

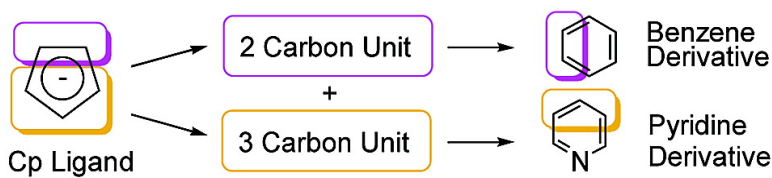
Communication

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*J. Am. Chem. Soc.*, **2003**, 125 (32), 9568-9569 • DOI: 10.1021/ja027234y • Publication Date (Web): 17 July 2003

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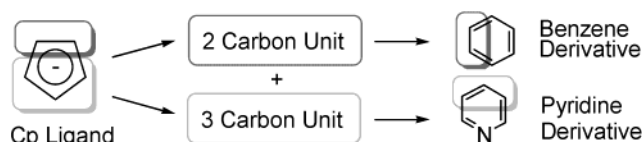
## Unprecedented Double C–C Bond Cleavage of a Cyclopentadienyl Ligand

Zhenfeng Xi,<sup>\*,†</sup> Kimihiko Sato,<sup>‡</sup> Ye Gao,<sup>†</sup> Jianming Lu,<sup>†</sup> and Tamotsu Takahashi<sup>\*,‡</sup>

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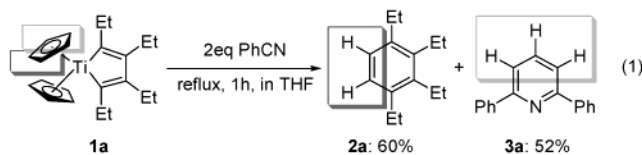
Received June 9, 2002; E-mail: tamotsu@cat.hokudai.ac.jp

Carbon–carbon bond cleavage is one attractive target of organic chemistry.<sup>1–3</sup> However, in most cases, the carbon–carbon bond cleavage reaction is limited to the ring opening, or elimination of small molecules, intramolecular rearrangement reactions, or metal–complex formation of the intermediates. From the point of view of organic synthesis, conversion of the cleaved fragments into useful organic molecules is more attractive and important. In this contribution, we report an unprecedented double C–C bond cleavage of a cyclopentadienyl ligand and transformation of the resulting two pieces such as a two-carbon unit and a three-carbon unit into a benzene derivative and a pyridine derivative, respectively, in one-pot (Figure 1).<sup>4</sup>



**Figure 1.** Formation of a benzene derivative and a pyridine derivative from a cyclopentadienyl ligand via cleavage of two C–C bonds and selective C–C formation.

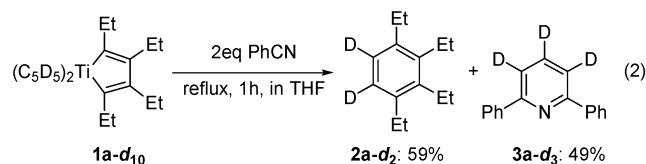
Reaction of titanacyclopentadiene **1a**,<sup>5</sup> which was generated in situ from  $\text{Cp}_2\text{TiBu}_2$  and 2 equiv of 3-hexyne, with 2 equiv of PhCN in THF at reflux for 1 h resulted in the formation of 1,2,3,4-tetraethylbenzene, **2a**, and 2,6-diphenylpyridine, **3a**, in 60 and 52% yields, respectively (eq 1). In addition to PhCN, a variety of nitriles,



such as *p*-F-C<sub>6</sub>H<sub>4</sub>CN, *p*-MeC<sub>6</sub>H<sub>4</sub>CN, and PrCN were found to be effective for the above novel reaction, resulting in the formation of **3b**, **3c**, and **3d**, respectively, as well as the formation of **2a**. Treatment of the reaction mixtures with DCl or I<sub>2</sub> instead of hydrolysis also afforded the same products **2** and the corresponding pyridine derivatives **3** (eq 1), which indicates that free benzene derivatives **2** and free pyridine derivatives **3** were formed in this reaction. Monitoring of the reaction of **1a** with 2 equiv of PhCN at 40 °C revealed that **2a** was formed first and then **3a** appeared with a time-lag.

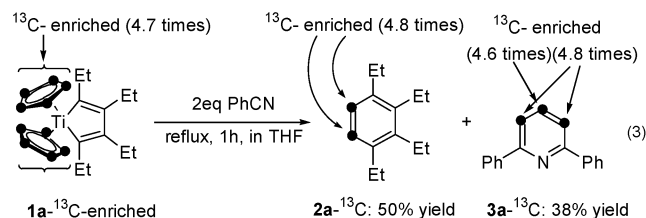
(C<sub>5</sub>D<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub> was prepared from C<sub>5</sub>D<sub>5</sub>Li and TiCl<sub>4</sub> and used for this reaction instead of Cp<sub>2</sub>TiCl<sub>2</sub>. Surprisingly, the reaction of **1a** with PhCN afforded dideuterated tetraethylbenzene **2a-d<sub>2</sub>** and 3,4,5-

trideutero-2,6-diphenylpyridine **3a-d<sub>3</sub>** with more than 97% deuterium incorporation (eq 2). Their <sup>13</sup>C NMR spectra clearly showed



the positions of those deuteriums in **2a-d<sub>2</sub>** and **3a-d<sub>3</sub>**. This indicates that the two CH moieties in tetraethylbenzene **2a** are from the Cp ligand of **1a** and the remaining three CH moieties of the Cp ligand were trapped as diphenylpyridine **3a**.

Furthermore, to obtain the direct evidence for the C–C bond-tearing reactions of the Cp ligand into two pieces, we synthesized <sup>13</sup>C-enriched Cp<sub>2</sub>TiCl<sub>2</sub> (4.7 times <sup>13</sup>C enriched in Cp ligands) and carried out the same reaction as for deuterium experiment. The results are shown in (eq 3) and the <sup>13</sup>C NMR study clearly showed that C5 and C6 carbons of 1,2,3,4-tetraethylbenzene were <sup>13</sup>C-enriched (4.7 times) and C3, C4, and C5 carbons of 2,6-diphenylpyridine were also <sup>13</sup>C-enriched (4.6 times). This result is completely consistent with the deuterium experiments.



As a whole, two carbon–carbon bonds of a cyclopentadienyl ligand were cleaved and torn into two pieces, a two-carbon unit and a three-carbon unit. The two-carbon unit was trapped by titanacyclopentadienyl moiety to form tetraethylbenzene **2a**, and the three-carbon unit was trapped by 2 equiv of benzonitrile to afford diphenylpyridine **3a**.

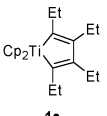
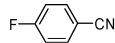
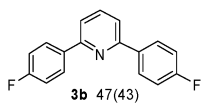
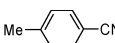
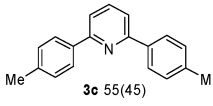

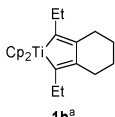
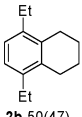
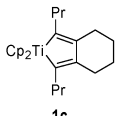
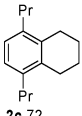
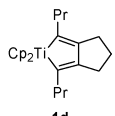
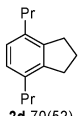
On the other hand, reaction of **1a** with <sup>13</sup>C-labeled PhCN gave the benzene derivative **2a** in 59% yield in which <sup>13</sup>C was not incorporated. Pyridine was obtained in 52% yield, and the carbons attached to a Ph group were <sup>13</sup>C enriched.

In addition to the above monocyclic titanacyclopentadiene **1a**, bicyclic titanacyclopentadiene **1b**, **1c**, and **1d** could also undergo the same reactions and afforded **2b**, **2c**, and **2d** in 50, 72, and 70% yields, respectively, along with the formation of **3a** in 56, 47, and 45% yields, respectively. Results are shown in Table 1 to understand whether this reaction proceeds via an intramolecular pattern or an intermolecular way, a mixture of **1e-d<sub>10</sub>** (R = Pr) and **1f** (R = Me) in a 1:1 molar ratio was treated with PrCN. As shown in eq 4, only the corresponding intramolecular coupling products, **2e-d<sub>2</sub>** and **2f** were obtained. This clearly indicates that the benzene

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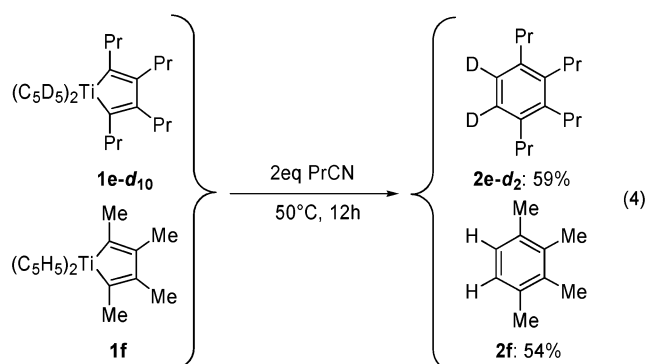
<sup>‡</sup> Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, and CREST, Japan Science and Technology Corporation (JST).

**Table 1.** Formation of Benzene Derivatives and Pyridine Derivatives from Cyclopentadienyltitanacyclopentadienes

Titanacyclopentadiene	R-CN	Conditions	Benzene (%)	Pyridine (%)
	PhCN	50°C 12h	<b>2a</b> 62 (45)	<b>3a</b> 46(45)
<b>1a</b>	PhCN	reflux 1h	<b>2a</b> 60	<b>3a</b> 52
<b>1a</b>		reflux 1h	<b>2a</b> 66(51)	 <b>3b</b> 47(43)
<b>1a</b>		reflux 1h	<b>2a</b> 68(50)	 <b>3c</b> 55(45)
<b>1a</b>	Pr-CN	reflux 1h	<b>2a</b> 59 (39)	 <b>3d</b> 54 (27)
	PhCN	reflux 1h	 <b>2b</b> 50(47)	<b>3a</b> 56(43)
	PhCN	50°C 24h	 <b>2c</b> 72	<b>3a</b> 47
	PhCN	50°C 20h	 <b>2d</b> 70(52)	<b>3a</b> 45

GC yields. Isolated yields were shown in parentheses. <sup>a</sup> See ref 2k.

formation from two carbons of a Cp ligand and a titanacyclopentadiene moiety proceeds intramolecularly.



After the reaction of **1a** with 2 equiv of PhCN, 0.1 equiv of unreacted PhCN was recovered in the reaction mixture. Hydrolysis and distillation of the reaction mixture gave 1.21 equiv of ammonia which was detected by indophenol method. Since **3a** was formed in 52% yield, more than 90% of N was detected. The origin of ammonia may be titanium nitride or titanium imide complexes. However, we did not observe the clean formation of some specified species.

In addition, we synthesized a tetraethyltitanacyclopentadiene with one methylcyclopentadienyl ligand and a pentadeuterated Cp ligand. When it was treated with PhCN, only **2a** and 4-methyl-2,5-diphenylpyridine were obtained as benzene derivatives and pyridine derivatives, respectively, from the methylcyclopentadienyl ligand. No formation of **3a** from the methylcyclopentadienyl ligand was observed. This clearly shows that the pyridine is formed from the rest of the C3 unit of cyclopentadienyl ligand after formation of the benzene derivative.

Recently Rosenthal and co-workers reported an interesting ring opening of the Cp ligand of bicyclic bis- $\eta^5$ -cyclopentadienyltitanacyclopentadienes such as **1b** and an intramolecular C–C coupling to form a stable  $\eta^4, \eta^3$ -dihydroindenyltitanium complex bearing a Ti–allyl moiety.<sup>2k,m</sup> Although we must await for further investigations to elucidate the reaction mechanism, one possible reaction path is via indene derivative formation by coupling of a Cp ligand with titanacyclopentadiene moiety.

**Acknowledgment.** We thank Mr. Y. Kuzuba for his assistance in experiments. A part of this work was supported by National Science Fund for Distinguished Young Scholars (29825105), the Major State Basic Research Development Program (G2000077502-D), and National Natural Science Foundation of China.

**Supporting Information Available:** Experimental details and spectra data for all new compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA027234Y