

# Cu(I)-mediated cycloaddition reaction of zirconacyclopentadienes with fumaronitrile and application for synthesis of monocyno-substituted pentacenes

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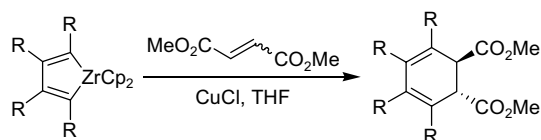
**Abstract**—Cu(I)-mediated reactions of zirconacyclopentadienes with fumaronitrile afforded the corresponding dicyanocyclohexadiene and benzonitrile derivatives in good yields. These products were selectively prepared by controlling the reaction temperature. Furthermore, the reaction was applicable for monocyno-substituted pentacene derivatives.

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Transition-metal mediated cycloaddition reactions of unsaturated molecules such as alkynes, alkenes, and so on have been widely applied for construction of carbocyclic and heterocyclic skeletons.<sup>1</sup>

We have developed a series of cycloaddition reactions of zirconacycles with various unsaturated compounds to afford the corresponding cycloadducts in good to excellent yields.<sup>2–4</sup> In general the reaction produces a formal [4+2] cycloadduct. When a zirconacyclopentadiene reacts with an alkyne in the presence of copper(I) or nickel(II) salt, the corresponding benzene derivatives were produced.<sup>2</sup> The reactions of zirconacyclopentadienes with dimethyl fumarate or maleate, the corresponding 1,3-cyclohexadiene derivative was obtained having trans configuration of the two ester groups as shown in **Scheme 1**.<sup>2d,e</sup>

During the further investigation of the zirconium-mediated cycloaddition reactions, we found that the reaction of zirconacyclopentadienes **1** with fumaronitrile afforded two types of formal [4+2] cycloadducts, dicyanocyclohexadiene **2** and benzonitrile **3** as shown in **Scheme 2**. It is interesting to note that the formation of **2** and **3**

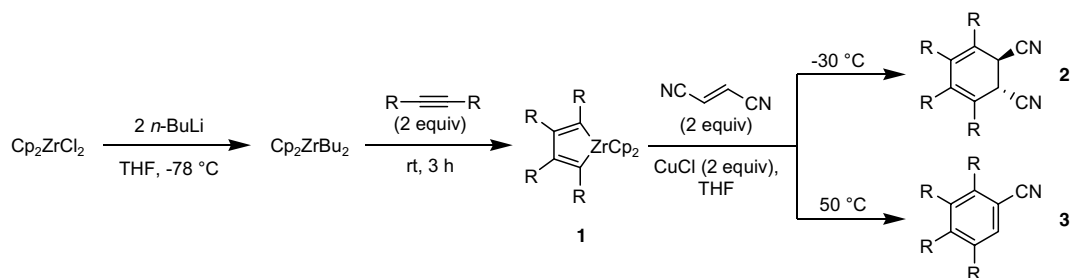


**Scheme 1.**

is dependent on the reaction temperature. Furthermore, the reaction was applied for the synthesis of monocyno-substituted pentacenes.<sup>5</sup>

A typical experimental procedure is as follows (**Scheme 2**): To a solution of zirconacyclopentadiene **1a** prepared from  $\text{Cp}_2\text{ZrCl}_2$  (1.1 mmol), *n*-BuLi (2.2 mmol), and 3-hexyne (2.0 mmol) in THF,<sup>6</sup> fumaronitrile (2.2 mmol), and CuCl (2.2 mmol) were added and the mixture was stirred at room temperature for 3 h. After quenching with 3 M aqueous HCl and usual work-up afforded a mixture of the corresponding dicyanocyclohexadiene **2a** and benzonitrile **3a** in 39% and 40% yields, respectively. The trans configuration of the two cyano groups in cyclohexadiene **2a** was confirmed by X-ray crystallographical analysis. The formation of benzonitrile **3** is significantly different from the reaction with dimethyl fumarate or maleate as shown in **Scheme 1**.

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Scheme 2.

**Table 1.** Reaction of zirconacyclopentadienes with fumaronitrile in the presence of CuCl at room temperature

Entry	Zirconacyclopentadiene	Time (h)	Yield <sup>a</sup> (%)		
			2	3	
1		<b>1a</b> (R = Et)	3	39	40
2		<b>1b</b> (R = Pr)	3	29	33
3		<b>1b</b> (R = Pr)	24	19	41
4		<b>1c</b> (R = Ph)	3	—	44
5		<b>1d</b> (R = Pr)	3	22	51
6		<b>1e</b> (R = Ph)	3	—	50

<sup>a</sup> Isolated yields.

**Table 1** summarizes the result of the reactions of a series of zirconacyclopentadienes with fumaronitrile at room temperature. The product ratio of cyclohexadiene **2** to benzonitrile **3** was dependent on the reaction time and substituents on the zirconacycles employed. When the reaction of zirconacyclopentadiene **1a** or **1b** with fumaronitrile was carried out at room temperature for 3 h, the product ratio of **2–3** was almost 1:1 (entries 1 and 2). On the other hand, when the reaction time was prolonged for 24 h, the amount of benzonitrile **3b** increased with decrease of cyclohexadiene **2b** (entry 3). This suggested that conversion of cyclohexadiene **2** into **3** occurred during the reaction.

In contrast to the alkyl-substituted zirconacycles, tetraphenyl-substituted one **1c** afforded the corresponding benzonitrile **3c** as a single product (entry 4). The same tendency was observed in the reactions with bicyclic zirconacyclopentadienes, that is, the mixture of cyclohexadiene **2d** and benzonitrile **3d** was obtained from the reaction with alkyl-substituted zirconacycle **1d**, whereas only the corresponding benzonitrile derivative **3e** was obtained from phenyl-substituted **1e** (entry 6).

It is worth noting that by controlling the reaction temperature highly selective formation of each product was achieved. **Table 2** summarized the results of temperature-dependence of the cycloaddition reactions. When the reactions were carried out at 50 °C, the corresponding benzonitrile derivatives **3** were obtained as single products (entries 1, 3, and 6). On the other hand, only

**Table 2.** Temperature-dependence of the reaction of zirconacyclopentadienes with fumaronitrile

Entry	Zirconacyclopentadiene	Temp (°C)	Yield <sup>a</sup> (%)		
			2	3	
1		<b>1a</b> (R = Et)	50	—	74(64)
2		<b>1a</b> (R = Et)	−30	(75)	—
3		<b>1b</b> (R = Pr)	50	—	78(64)
4		<b>1b</b> (R = Pr)	−30	(70)	—
5		<b>1c</b> (R = Ph)	−30	(43)	—
6		<b>1d</b>	50	—	82(66)
7		<b>1d</b>	−30	(87)	—

<sup>a</sup> GC yields. Isolated yields were given in parentheses.

cyclohexadienes **2** were produced at −30 °C in comparable yields (entries 2, 4, 5, and 7).

Interestingly, the cycloaddition of zirconacycle **1** with fumaronitrile occurred only at the C=C bond to afford the carbocycles **2** and **3**. No pyridine derivatives via the cycloaddition at the C≡N bond were observed. This is striking contrast to the reaction of cobaltacyclopentadiene with acrylonitrile to afford a mixture of the corresponding cyclohexadiene and pyridine derivatives.<sup>7</sup> Thus, the carbocycle-selective nature is a unique characteristic of the present Zr-mediated reaction.

**Table 3** shows the results of the reaction of zirconacyclopentadiene **1** with maleonitrile. Compared with fumaronitrile, the reactivity of maleonitrile was lower, and at −30 °C the reaction did not take place (entry 1). At 0 °C, the reaction with zirconacycle **1b** (R = Pr) proceeded to afford the corresponding *cis*-dicyanocyclohexadiene **4b** along with a small amount of *trans*-isomer **2b** (entry 2). At room temperature, the ratio of *cis*-isomer **4b** was decreased on increasing the ratio of *trans*-isomer **2b** and benzonitrile **3b** (entry 3). This suggests that isomerization of *cis*-isomer **4b** into *trans*-isomer **2b** occurred during the reaction. The similar phenomena were observed in the reaction of zirconacycle **1a** (R = Et), entries 4 and 5). The difference of the product ratios between the reaction of **1a** (R = Et) and **1b** (R = Pr) could be attributed to the different steric effects of their substituents.

The reaction was applied for the synthesis of mono-cyano-substituted pentacenes as shown in **Scheme 3**. In

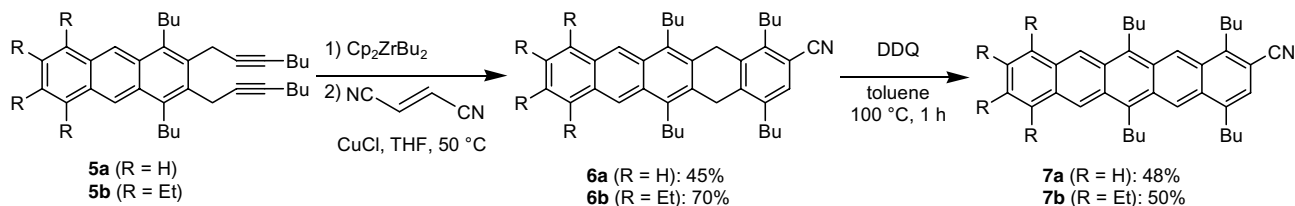
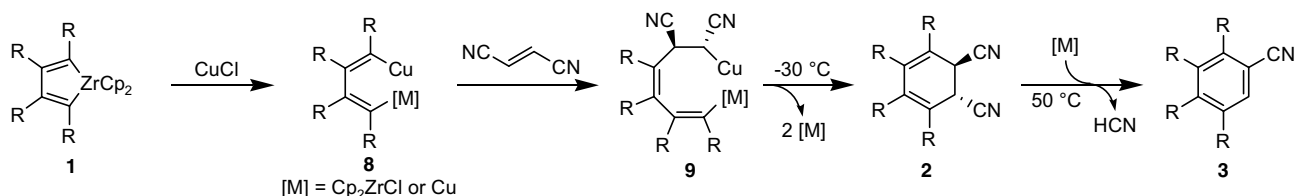
**Table 3.** Reaction of zirconacyclopentadienes with maleonitrile

Entry	R	Temp	Yield <sup>a</sup> (%)		
			4	2	3
1	Pr	-30 °C	0	0	0
2	Pr	0 °C	72	2	0
3	Pr	rt	7	28	41
4	Et	0 °C	29	14	32
5	Et	rt	0	15	55

<sup>a</sup> NMR yields.

1997, it was reported that non-substituted pentacene had high carrier mobility comparable to amorphous silicon.<sup>8</sup> Since then non-substituted pentacene has shown the highest carrier mobility among organic compounds as an organic film. However, non-substituted pentacene has a critical problem, which is insoluble in organic solvents at ambient temperature. Therefore, we reported the preparation method (homologation method) of the substituted pentacenes as soluble pentacenes.<sup>5,9</sup> The substituents can control the properties of pentacenes. After our report, several groups reported substituted pentacene derivatives.<sup>10–14</sup>

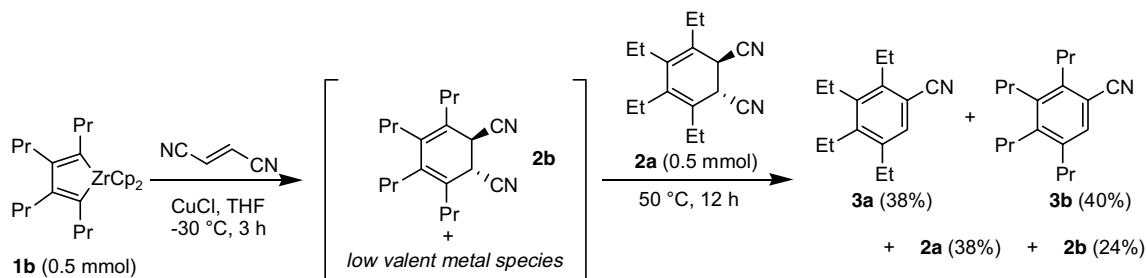
Here, we applied our novel method to the formation of monocyano-substituted soluble pentacenes. In this reaction, the same reaction conditions were used for bis(propargyl)anthracenes **5a,b** to afford the corresponding monocyano-substituted dihydropentacenes **6a,b**, in 45% and 70% yield, respectively. These dihydropentacene derivatives were aromatized with DDQ to produce the corresponding monocyano-pentacenes **7a,b** as dark-blue solid in 48% and 50% yield, respectively.

**Scheme 3.****Scheme 4.**

A plausible mechanism for the reaction of a zirconacyclopentadiene with fumaronitrile is shown in Scheme 4. In the reaction of zirconacyclopentadiene **1** with CuCl, transmetalation between zirconium and copper(I)<sup>15,16</sup> occurs to generate dimetalated butadiene intermediate **8**, which adds to fumaronitrile to produce intermediate **9**. Then, oxidative ring closing of **9** can produce cyclohexadiene **2** along with elimination of the low valent metal species. At low temperature, **2** is stable. After treatment of the low valent metal species with 3 M HCl, **2** is isolated as a single product. At 50 °C, **2** reacts with the low valent metal species, which act as a base to remove HCN from **2**. As a result, benzonitrile **3** is formed as a single product.

In order to make clear the elimination of HCN from the once formed **2** in the solution, the following reactions were carried out. First, the reaction mixture of zirconacyclopentadiene **1a** (R = Et) with fumaronitrile and CuCl was quenched by D<sub>2</sub>O. No deuterated products were obtained. This indicates that metalated species of **2** or **3** were not formed as the products before hydrolysis at low temperature. In addition, to the reaction mixture of **1b** with fumaronitrile, which gives **2b** as a product, dicyanocyclohexadiene **2a** was added as shown in Scheme 5. Then dicyanocyclohexadiene **2a** was converted into **3a**. This result suggests that the reaction mixture after formation of cyclohexadiene **2** is basic enough to cause the elimination of HCN from **2**. These results strongly support our proposed mechanism, which explains the temperature-dependent products.

In summary, cycloaddition reaction of zirconacyclopentadiene with fumaronitrile was demonstrated. Although a mixture of cyclohexadiene **2** and benzonitrile **3** was obtained from the reaction at room temperature, a simple control of the reaction temperature led to selective preparation of each product. Furthermore, the method was applied to synthesize monocyano-substituted pentacenes.



Scheme 5.

### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.075.

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