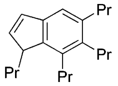
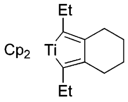
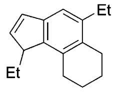
4a

Resulting from the structure of **3a**, the indene derivative **2a** has one unexpected Et group in the five-membered ring, and three Et groups are in the six-membered ring of the indene. For other titanacyclopentadienes, such as **1b** and **1c**, the same types of indene derivatives were formed with the alkyl group migration in 25 and 17% yield, respectively, after workup under air, as shown in Table 1.

Table 1. Formation of Indene Derivatives

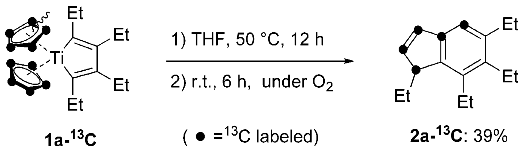


(6)

Entry	Titanacyclopentadiene		Product		Oxidant and conditions	Yield (%)[a]
1		**1a**		**2a**	under air, r.t., 6 h	(31)
					CH_3I (3eq), 50 °C, 6 h	59 (45)
					CH_3I (3eq), r.t., 6 h	57
					CH_2Br_2 (3eq), r.t., 6 h	51
					$CHBr_3$ (3eq), r.t., 6 h	46
					n-BuI (3eq), r.t., 6 h	52
2		**1b**		**2b**	under air, r.t., 6 h	(25)
					MeI (3eq), 50 °C, 24 h	(34)
3		**1c**		**2c**	under air, r.t., 6 h	(17)
					MeI (3eq), 50 °C, 6 h	(49)

[a] GC yields. Isolated yields are given in parentheses.

To make clear which carbons in **2a** come from the Cp ligand of **1a**, ^{13}C-labeled titanacyclopentadiene **1a-^{13}C** was used as the starting material for this reaction.[4] The ^{13}C NMR spectrum of the product **2a-^{13}C** showed that those ^{13}C-enriched five carbons of the Cp ligand were found in the positions of the indene derivative **2a-^{13}C**, as shown in eq 2. This clearly indicates that not only migration of an ethyl group but also cleavage of a cyclopentadienyl ligand itself is involved in this reaction.



(2)

1a-^{13}C (● = ^{13}C labeled) **2a-^{13}C**: 39%

The position of the Cp carbons in **2a** reminded us of the Rosenthal's titanium complex **5c**[2] with the similar Cp carbon positions as shown below.

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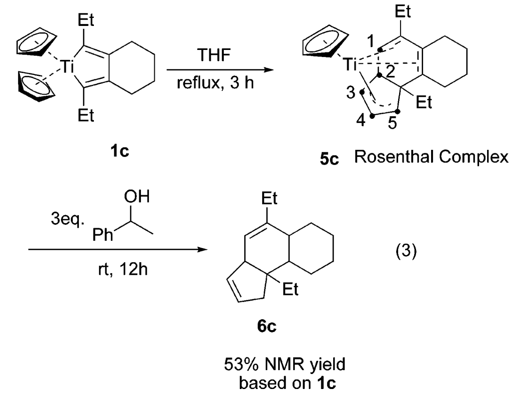
The difference between Rosenthal complex **5c** and our product **2c**, for example, is the position of the one Et group. In the Rosenthal complex, the fourth Et group is at the bridge-head position. However, in our product **2c**, the Et group is in the five-membered ring of indene **2c**. This prompted us to hypothesize that the dihydroindenyl titanium complex **5c** might be the intermediate of our reaction product **2c**.

Therefore, we synthesized the complex **5c** according to the literature.[2] Protonolysis of the complex **5c** with α-phenethyl alcohol actually afforded **6c** with one Et group at the bridge-head.



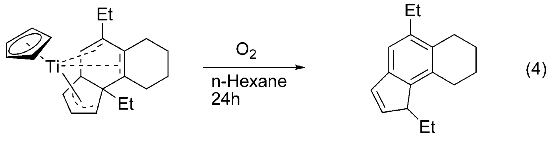
1c

5c Rosenthal Complex

6c

53% NMR yield based on **1c**

The complex **5c** was treated with oxygen for 24 h. NMR analysis of the resulting mixture showed that the ethyl group-migrated product **2c** was surprisingly formed in 75% yield (eq 4). This clearly indicates that the migration of an ethyl group proceeds after formation of the Rosenthal's complex **5c**.



5c

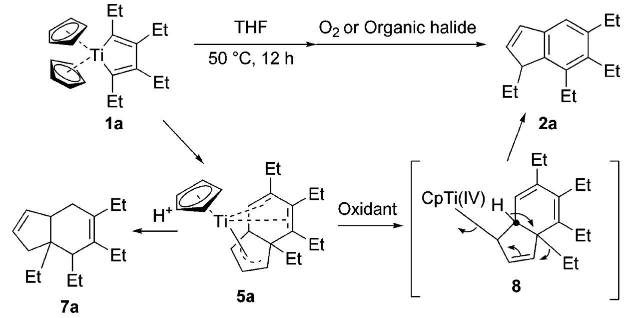
2c: 75% NMR yield

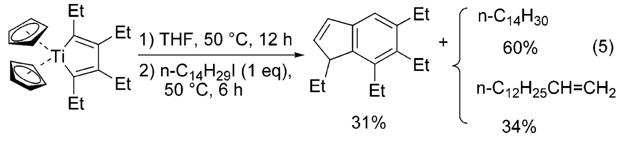
In a similar way, titanacyclopentadiene **1a** was converted to **5a** in 85% NMR yield after heating at 50 °C for 12 h. Protonolysis of **5a** with phenethyl alcohol gave **7a** in 31% yield. The treatment of **5a** under air for 6 h gave **2a** in 54% yield.

From these results, a possible mechanism is shown in Scheme 1. Treatment of a titanacyclopentadiene **1a** at 50 °C gives the corresponding dihydroindenyl complex **5a**. In the complex **5a**, both the diene moiety and allyl moiety of the dihydroindene simultaneously coordinate to the titanium center as shown in the structure of **5c**.[2] The oxidation state of the titanium metal center of the complex **5a** is 2. Thus the dihydroindene derivative strongly coordinates to titanium through the diene and allyl moieties. To liberate the diene moiety from titanium, oxidation of titanium is an efficient method. Treatment of the complex **5a** with air oxidizes the titanium metal center from 2 to 4, and then, the diene moiety of the diene does not coordinate to titanium metal center in **8**. As shown in Scheme 1, a liberated cyclohexadiene moiety is aromatized by elimination of a hydrogen atom, and at the same time, one ethyl group at the bridge-head migrates to the allylic position of allyltitanium, which gives the final product **2a**.

According to the proposed reaction mechanism, oxidation is the key step for the migration of the alkyl group. Investigation of the oxidation of **5a** with various oxidants suggested that the treatment with alkyl halides is effective. For example, treatment of **5a** in situ prepared with 3 equiv of MeI improved the yield of **2a** up to 59%. This method was also useful for **5c**. The product **2c** was obtained in 49% yield.

Scheme 1. A Possible Reaction Mechanism





To check the fate of the alkyl iodide, 1-iodotetradecane was used for the reaction with **5a** in situ prepared from **1a**. When 1 equiv of 1-iodotetradecane was added to **5a** as an oxidant, indene derivative **2a** (31%) was obtained. In addition, tetradecane (60%) and 1-tetradecene (34%) were formed after hydrolysis, respectively, from 1-iodotetradecane. The formation of tetradecane and 1-tetradecene suggests that the oxidative addition of 1-iodotetradecane to **5a** proceeded, and the tetradecyl group was converted into tetradecane and 1-tetradecene on the titanium metal center.

In summary, we found the formation of the indene derivatives from titanacyclopentadienes with unusual migration of an alkyl group by oxidation of a titanium metal center. However, the unusual positioning of Cp carbons in the indene product is still mysterious.[8] We must await further investigation for clarity of this point.

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Supporting Information Available: Structure and X-ray analysis data for **3a**, details of the experimental procedure, and analytical data for compounds **2a**−**c**, **3a**, **5a**, **6c**, and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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