Substituent-Dependent Selective Replacement of Alkyne Moieties of Zirconacyclopentadienes *via* C-C Bond Cleavage Reaction

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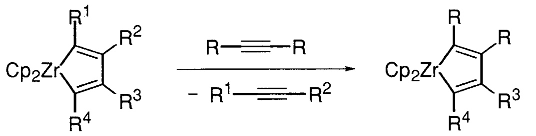
Replacement of an alkyne moiety of zirconacyclopentadienes via β,β'-carbon-carbon bond cleavage was highly dependent on their substituents. Complete differentiation between diphenylacetylene and 4-octyne in the reaction with butyronitrile was demonstrated.

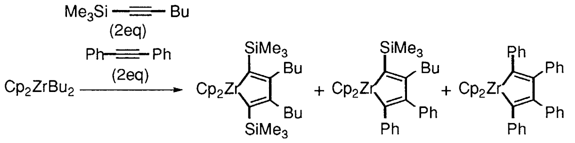
Metallacycles are known to show β,β'-carbon-carbon bond cleavage reactions.[1-3] We have investigated the cleavage reactions of zirconacycles and have used these reactions for organic syntheses.[1-3] During the course of our studies, we found that the cleavage reaction of zirconacyclopentadienes was dependent on their substituents. In this paper we would like to report the substituent-dependent selective replacement of an alkyne moiety of zirconacyclopentadienes via selective β,β'-carbon-carbon bond cleavage (eq 1).



(1)

It is well known that when alkynes are treated with zirconocene (II) complexes, dimerization of alkynes proceeds on zirconocene to give zirconacyclopentadienes quantitatively. When a mixture of two different alkynes was used, three different zirconacyclopentadienes are expected to be statistically formed. In fact, when a mixture of 2 eq of 1-trimethylsilyl-1-hexyne and 2 eq of diphenylacetylene reacted with Cp_2ZrBu_2 (Negishi reagent)[4] at room temperature, a mixture of three zirconacyclopentadienes **1a**, **2** and **3** was obtained (eq 2). The compound **2** was the major product.

Table 1. Yields of zirconacyclopentadienes by the reaction of Cp_2ZrBu_2 with a mixture of 2 eq of 1-trimethylsilyl-1-hexyne and 2 eq of diphenylacetylene



(2)

1a **2** **3**

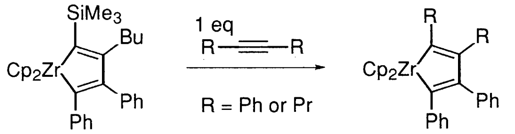
	Products Yields/%[a]		
	1a	**2**	**3**
r.t., 3 h	12	83	4
50 °C, 1 h	2	55	32
50 °C, 3 h	3	18	60
50 °C, 6 h	4	2	76
50 °C, 15 h	2	0	79

[a] Yields were determined by GC after hydrolysis.

However, when the mixture was stirred at 50 °C, surprisingly, the yield of **3** increased with decrease of that of **2** and **1a**. After stirring at 50 °C for 15 h, zirconacyclopentadienes **1a** and **2** almost disappeared (2% and 0% yield for **1a** and **2**, respectively), and **3** was selectively obtained in 79% yield as shown in Table.

In order to elucidate the puzzle of this unusual selective coupling of alkynes, we carried out the following reactions and found a selective stepwise replacement of an alkyne moiety of zirconacyclopentadienes. When zirconacyclopentadiene **2**, which was selectively prepared by our method,[3] was treated with one equiv of diphenylacetylene at 50 °C, **3** was formed in quantitative yield along with the formation of free 1-trimethylsilyl-1-hexyne (eq 3). The complex **2** completely disappeared. Use of 4-octyne instead of diphenylacetylene for zirconacyclopentadiene **2** afforded unsymmetrical zirconacyclopentadiene **4** in 77% yield (eq 3). Noteworthy is that 1-trimethylsilyl-1-hexyne moiety of **2** was replaced with high selectivity (>98%). No formation of **5a** was observed. Further addition of 4-octyne to **4** did not give **6**. Similar selective replacement was observed for **7**. Reaction of **7** with 4-octyne at 50 °C for 3 h afforded **4** in 83% yield with >97% selectivity. In this reaction t-Bu substituted alkyne moiety was selectively replaced.

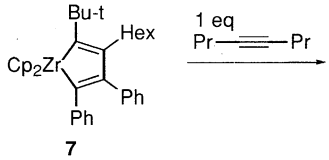
These results clearly indicated that when zirconacyclopentadienes **2** and **7** were treated with an alkyne such as diphenylacetylene and 4-octyne, one alkyne moiety with a bulky substituent such as 1-trimethylsilyl-1-hexyne moiety for **2** and t-Bu substituted alkyne for **7** was replaced with high selectivity via β,β'-carbon-carbon bond cleavage of zirconacyclopentadienes. This type of highly substituent-dependent selective replacement of an alkyne moiety via β,β'-



(3)

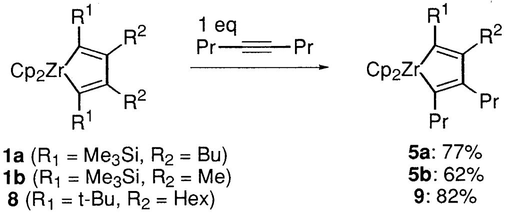
2

3: quantitative (R = Ph)
4: 77% (R = Pr)
(>98% selectivity)



4: 83% (4)

7



(5)

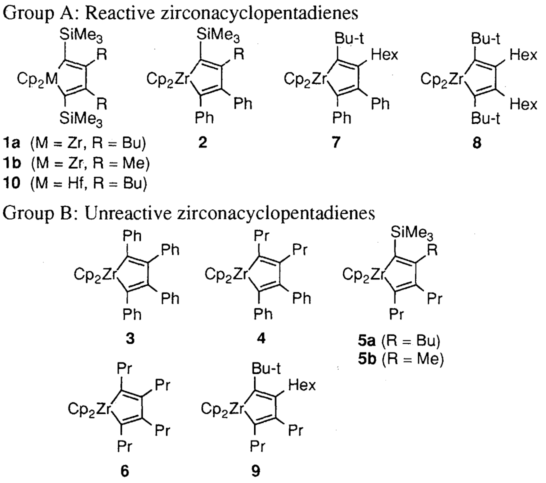
1a (R_1 = Me_3Si, R_2 = Bu)
1b (R_1 = Me_3Si, R_2 = Me)
8 (R_1 = t-Bu, R_2 = Hex)

5a: 77%
5b: 62%
9: 82%

carbon-carbon bond cleavage of zirconacycles is unprecedented, to the best of our knowledge.

Zirconacyclopentadienes with two trimethylsilyl groups or two t-Bu group such as **1a**, **1b** and **8** also showed the replacement of alkynes in a similar way. Treatment of **1a**, **1b** and **8** with 4-octyne gave unsymmetrical zirconacyclopentadienes **5a**, **5b** and **9**, in 77%, 62% and 82% yield, respectively (eq 4). In the case of hafnacyclopentadiene **10**, one 1-trimethylsilyl-1-hexyne moiety was replaced by 4-octyne in 60% yield at reflux in toluene. Interestingly, zirconacyclopentadiene **5** or **9**, which has a bulky substituent such as trimethylsilyl group and t-Bu group, did not react with diphenylacetylene or 4-octyne at all at 50 °C. This is in sharp contrast to the reaction of **2** or **7**. Reaction rate of **1b** with 4-octyne at 50 °C obeyed first order rule and the rate constant at 50 °C was 2.4×10^{-5}/sec. However, no significant change was observed by NMR study of **1b** at higher temperature.

The following is the classification of reactive (Group A) or unreactive zirconacyclopentadienes (Group B) for alkyne replacement via β,β'-carbon-carbon bond cleavage. At least one sterically hindered substituent such as trimethylsilyl group and t-Bu group was required at α-position of zirconacyclopentadienes. However, when only one sterically hindered substituent was in the α-position of a zirconacyclopentadiene ring, the replacement reaction was dependent on the other substituent at α'-position. If the other substituent at α'-position is an alkyl group such as propyl group, the replacement reaction did not proceed, but in the case of phenyl group the reaction proceeded.


Group A: Reactive zirconacyclopentadienes

1a (M = Zr, R = Bu)
1b (M = Zr, R = Me)
10 (M = Hf, R = Bu)
2
7
8

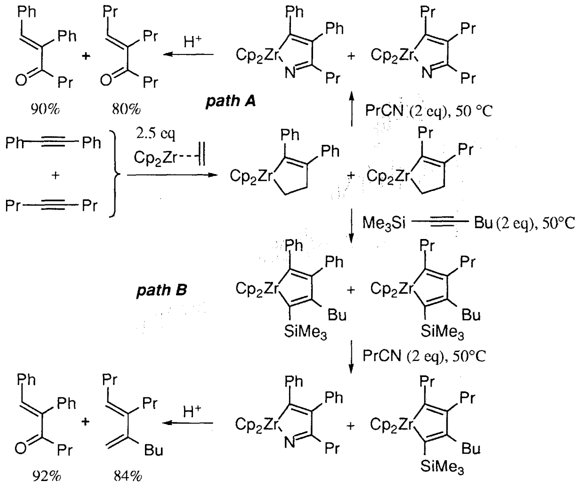
Group B: Unreactive zirconacyclopentadienes

3
4
5a (R = Bu)
5b (R = Me)
6
9

Figure 1. Classification of zirconacyclopentadienes for β,β'-carbon-carbon bond cleavage reaction

Although it is not clear yet why the β,β'-carbon-carbon bond of zirconacyclopentadienes is dependent on the substituents, we could demonstrate an interesting reaction which differentiates 4-octyne from diphenylacetylene in the mixture as follows (Scheme 1). It is known that both alkynes, 4-octyne and diphenylacetylene react with zirconocene-ethylene complex and butyronitrile in this order to give α,β-unsaturated ketones in good yields (path A).[2c] However, addition of trimethylsilylacetylene after treatment of zirconocene-ethylene complex afforded completely different products for diphenylacetylene and 4-octyne (path B). After hydrolysis, α,β-unsaturated ketone was obtained from diphenylacetylene, whereas a diene was obtained after desilylation from 4-octyne. No formation of the corresponding α,β-unsaturated ketone from 4-octyne was observed. The formation of a diene from diphenylacetylene was not detected. For zirconium chemistry, such complete differentiation between diphenylacetylene and 4-octyne is unprecedented.

Scheme 1.



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