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Coupling of the R−Cp or Indenyl Ligand with the Diene Moiety of Bis(substituted cyclopentadienyl)- or Bis(indenyl)zirconacyclopentadienes

Shenyong Ren,[†] Eri Igarashi,[†] Kiyohiko Nakajima,[‡] Ken-ichiro Kanno,[†] and Tamotsu Takahashi*,[†]

Catalysis Research Center and Graduate School of Life Sciences, Hokkaido University, and SORST, Japan Science and Technology Agency (JST), Kita-ku, Sapporo 001-0021, Japan, and Department of Chemistry, Aichi University of Education, Igaya, Kariya 448-8542, Aichi, Japan

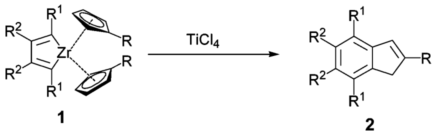
Received December 14, 2008; E-mail: tamotsu@cat.hokudai.ac.jp

Although the cyclopentadienyl (Cp) ligand has been used as an inert ligand on transition metals for long time, some reactions of Cp ligands have been reported for Ti and Co cyclopentadienyl complexes.[1−5] The first example of the coupling of a Cp ligand with a diene moiety in dicyclopentadienyltitanacyclopentadienes was reported by Rosenthal and co-workers. Titanium dihydroindene complexes were formed when dicyclopentadienyltitanacyclopentadienes were heated.[2] However, such a coupling of the Cp ligand did not proceed for zirconacyclopentadienes. To the best of our knowledge, there is no example of the coupling of the Cp ligand with a diene moiety in zirconacyclopentadienes.

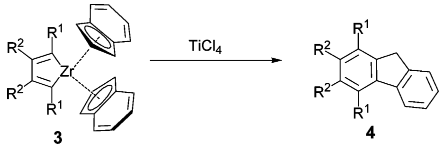
Very recently, we reported that treatment of titanacyclopentadienes with $TiCl_4$ induced coupling of the Cp ligand with the diene moiety to give chlorodihydroindene derivatives.[6] In fact, tetraphenyltitanacyclopentadiene[7] reacted with $TiCl_4$ to give the coupling products in 20−30% combined yield at room temperature, whereas the Zr analogue, tetraphenylzirconacyclopentadiene (**1a**: $R^1 = R^2 =$ Ph, R = H),[8] did not give any coupling products. Comparison with the structure of Ti complex[7,8] showed that the distance between the Cp carbons and the diene carbons attached to Zr in **1a** is longer than that in the Ti analogue by more than 0.2 Å.

This prompted us to investigate the coupling of the Cp ligand with the diene moiety in zirconacyclopentadienes, and we found that the coupling reaction occurs in the case of zirconacyclopentadienes with substituted Cp ligands.

Here we report the first example of the coupling of Cp or indenyl ligand with the diene moiety in zirconacyclopentadienes to give indene or fluorene derivatives, respectively (eqs 1 and 2):



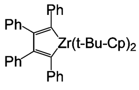
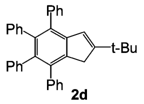
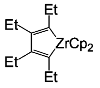
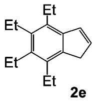
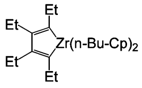
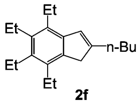
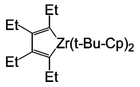
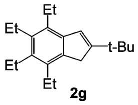
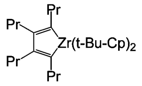
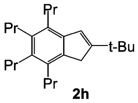
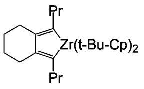
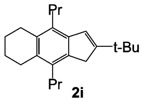
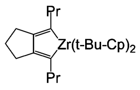
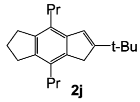
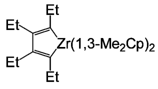
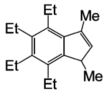
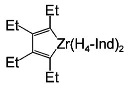
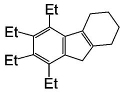
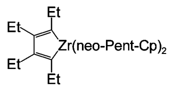
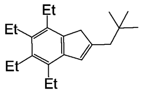
(1)



(2)

First we investigated Me- or *n*-Bu substituted dicyclopentadienylzirconacyclopentadienes. [$R^1 = R^2 =$ Ph; R = Me (**1b**), *n*-Bu (**1c**)]. No formation of the coupling product was observed. However, introduction of a *t*-Bu substituent on the Cp ligand changed the situation. When zirconacyclopentadiene **1d** with the *t*-Bu-Cp ligand ($R^1 = R^2 =$ Ph, R = *t*-Bu) was treated with 4 equiv of $TiCl_4$ at room temperature in THF for 3 h, 4,5,6,7-tetraphenylindene **2d** was surprisingly obtained in 45% yield.

Table 1. Coupling Reaction between the Substituted Cp Ligand and the Diene Moiety in **1d**−**m**[a]

Entry	Zirconacyclopentadiene	Product	Yield/%[b]
1	 **1d**	 **2d**	45(37)
2	 **1e**	 **2e**	27(15)
3	 **1f**	 **2f**	35(17)
4	 **1g**	 **2g**	93(75)
5	 **1h**	 **2h**	90(77)
6	 **1i**	 **2i**	75(62)
7	 **1j**	 **2j**	63(55)
8	 **1k**	 **2k**	29(21)
9[c]	 **1l**	 **2l**	70(63)
10	 **1m**	 **2m**	47(38)

[a] Conditions: $TiCl_4$ (4 equiv), THF, rt, 3 h. [b] GC or NMR yields. Isolated yields are given in parentheses. [c] H_4-Ind = tetrahydroindenyl.

[†] Hokkaido University and SORST.
[‡] Aichi University of Education.

10.1021/ja809401s CCC: $40.75

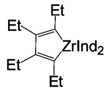
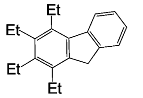
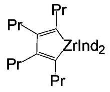
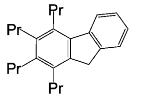
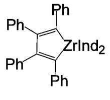
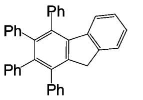
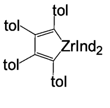
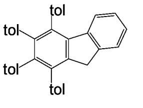
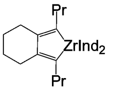
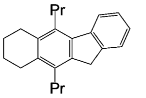
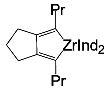
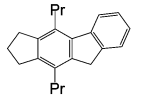
We further investigated the reactivity of various zirconacyclopentadienes with substituted Cp ligands, and the results are shown in Table 1. Alkyl-substituted diene moieties showed higher reactivity. The tetraethyldiene moiety in **1e** could react even with nonsubstituted Cp ligand to give the corresponding product **2e** in 27% yield. The combination of *t*-Bu-substituted Cp ligand and Et-substituted diene in **1g** afforded the coupling product in 93% yield.

Other *t*-Bu-substituted zirconacyclopentadienes **1h**−**j** also afforded the corresponding products in high yields. Reaction of **1k** with 1,3-dimethyl-Cp ligand gave **2k** in 29% yield. With tetrahydroindenyl ligand **1l** and neopentyl-substituted Cp ligand **1m**, the products **2l** and **2m** were obtained in 70 and 47% yield, respectively. In the case of **1m**, its hydrolysis product, 4,5-diethyl-3,5-octadiene was formed in 25% yield, and the formation of the 3-chloro-4,5-diethyl-3,5-octadiene byproduct was observed in 8% yield. Zirconacyclopentadienes with a Me_3Si substituent on the Cp ligand did not give the coupling product. In the case of an *i*-Pr substituent, the coupling product was formed in very low yield (5%).

To clarify the high reactivity of zirconacyclopentadienes with *t*-Bu-substituted Cp ligands, the structure of **1d** was verified by X-ray analysis. The distance between the Cp carbons and the diene carbons attached to zirconium was not significantly different from that in **1a**. The reaction mechanism involves the coordination of $TiCl_4$ from the back side of the zirconacyclopentadiene. Therefore, pushing of the Cp ligands with sterically hindered substituents by $TiCl_4$ causes one double bond of a Cp ligand to slip out and in turn react with the diene moiety by Diels−Alder reaction or stepwise coupling, as shown in the case of Ti.[2,6]

We investigated further and found that indenyl ligands are highly reactive toward coupling with their diene moieties. Bis(indenyl)zirconacyclopentadienes **3a**−**f** were prepared by the reaction of Ind_2ZrBu_2 and 2 equiv of alkynes or 1 equiv of diynes. The structure of **3d** was determined by X-ray analysis. These complexes were treated with 4 equiv of $TiCl_4$ in toluene at room temperature for 1 h, and fluorene derivatives **4a**−**f** were obtained in moderate to high yields (Table 2). Reactions of **3a** with various metal halides were investigated. $TiBr_4$ gave a result similar to $TiCl_4$. TiI_4 was not effective. Group 4 and group 5 metal halides such as $ZrCl_4$ and $TaCl_5$ did not give the product at all.

Table 2. Coupling Reaction with the Diene Moiety in Bis(indenyl)zirconacyclopentadienes[a]

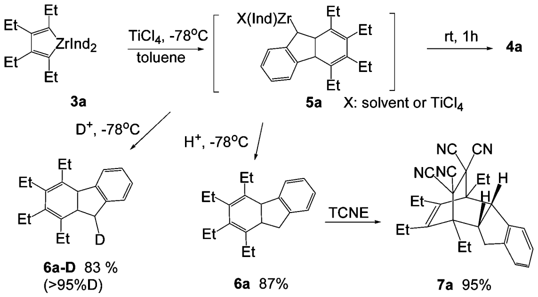
Entry	Zirconacyclopentadiene		Product		Yield/%[b]
1		3a		4a	90(72)
2		3b		4b	88(70)
3		3c		4c	58(40)
4		3d		4d	44(32)
5		3e		4e	73(58)
6		3f		4f	67(55)

[a] Conditions: $TiCl_4$ (4 equiv), toluene, rt, 1 h. [b] GC or NMR yields. Isolated yields are given in parentheses.

The distance between the indenyl and diene carbons in **3d** is not significantly different from that in **1a** or **1d**. The high reactivity can be attributed to the pushing of the indenyl ligands by $TiCl_4$ coordination from the back side of the zirconacyclopentadiene.

A mixture of **1g** and **3b** was treated with $TiCl_4$ at room temperature for 3 h. After hydrolysis, products **2g** and **4b** were obtained. No formation of **2h** and **4a** was detected. This clearly indicates that the coupling reaction is *intramolecular*.

When the reaction of **3a** with $TiCl_4$ was carried out at −78 °C, formation of Zr-containing intermediate **5a** was detected. Hydrolysis of **5a** at −78 °C gave dihydrofluorene **6a** in 87% yield. Deuterolysis instead of hydrolysis afforded **6a-D** in 83% yield with >95% D incorporation. Compound **6a** was converted into **7a** with TCNE, and the structure of **7a** was verified. Treatment of **5a** at room temperature gave free **4a**, which can be explained by β-hydrogen elimination from **5a**. This explains why chlorodihydroindene was not formed in the case of **2a**−**m**: β-hydrogen elimination proceeded in the case of Zr, in sharp contrast to the case of Ti, where chlorination proceeded with $TiCl_4$.



Further investigation in the area of coupling of substituted Cp ligands of zirconacycles is in progress.

Supporting Information Available: Experimental details, spectral data for all new compounds, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA809401S