844 *Organometallics* **2011,** *30,* 844–851
DOI: 10.1021/om101020u

ORGANOMETALLICS
Article

Coupling Reaction of a Cyclopentadienyl Ligand with a Dienyl or Alkenyl Moiety on Titanocene

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Received October 28, 2010

Coupling reactions of a cyclopentadienyl (Cp) ligand with a dienyl or alkenyl ligand on dienyl- or alkenyltitanocenes proceeded to give dienylcyclopentadiene or alkenylcyclopentadiene derivatives in good to high yields. Dienyltitanocene derivatives were prepared by protonation of bis(cyclopentadienyl)titanacyclopentadienes with carboxylic acids. Chlorodienyltitanocene derivatives were formed by the reaction of titanacyclopentadienes with NCS. Alkenyltitanocene derivatives were prepared by the reaction of titanacyclopentene, which were prepared from Cp_2TiEt_2 and alkynes, with *t*-BuOH. The structure of the alkenyltitanocene (in the case of 1,2-diphenylethenyl) was determined by X-ray analysis of the single crystal. These dienyl-, chlorodienyl-, or alkenyltitanocenes were treated with azobenzene at 50 °C for 6 h, and the corresponding dienylcyclopentadienes, chlorodienylcyclopentadienes, and alkenylcyclopentadiene derivatives were obtained in good to high yields. This result supports the existence of the stepwise mechanism for the coupling reaction of a Cp ligand with a diene moiety of titanacyclopentadienes, giving indene derivatives in the presence of azobenzene.

1. Introduction

The cyclopentadienyl ligand has been believed to be "inert" for various reactions for a long time.[1] Rosenthal and his coworkers reported a pioneer work of the coupling reaction of the Cp ligand with a diene moiety of titanacyclopentadienes and a rearranged dihydroindene titanium complex as shown in Scheme 1.[2]

Recently we found titanacyclopentadienes **1** reacted with benzonitrile, leading to double C−C cleavage of one Cp ligand into two units, a 2C unit annualized with a diene moiety to give benzene derivatives and a 3C unit constructing pyridine derivatives with the added nitrile (Scheme 2).[3a] We also reported a novel alkyl group migrated indene formation by oxidation of the Rosenthal type of complex. C−C cleavage of the Cp ligand was detected by ^{13}C-enriched experments.[3b] Furthermore, complexes **1** reacted with $TiCl_4$ to afford chlorodihydroindene derivatives without C−C cleavage on the Cp ligand.[3c] More recently, we reported that the once cleaved C−C bond of Cp was recombined in the indene product when the Rosenthal-type complex was treated with azobenzene.[3d] The unusual reaction of the Cp ligand was also found to occur smoothly in a zirconium analogue when it bears the indenyl or substituted Cp ligands.[3e]

Very recently we clearly indicated from the kinetic study and ^{13}C labeled experiment that the coupling of Cp with the diene moiety occurred without the ring-opening of the Cp ligand giving **2** as the first step (Scheme 3).[3d] In the second step, the coupling product was gradually converted into the Cp ring-opening product **3**. We also indicated that there was equilibrium between complexes **2** and **3**. For this conversion, we proposed the metathesis mechanism to explain the Cp ring-opening reaction on titanium.[3d]

However, as for the coupling of the Cp ligand and the diene moiety of the titanacyclopentadiene, there are two possible pathways (Scheme 4). One is a concerted mechanism, such as a Diels−Alder-type reaction of a carbon−carbon double bond of a slipped Cp ligand on titanium(II) with the diene moiety. The other is a stepwise coupling reaction of the Cp ligand with the diene moiety on titanium(IV).

Although there are several coupling reactions of a Cp ligand with a diene moiety[2,3] and a theoretical study for the coupling,[4] there is no such study on the coupling

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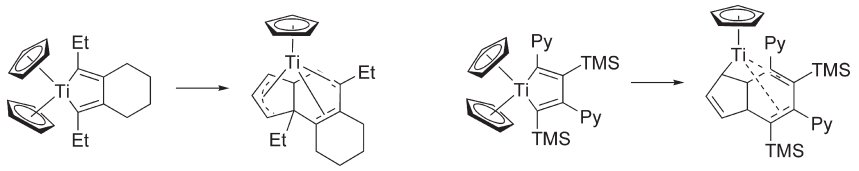
(1) Recent review article on metallocenes; see: Takahashi, T.; Kanno, K. Metallocene in Regio- and Stereoselective Synthesis. In *Topics in Organometallic Chemistry*; Takahashi, T., Ed.; Springer: Berlin, 2005; Vol. *8*, p 217. For reactions of Cp ligand except titanacyclopentadienes, see: (c) Giolando, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 6455. (d) Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc.* **1996**, *118*, 5508. (e) Dzwinniel, T. L.; Stryker, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 9184.

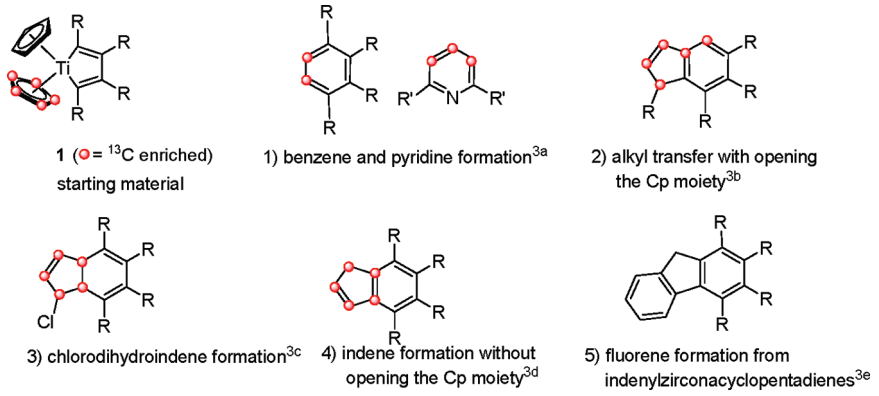
(2) (a) Tillack, A.; Baumann, W.; Lefeber, O. C.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *J. Organomet. Chem.* **1996**, *520*, 187. Several related reports from Prof. Rosenthal's group; see: (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884. (c) Rosenthal, U.; Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. *J. Organomet. Chem.* **1995**, *503*, 221. (d) Thomas, D.; Peulecke, N.; Burlakov, V. V.; Heller, B.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U.; Beckhaus, R. Z. *Anorg. Allg. Chem.* **1998**, *624*, 919.

 Published on Web 02/03/2011

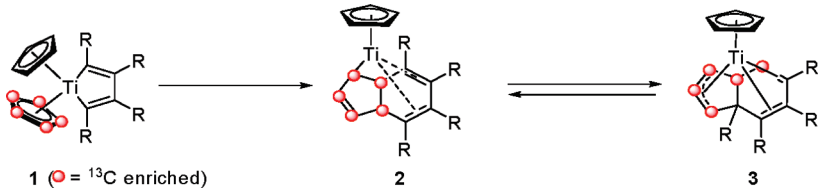
Scheme 1. Rosenthal's Pioneer Work for the Formation of Dihydroindenyl Titanium Complexes from Titanacyclopentadienes



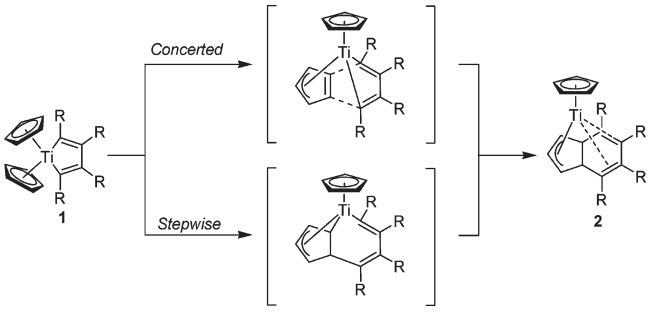
Scheme 2. Various Products from Titanacyclopentadienes 1 and a Zirconium Analogue



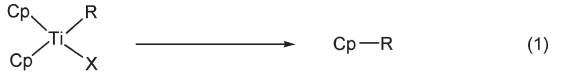
Scheme 3. Coupling of the Cp Ligand with the Diene Moiety and Rearrangement of the Dihydroindenyl Moiety



Scheme 4. Concerted Mechanism and Stepwise Mechanism for the Coupling of Cp with the Diene Moiety of Titanacyclopentadienes



reaction of the Cp ligand with an alkenyl or dienyl moiety group on titanocene as shown in eq 1, to the best of our knowledge.



R = alkenyl or dienyl

This situation prompted us to investigate the coupling reaction of the Cp ligand with dienyl or alkenyl groups on titanocene complexes. We found such coupling reactions occurred smoothly and were facilitated by azobenzene. In this paper we would like to report the coupling reaction of the Cp ligand on titanium, as shown in Scheme 5.

2. Results

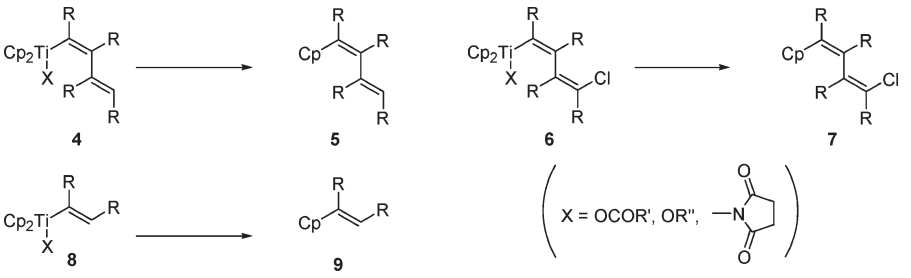
2.1. Coupling Reaction of a Cp Ligand with a Dienyl Ligand on Titanocene. Dienyltitanocene complexes **4** were prepared by protonation of titanacyclopentadiene **1** with carboxylic acids.[5] For example, preparation and quenching of dienyltitanocene **4b$_4$** are shown in Scheme 6. In THF, bis(cyclopentadienyl)titanacyclopentadiene **1b** was treated with 1 equiv of dichloroacetic acid to afford **4b$_4$** in 93% yield. NMR study of the dienyltitanocene **4b$_4$** revealed an alkenyl proton at 4.73 ppm as a triplet in the ^{1}H NMR spectrum and four alkenyl carbons at 129.4 (CH), 144.1 (C), 147.1 (C), and 192.8 (C−Ti) ppm in the ^{13}C NMR spectrum. The chemical shift of 192.8 ppm is very characteristic and is easily assigned to the carbon attached to the titanium metal center. Deuterolysis

(3) Our related reports on this topic; see: (a) Xi, Z.; Sato, K.; Gao, Y.; Lu, J.; Takahashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9568. (b) Takahashi, T.; Kuzuba, Y.; Kong, F.; Nakajima, K.; Xi, Z. *J. Am. Chem. Soc.* **2005**, *127*, 17188. (c) Takahashi, T.; Song, Z.; Sato, K.; Kuzuba, Y.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2007**, *129*, 11678. (d) Takahashi, T.; Song, Z.; Hsieh, Y.-F.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2008**, *130*, 15236. (e) Ren, S.; Igarashi, E.; Nakajima, K.; Kanno, K.; Takahashi, T. *J. Am. Chem. Soc.* **2009**, *131*, 7492.

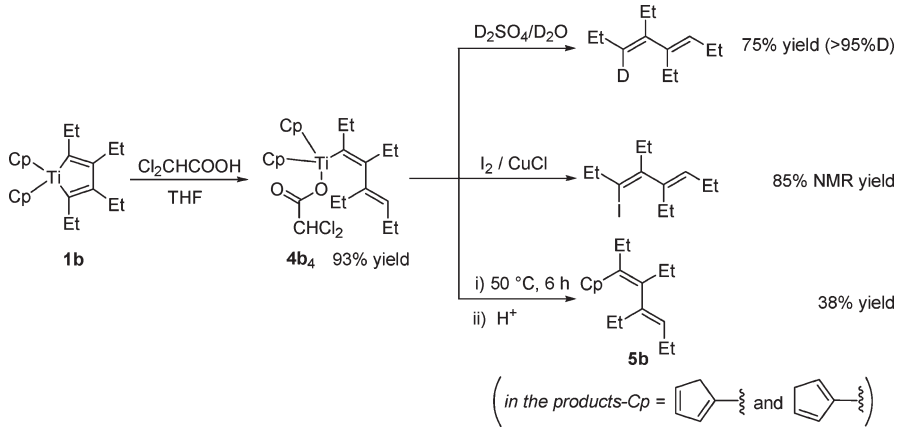
(4) Suresh, C. H.; Koga, N. *Organometallics* **2006**, *25*, 1924.

(5) Titanacyclopentadienes **1** and titanacyclopentenes **10** were prepared according to the following literature. See: Sato, K.; Nishihara, Y.; Huo, S.; Xi, Z.; Takahashi, T. *J. Organomet. Chem.* **2001**, *633*, 18.

Scheme 5



Scheme 6. Generation and Quenching of Dienyltitanocene $4b_4$



and iodination of $\mathbf{4b_4}$ gave the corresponding deuterated and iodinated dienes in 75% yield with >95% deuterium incorporation and 85% NMR yield, respectively. These results unambiguously showed the formation of dienyltitanocene **4b** in high yield.

When *in situ* prepared dienyltitanocene $\mathbf{4b_4}$ was heated at 50 °C for 6 h in THF, the corresponding coupling product, dienylcyclopentadiene **5b**, was obtained as a mixture of the double-bond positional isomers in 38% combined yield after protonolysis.

As we reported in the communication,[3d] the coupling reaction of a Cp ligand and the diene moiety of titanacyclopentadienes giving indene derivatives was facilitated by addition of azobenzene. Surprisingly, the same positive effect of azobenzene was observed in this case. The yield of **5b** was remarkably improved to 92% when $\mathbf{4b_4}$ was heated in the presence of azobenzene (Table 1, entry 5).

Various carboxylic acids were employed for the reaction with **1b** to afford $\mathbf{4b_{1-9}}$, as shown in Table 1. Complexes $\mathbf{4b_{1-9}}$ were treated with azobenzene to give coupling product **5b** in yields of 45−95% (entries 3−10).

Under the optimized conditions, complexes **1a**−**d** were treated first with dichloroacetic acid at −15 °C. The mixture was gradually warmed to room temperature and stirred overnight to afford **4a**−**d**. After addition of 2 equiv of azobenzene, the reaction mixture was stirred at 50 °C for 6 h. Hydrolysis of the reaction mixture gave **5a**−**d** in excellent yields from 92% to 98% (entries 1, 5, 12, and 13). When picolinic acid-d_1 was employed to generate $\mathbf{4b_9}$-**D**, **5b-D** was obtained in 83% yield with 86% deuterium incorporation (entry 11).[6]

In the coupling reaction of Cp with diene moiety giving indene derivatives from titanacyclopentadienes, the driving force was the sterical hindrance. Zr analogues did not show such coupling reactions. But when the *t*-Bu group was introduced to the Cp ligand of zirconacyclopentadienes, even in the case of Zr, the coupling reaction proceeded. Therefore, the driving force of the coupling reaction of Cp with alkenyl or dienyl on Ti is the sterical hindrance around the Ti center.

2.2. Coupling of a Cp Ligand with a Chlorodienyl Moiety on Titanium. In a further investigation, *N*-chlorosuccinimide (NCS) was employed to cleave one of the two Ti−C bonds of a titanacyclopentadiene instead of hydrolysis (Scheme 7).[7] Chlorodienyltitanocenes **6** were prepared by treatment of titanacyclopentadienes **1** with 1.2 equiv of NCS. The formation of complex **6b** was checked by protonolysis, deuterolysis, and iodonation. Protonolysis with concentrated HCl afforded chlorobutadiene in 92% NMR yield. Deuterolysis and iodonation gave the corresponding deuterated products in 85% yield (85% D) and chloroiodobutadiene in 90% yield.

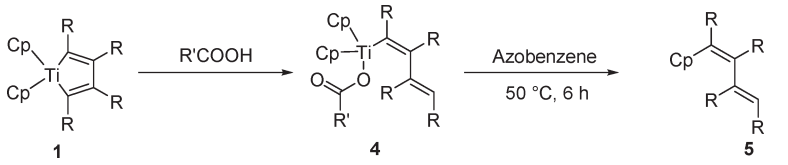
Then the formed complex **6b** was heated at 50 °C for 6 h. After workup, the coupling product **7b** was obtained as a mixture of two double-bond positional isomers in 35% combined yield. When azobenzene was added to the reaction, the yield dramatically increased to 80% (Table 2, entry 2).

The coupling reaction was applied to various substrates, and the results are summarized in Table 2. The reactions of **6a** and **6c** with azobenzene afforded the corresponding products **7a** and **7c** in 85% and 91% yields, respectively (entries 1 and 8). The cyclic **6d** gave the coupling product **7d** in 75% yield (entry 9).

(6) Gilbert, A. M.; Failli, A.; Shumsky, J.; Yang, Y.; Severin, A.; Singh, G.; Hu, W.; Keeney, D.; Petersen, P. J.; Katz, A. L. *J. Med. Chem.* **2006**, *49*, 6027.

(7) Kanno, K.; Igarashi, E.; Zhou, L.; Nakajima, K.; Takahashi, T. *J. Am. Chem. Soc.* **2008**, *130*, 5624.

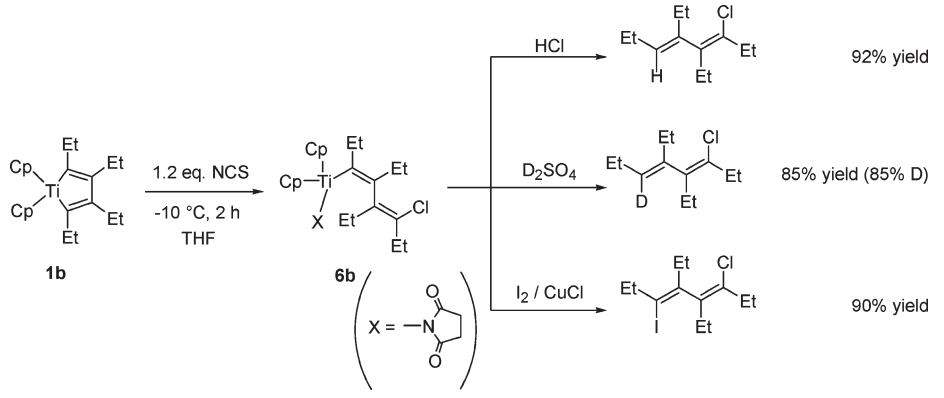
Table 1. Formation of Dienylcyclopentadienes 5



Entry	Carboxylic acids	Dienyltitanium complex **4**[a]	Products **5**[b]	Yield (%)[c]
1	$Cl_2CHCOOH$	**4a**	**5a**	98 (86)
2	HCOOH	**4b**$_1$	**5b**	81
3	CH_3COOH	**4b**$_2$	**5b**	45
4	$ClCH_2COOH$	**4b**$_3$	**5b**	73
5	$Cl_2CHCOOH$	**4b**$_4$	**5b**	92 (79)
6	Cl_3CCOOH	**4b**$_5$	**5b**	82
7	CF_3COOH	**4b**$_6$	**5b**	60
8	PhCOOH	**4b**$_7$	**5b**	46
9	C_6F_5COOH	**4b**$_8$	**5b**	95
10	picolinic acid	**4b**$_9$	**5b**	83
11	picolinic acid-d_1	**4b**$_9$**-D**	**5b-D**	83 (85% D)
12	$Cl_2CHCOOH$	**4c**	**5c**	94 (80)
13	$Cl_2CHCOOH$	**4d**	**5d**	95 (81)

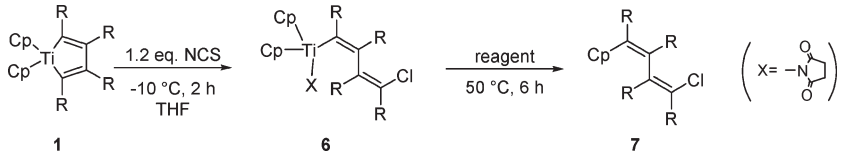
[a] Dienyltitanium **4** were prepared *in situ* by the reaction of carboxylic acid with **1**. [b] A mixture of double-bond regioisomers. [c] Combined NMR yields of two isomers. Isolated yields are in parentheses.

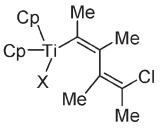
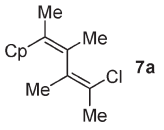
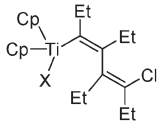
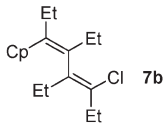
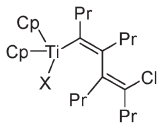
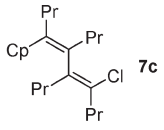
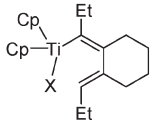
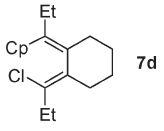
Scheme 7. Synthesis of Bis(cyclopentadienyl)chlorodienyltitanocene Derivatives



As for a facilitation effect, various reagents were examined instead of azobenzene, and it was found that allyl chloride and propargyl bromide also showed a similar effect. The results are shown in Table 2. When **6b** was treated with allyl chloride and propargyl bromide, **7b** was obtained in high yields (entries 3 and 4). Pyrazine and triphenylphosphine

Table 2. Coupling Reaction of a Cyclopentadienyl Ligand with a Chlorodienyl Ligand on Titanocene



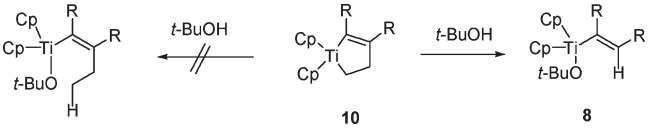
Entry	Chlorodienyltitanocene **6**[a]		Reagent	Product **7**[b]		Yield (%)[c]
1		**6a**	azobenzene		**7a**	85 (67)
2		**6b**	azobenzene		**7b**	80 (60)
3	**6b**		allyl chloride	**7b**		90
4	**6b**		propargyl bromide	**7b**		92
5	**6b**		pyrazine	**7b**		68
6	**6b**		triphenylphosphine	**7b**		58
7	**6b**		-	**7b**		35
8		**6c**	azobenzene		**7c**	91 (72)
9		**6d**	azobenzene		**7d**	75 (57)

[a] Compounds **6** were prepared *in situ* by the reaction of **1** with NCS. [b] A mixture of two double-bond regioisomers. [c] Combined NMR yields of isomers. Isolated yields are in parentheses. Entries 3 and 4 are GC yields.

also showed small effects (entries 5 and 6), compared with the control experiment without additives (entry 7). Since the coupling reaction can be regarded as reductive elimination, reagents that can oxidize the Ti(II) metal center have positive effects. Allyl chloride or propargyl bromide plays a role in the oxidation of the Ti metal center by oxidative addition. On the other hand, azobenzene, pyrazine, or triphenylphosphine coordinates to the Ti(II) metal center to push two ligands together on titanium toward the coupling reaction and stabilize the resulting titanium complex. However to our disappointment, the identification of the remaining "CpTi" species after the reductive elimination has not been successful at this moment, since several peaks appear in the Cp area in the proton NMR spectrum.

2.3. Preparation of Alkenyltitanocenes and Coupling of the Cp Ligand with the Alkenyl Moiety on Titanium. The results obtained above prompted us to investigate the coupling of the Cp ligand with a simpler alkenyl ligand than the dienyl ligand as an sp^2 carbon. We tried to prepare alkenyltitanocenes by protonation of titanacyclopentenes **10**, which we previously prepared.[5] It is interesting to note that when a titanacyclopentene, which was conveniently prepared from Cp_2TiEt_2 and an alkyne, was treated with *t*-BuOH, the expected

Scheme 8. Formation of Alkenyltitanocene from Titanacyclopentene 10 by the Reaction with *t*-BuOH



1,2-disubstituted butenyltitanocene was not formed. Instead, disubstituted ethenyltitanocene **8** was obtained (Scheme 8). The structure of one of the complexes (R = Ph, **8e**) was determined by X-ray analysis, as shown in Figure 1. This suggests that titanacyclopentene **8** is in equilibrium with the titanocene(alkyne)(ethylene) complex.[8] Ethylene was eliminated by addition of *t*-BuOH, and protonolysis of alkyne on titanium proceeded to afford the alkenyltitanocene derivative **8**.

The prepared alkenyltitanocene **8** was treated with azobenzene. As expected, alkenylcyclopentadienes **9** were obtained as a mixture of two isomers when R was an alkyl group (Scheme 9).

(8) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564.

Table 3 shows the result of the Cp coupling reaction with an alkenyl ligand on titanium. The complex **10a**, which was prepared by our reported method,[5] was treated with *t*-BuOH at room temperature for 24 h to afford complex **8a**. Azobenzene was added, and the reaction mixture was stirred at 50 °C for an additional 6 h. After workup, alkenyl-Cp derivative **9a** was obtained as two isomers in 71% combined yield. Ethylene was released in this reaction. Without azobenzene, only 10% of product **9a** was formed.

Instead of *t*-BuOH, *n*-BuOH, *sec*-BuOH, and EtOH were used (Table 3, entries 2−4), and the same coupling product was obtained in those cases in comparable yields.

It is interesting to note that complex **8e** (R = Ph) did not give the corresponding coupling product. This reaction requires electron-donating substituents. Complexes **10b**,**c**,**d** with other alkyl substituents reacted with alcohol and azobenzene in this order to give the corresponding products **9b**,**c**,**d** in yields of 76%, 64%, and 65%, respectively (entries 5−7).

When *n*-BuOD was employed to react with **10a** at room temperature, and then azobenzene was added, deuterated product **9a-D** was obtained in 55% yield with 98% deuterium incorporation (Scheme 10).

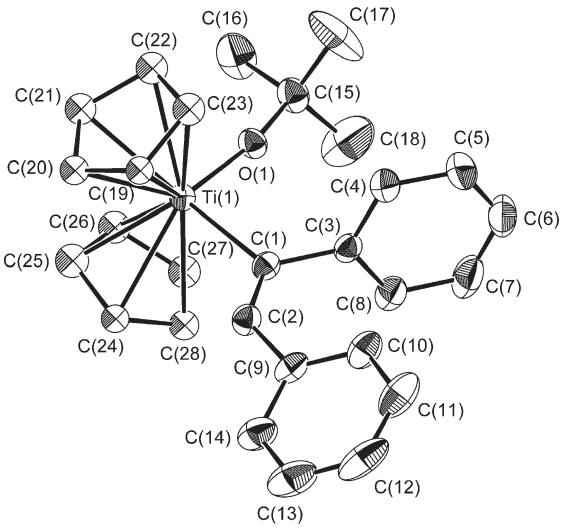
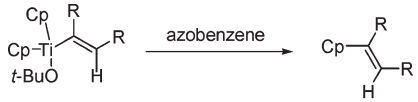
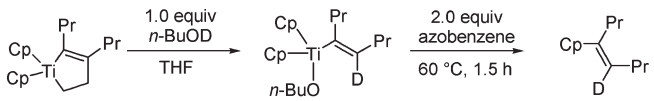


Figure 1. Perspective View of Diphenylethenyltitanocene **8e**.

Scheme 9. Coupling of the Cp Ligand with an Alkenyl Moiety on Titanocene



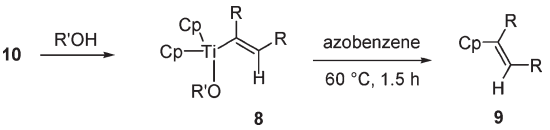
Scheme 10. Formation of Deuterated Alkenyltitanocene and Its Coupling Reaction

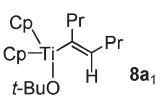
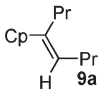
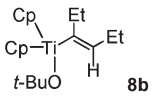
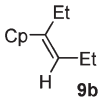
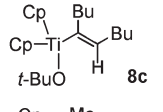
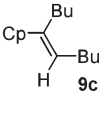
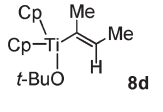
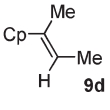


3. Conclusion

We observed the coupling reaction of a dienyl or alkenyl ligand with a Cp ligand on titanium metal. In the formation of dihydroindenyl titanium complexes **2** from titanacyclopentadienes **1**, this result indicates that a stepwise mechanism

Table 3. Coupling of the Cp Ligand with an Alkenyl Ligand of Alkenyltitanocene



Entry	Alcohol	Complex **8**[a]	Product **9**[b]	Yield /%[c]
1	*t*-BuOH	 **8a**$_1$	 **9a**	71(55)
2	*sec*-BuOH	**8a**$_2$	**9a**	65
3	*n*-BuOH	**8a**$_3$	**9a**	58
4	EtOH	**8a**$_4$	**9a**	65
5	*t*-BuOH	 **8b**	 **9b**	76(61)
6	*t*-BuOH	 **8c**	 **9c**	64(51)
7[d]	*t*-BuOH	 **8d**	 **9d**	65(47)

[a] Complexes **8** were prepared *in situ* by the reaction of **10** with alcohol. [b] A mixture of two double-bond regioisomers. [c] Combined NMR yields of isomers. Isolated yields are in parentheses. [d] The product **9d** polymerized in net.

that involves coupling of a dienyl moiety on titanium is possible.

4. Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk line techniques. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF), benzene, toluene, and hexane were refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Pyridine-2-carboxylic acid was deuterated through recrystallization in D_2O.[6] Bis(cyclopentadienyl)titanacyclopentadiene **1** and bis(cyclopentadienyl)titanacyclopentene **10** were prepared as we reported before.[5]

Preparation of 4b$_4$. A solution of Cp_2TiCl_2 (598 mg, 2.4 mmol) in THF (10 mL) was cooled to −78 °C, and *n*-BuLi (1.58 M in hexane, 3.0 mL, 4.8 mmol) was added dropwise to the solution. After stirring for 1 h at −78 °C, 3-hexyne (4.0 mmol) was added and the mixture was stirred for 3 h at −10 °C, to form bis(cyclopentadienyl)titanacyclopentadiene **1b** in the dark green solution. The solvent was removed under reduced pressure. To the residue was added 8 mL of hexane, the precipitated LiCl was removed by filtration, and the filtrate was concentrated to afford a yellow-green solid, **1b**.

A capped 5 mm Ø NMR tube was charged with 0.5 mL of a benzene-d_6 solution of the above prepared **1b** (21 mg, 66 μmol) under argon, and dichloromethane (6.4 μL, 100 μmol) was added as the internal standard. After the NMR measurement, the mixture was treated with dichloroacetic acid (5.4 μL, 66 μmol), and the color of the mixture changed instantly from yellow-green to red. ^{1}H NMR spectroscopy revealed that **4b$_4$** was formed in >93% yield. To this **4b$_4$** was added additional dichloroacetic acid (10.8 μL, 132 μmol), and the color of the mixture changed instantly to yellow with the formation of dienyl derivative in 96% yield.

Furthermore, to the *in situ* generated **4b$_4$** was added 0.1 mL of a benzene-d_6 solution of azobenzene (0.3 mmol), the sealed NMR tube was treated at 50 °C for 6 h, and the dienyl-Cp derivative **5b** was formed in 72% yield (the characterization of **5b** is listed in the following sections).

4b$_4$: ^{1}H NMR (C_6D_6, Me_4Si) 0.88 (dt, J = 7.5, 1.6 Hz, 3 H), 0.97 (dt, J = 7.5, 1.6 Hz, 3 H), 0.99 (dt, J = 7.0, 1.2 Hz, 3 H), 1.06 (dt, J = 7.5, 1.6 Hz, 3 H), 1.52−1.56 (m, 2 H), 1.67−1.86 (m, 6 H), 4.73 (t, J = 7.0 Hz, 1 H), 5.41 (s, 1 H), 5.76 (s, 10 H); ^{13}C NMR (C_6D_6, Me_4Si) 12.9, 14.5, 14.6, 16.0, 21.6, 25.5, 26.1, 26.3, 68.3, 115.0, 129.4, 144.1, 147.1, 166.1, 192.8.

Deuterolysis and Iodination of 4b$_4$. To a dark green solution of bis(cyclopentadienyl)titanacyclopentadiene **1b**, which was prepared in 2.0 mmol scale, was added 2.0 mmol of dichloroacetic acid, and the mixture was stirred for 1.5 h at −15 °C to afford a red solution of **4b$_4$**. The reaction mixture was treated with 1 mL of D_2SO_4 (10% D_2O solution) at this temperature and was allowed to warm to room temperature overnight. The mixture was diluted with 5 mL of water, extracted with hexane, dried over $MgSO_4$, and concentrated. The residue was analyzed by ^{1}H NMR spectroscopy in benzene-d_6 with dichloromethane (63.8 μL, 1.0 mmol) as an internal standard to reveal the formation of deuterated diene in 75% yield (>95% D) and **5b** in 25% yield. When **4b$_4$** was treated with I_2 (3.0 mmol) and CuCl (1.0 mmol), the iododiene was formed in 85% NMR yield.

Representative Procedure for Preparation of Dienyltitanocenes 4 and the Following Coupling Reaction to Form Dienyl-Cp 5. To a solution of bis(cyclopentadienyl)titanacyclopentadiene **1**, which was prepared from Cp_2TiCl_2 (598 mg, 2.4 mmol) in 10 mL of THF, *n*-BuLi (1.58 M in hexane, 4.8 mmol), and an alkyne (4.0 mmol) or a diyne (2.0 mmol) was added 2.0 mmol of dichloroacetic acid, and the mixture was stirred for 5 h at room temperature to afford complexes **4** (small amount of the coupling products **5** were formed unavoidably). After addition of 2.4 mmol of azobenzene, the mixture was heated to 50 °C and stirred for 6 h. The resulting solution was cooled to room temperature, and aqueous $NaHCO_3$ (2 mL) was added to quench the reaction. The mixture was extracted with hexane, and the organic phase was dried over $MgSO_4$. After removal of volatiles *in vacuo*, the residue was analyzed by ^{1}H NMR spectroscopy in benzene-d_6 with dichloromethane or dioxane as an internal standard. Then the residue was subjected to column chromatography on silica gel (hexane containing 3% of Et_3N as eluent) to afford cyclopentadienyl derivatives **5**.

(2*Z*,4*E*)-2-(Cyclopentadienyl)-3,4-dimethylhexa-2,4-diene (5a). Product **5a** was obtained as a mixture of double-bond positional isomers of the cyclopenadienyl moiety. Combined NMR yield of 98%. Isolated yield of 86%. Colorless oil.

The ratio of two isomers major:minor = 2.2:1. ^{1}H NMR (C_6D_6, Me_4Si): 1.44 (qq, J = 6.8 Hz, 1.5 Hz, major − 3 H), 1.48 (qq, J = 6.8 Hz, 2.2 Hz, minor − 3 H), 1.61−1.64 (m, major − 3 H), 1.66−1.70 (m, minor − 3 H), 1.78−1.82 (m, major − 3 H, minor − 3 H), 1.87−1.91 (m, major − 3 H), 1.93−1.95 (m, minor − 3 H), 2.81−2.85 (m, minor − 2 H), 3.05−3.09 (m, major − 2 H), 5.21 (qq, J = 6.8 Hz, 1.5 Hz, major − 1 H), 5.30 (qq, J = 6.8 Hz, 1.5 Hz, minor − 1 H), 6.05−6.09 (m, minor − 1 H), 6.22−6.28 (m, major − 1 H, minor − 1 H), 6.37−6.42 (m, major − 1 H), 6.46−6.51 (m, major − 1 H), 6.64 (dq, J = 5.3 Hz, 1.5 Hz, minor − 1 H). ^{13}C NMR (C_6D_6, Me_4Si): 13.5, 13.7, 15.5, 15.8, 18.8, 19.36, 19.39, 20.8, 40.9, 43.7, 121.1, 123.0, 125.3, 125.4, 127.4, 129.3, 131.0, 131.7, 132.6, 135.8, 136.5, 136.9, 139.1, 140.3, 149.6, 149.9. HRMS: calcd for $C_{13}H_{18}$, 174.1409; found, 174.1398.

Reaction of 1b with Picolinic Acid-d_1. Complex **1b** was treated with 1 equiv of picolinic acid-d_1 to give **4b-D**, which was followed by quenching with an excess amount of methanesulfonic acid (0.5 mL) to afford deuterated diene in 80% yield with 70% deuterium incorporation.

Complex **4b-D** reacted with azobenzene to afford **5b-D** and **5b′-D** in the combined NMR yield of 83% and were isolated as a colorless oil in a yield of 75% with 86% deuterium incorporation.

The ratio of two isomers major:minor =1.5:1. ^{1}H NMR (C_6D_6, Me_4Si): 0.82−1.10 (m, major − 12 H, minor − 12 H), 1.89−2.02 (m, major − 2 H, minor − 2 H), 2.04−2.27 (m, major − 4 H, minor − 4 H), 2.29−2.40 (m, major − 2 H, minor − 2 H), 2.80−2.84 (m, minor − 2 H), 3.04−3.08 (m, major − 2 H), 6.07−6.11 (m, minor − 1 H), 6.21−6.26 (m, major − 1 H, minor − 1 H), 6.40−6.43 (m, major − 1 H), 6.46−6.50 (m, major − 1 H), 6.61−6.66 (m, minor − 1 H).

Representative Procedure for Preparation Chlorodienyl-Cp Derivatives 7 from the *in Situ* Formed Chlorodienyltitanocene 6. To a solution of bis(cyclopentadienyl)titanacyclopentadiene **1**, which was prepared from Cp_2TiCl_2 (598 mg, 2.4 mmol) in 10 mL of THF, *n*-BuLi (1.58 M in hexane, 4.8 mmol), and an alkyne (4.0 mmol) or a diyne (2.0 mmol) was added 2.4 mmol of NCS, and the mixture was stirred for 2 h at −10 °C to afford the chlorodienyltitanocenes **6**. After addition of 4 mmol of azobenzene, the mixture was heated to 50 °C and stirred for 6 h. The resulting solution was cooled to room temperature, and aqueous $NaHCO_3$ (2 mL) was added to quench the reaction. The mixture was extracted with hexane, and the organic phase was dried over $MgSO_4$. After removal of volatiles *in vacuo*, the residue was analyzed by ^{1}H NMR spectroscopy in benzene-d_6 with dichloromethane or dioxane as an internal standard. Then the residue was subjected to column chromatography on silica gel (hexane containing 3% of Et_3N as eluent) to afford a mixture of cyclopentadienyl derivatives **7**.

(2*Z*,4*Z*)-5-Chloro-2-(cyclopentadienyl)-3,4-dimethylhexa-2,4-diene (7a). Product **7a** was obtained as a mixture of double-bond positional isomers. Combined NMR yield of 85%. Isolated yield of 67%. Light yellow oil.

The ratio of two isomers major:minor = 2.2:1. ^{1}H NMR (C_6D_6, Me_4Si): 1.50 (q, J = 1.1 Hz, major − 3 H), 1.55 (q, J = 1.1 Hz, minor − 3 H), 1.80 (q, J = 1.1 Hz, major − 3 H), 1.80−1.89 (m, major − 6 H, minor − 9 H), 2.80 (br d, J = 1.4 Hz,

minor − 2 H), 3.06 (dq, J = 1.4, 23 Hz, major − 1 H), 3.19 (dq, J = 1.4, 23 Hz, major − 1 H), 6.19−6.23 (m, minor − 1 H), 6.24−6.29 (m, major − 1 H, minor − 1 H), 6.47−6.54 (m, major − 2 H), 6.74 (dq, J = 1.5, 5.2 Hz, minor − 1 H). ^{13}C NMR (C_6D_6, Me_4Si): 18.0, 18.22, 18.27, 18.5, 18.7, 19.0, 21.8, 21.9, 41.2, 42.8, 123.9, 124.1, 126.2, 126.5, 128.2, 129.4, 132.3, 132.51, 132.54, 132.7, 133.2, 134.3, 135.7, 136.2, 148.4, 148.6. HRMS: calcd for $C_{13}H_{17}Cl$, 208.1018; found, 208.1013.

Reaction of 6b with Propargyl Bromide to Afford 7b. To a THF solution of tetraethyltitanacyclopentadiene **1b** (1.0 mmol scale) was added NCS (160 mg, 1.2 mmol) at 0 °C, and the mixture was stirred for 2 h. To the mixture was added propargyl bromide (0.18 mL, 2.0 mmol), and the mixture was stirred at 50 °C for 6 h. The reaction was quenched with 3 M aqueous HCl solution and extracted with hexane. The organic phase was washed with water, aqueous saturated $NaHCO_3$, and brine and dried over anhydrous sodium sulfate. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with hexane as an eluent to afford chlorobutadienylcyclopentadiene **7b** as a colorless oil (218 mg, 92% GC yield; 82% isolated yield). Compound **7b** was obtained as a mixture of the double-bond positional isomers in the cyclopentadiene ring in a ratio of 63:37.

The reactions with other organic halides also produced the same compound **7b**.

Representative Procedure for Preparation of Alkenyl-Cp Derivatives 9. A solution of bis(cyclopentadienyl)titanacyclopentene **10** was prepared as we described for **10e** from Cp_2TiCl_2 (598 mg, 2.4 mmol), EtMgBr (1.0 M in THF, 4.8 mmol), and an alkyne (2.0 mmol). To the reaction mixture was added azobenzene (4 mmol), and the mixture was stirred at 50 °C for 8 h. After cooling to room temperature, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ (2 mL). The mixture was extracted with hexane, and the organic phase was dried over $MgSO_4$. After removal of volatiles *in vacuo*, the residue was analyzed by ^{1}H NMR spectroscopy in benzene-d_6 with dichloromethane or dioxane as an internal standard. Then the residue was subjected to column chromatography on silica gel (hexane containing 3% of Et_3N as eluent) to afford a mixture of cyclopentadienyl derivatives **9**.

(*E*)-4-(Cyclopentadienyl)-oct-4-ene (9a). Product **9a** was obtained as a mixture of double-bond positional isomers. Combined NMR yield of 71%. Isolated yield of 55%. Colorless oil.

The ratio of two isomers major:minor = 2.9:1. ^{1}H NMR (C_6D_6, Me_4Si): 0.89−1.08 (m, major − 6 H, minor − 6 H), 1.38−1.53 (m, major − 2 H, minor − 2 H), 1.55−1.70 (m, major − 2 H, minor − 2 H), 2.10−2.25 (m, major − 2 H, minor − 2 H), 2.36−2.53 (m, major − 2 H, minor − 2 H), 2.96 (br s, minor − 2 H), 3.06 (br s, major − 2 H), 5.72 (t, J = 7.2 Hz, major − 1 H), 5.95 (t, J = 7.2 Hz, minor − 1 H), 6.18−6.24 (m, major − 1 H, minor − 1 H), 6.38−6.44 (m, major − 1 H, minor − 1 H), 6.51−6.57 (m, major − 1 H), 6.93−6.98 (m, minor − 1 H). ^{13}C NMR (C_6D_6, Me_4Si): 14.10, 14.12, 14.4, 14.5, 22.8, 23.0, 23.3, 23.4, 30.60, 30.63, 31.0, 31.3, 40.7, 41.7, 124.9, 126.40, 126.48, 128.5, 130.7, 132.1, 133.1, 133.4, 135.4, 136.3, 147.6, 149.4. HRMS: calcd for $C_{13}H_{20}$, 176.1565; found, 176.1571.

Formation of 8e by the Reaction of Bis(cyclopentadienyl)titanacyclopentene 10e with *t*-BuOH. It should be noted that in the case of diphenyltitanacyclopentene **10e**, the coupling reaction did not proceed to **9e** under the same conditions as for **9a−d**. Complex **10e** reacted with *t*-BuOH to afford air-stable yellow crystals of **8e** with a loss of ethylene. The structure of **8e** was determined by X-ray analysis. The deuterolysis of **8e** gave deuterated *cis*-stilbene in 96% GC yield, and the isolated yield was 89% with >99% deuterium incorporation. The same product was obtained again when **10e** reacted with *t*-BuOD followed by quenching with 3 N HCl.

To a THF solution of bis(cyclopentadienyl)titanacyclopentene **10e**, which was obtained in the same way as above, was added *t*-BuOH (2.4 mmol), and the mixture was stirred at 50 °C for 3 h. After removal of volatiles *in vacuo*, the residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 3:1 as eluent) to afford a yellow powder, **8e**. Suitable crystals for X-ray diffraction were obtained by dissolving **8e** in toluene and keeping it at −30 °C.

8e: ^{1}H NMR (C_6D_6, Me_4Si) 1.11 (s, 9 H), 6.06 (s, 10 H), 6.75 (s, 1 H), 7.01−7.53 (m, 10 H); ^{13}C NMR (C_6D_6, Me_4Si) 31.3, 83.7, 112.8, 123.6, 125.0, 126.3, 128.2, 128.6, 128.8, 133.7, 140.0, 155.5, 188.6; HRMS calcd for $C_{28}H_{30}OTi$, 430.1776; found, 430.1777.

Reaction of Bis(cyclopentadienyl)titanacyclopentene 10a with *n*-BuOD. The reaction was carried out in a similar method to the above method using *n*-BuOD reacted with **10a**. Product **9a-D** was obtained as a mixture of double-bond positional isomers. Combined NMR yield of 71%. Isolated yield of 55% (98% D). Colorless oil.

The ratio of two isomers major:minor = 2.9:1. ^{1}H NMR (C_6D_6, Me_4Si): 0.89−1.08 (m, major − 6 H, minor − 6 H), 1.38−1.53 (m, major − 2 H, minor − 2 H), 1.55−1.70 (m, major − 2 H, minor − 2 H), 2.10−2.25 (m, major − 2 H, minor − 2 H), 2.36−2.53 (m, major − 2 H, minor − 2 H), 2.96 (br s, minor − 2 H), 3.06 (br s, major − 2 H), 5.72 (t, J = 7.2 Hz, major − 1 H, 98% D incorporation), 5.95 (t, J = 7.2 Hz, minor − 1 H, 98% D incorporation), 6.18−6.24 (m, major − 1 H, minor − 1 H), 6.38−6.44 (m, major − 1 H, minor − 1 H), 6.51−6.57 (m, major − 1 H), 6.93−6.98 (m, minor − 1 H).

Supporting Information Available: Experimental part for compounds **5b−d**, **7b−d**, and **9b−d**, NMR spectra of new compounds, and X-ray analytical data for **8e**. This material is available free of charge via the Internet at http://pubs.acs.org.