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Reaction of a Double Bond of Zirconacyclopentadienes: Formation of 1,2,3,5-Tetrasubstituted Benzenes via the C−C Bond Cleavage

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Metalacyclopentadienes, which have been considered as intermediates for the formation of benzene derivatives from alkynes,[1] have shown various C−C bond formation reactions.[1,2] Reactions of metalacyclopentadienes mostly proceed at the metal-α-carbon bond (site *A*, Figure 1),[1,2] and some reactions are known to proceed at the *β*,*β*′-carbon−carbon bond (site *B*).[2d,h,3,4] However, to the best of our knowledge, there is no report for the reaction of the α,*β*-carbon−carbon double bond (site *C*) of metalacyclopentadienes. Herein we would like to report the first example of a reaction of the α,*β*-C═C bond (site *C*) in zirconacyclopentadienes and further transformation affording 1,2,3,5-tetrasubstituted benzene formation via the formal C−C bond cleavage of the zirconacyclopentadienes.

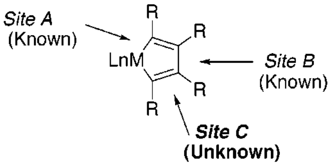


Figure 1. Reation sites of metalacyclopentadienes.

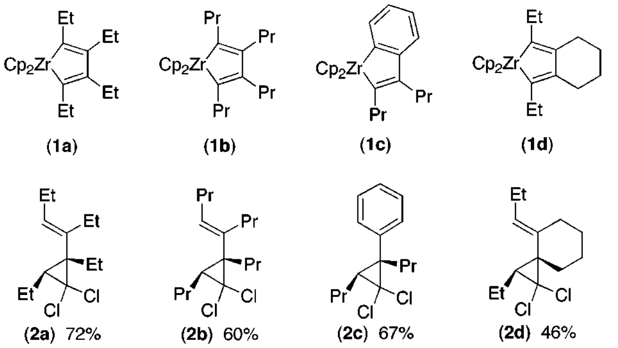


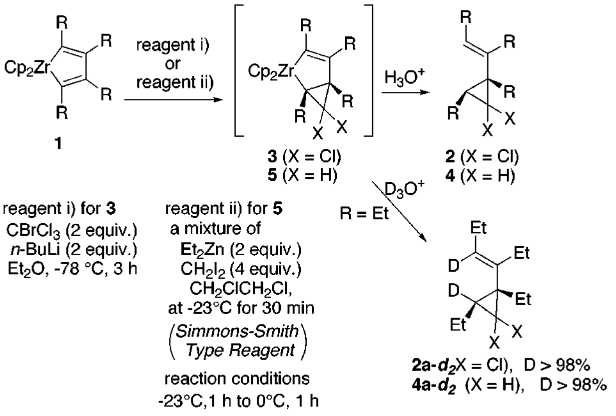
Figure 2. Formation of cyclopropanes from zirconacyclopentadienes (GC yields).

Initially, we studied the cyclopropanation reaction of zirconacyclopentadienes **1** with dichlorocarbene.[5] The dichlorocarbene was generated by the standard procedure in situ by the sequential addition of bromotrichloromethane and butyllithium in the solution of zirconacyclopentadienes **1** at −78 °C in Et_2O. After 3 h at the same temperature, the reaction mixture was hydrolyzed with 3 M HCl at −78 °C for several hours. Workup afforded the dichlorocyclopropanated products **2**.

Typical examples are given in Figure 2. Reactions of tetraalkylzirconacyclopentadienes **1a** and **1b**,[6] zirconaindene **1c**,[7] and bicyclic zirconacyclopentadiene **1d**[6] with dichlorocarbene afforded products **2a**, **2b**, **2c**, and **2d** in reasonable yields, respectively. Deuteriolysis of the reaction mixture prepared from **1a** with DCl/D_2O afforded **2a-*d*$_2$** with >98% of deuterium incorporation. This result proved that the α,*β*-carbon−carbon double bond of zirconacyclopentadiene **1** reacted with the carbene without interference with the Zr−C bonds to give 1-zirconabicyclo[3.1.0]hexene **3** as an intermediate.[8]

We assumed that the similar reaction could be achieved with a Simmons−Smith type cyclopropanation reagent[9] Thus a zirconacyclopentadiene **1** solution in dichloroethane was added to a solution of Simmons-Smith type reagent at −23 °C, stirred for 1h at the same temperature, warmed to 0 °C and stirred for additional 1 h. The formation of intermediate **5** was confirmed by ^{13}C NMR analysis of the reaction mixture.[10] The shifts for the carbon atoms connected to zirconium atom were observed at 188.20 ppm (sp^2 C) and 66.02 ppm (sp^3 C), which is agreement for with the observed data for similar compounds.[11] After quenching of the reaction mixture and workup, the corresponding cyclopropane derivatives **4** were obtained. Also, dideuterated product **4a-*d*$_2$** was obtained after deuteriolysis with >98% of deuterium incorporation (Scheme 1). Some typical examples are given in Table 1.

Scheme 1



It has been known that zirconacyclopentadienes do not directly react with CO[12] but that zirconacyclopentenes do.[13,14] In the next step, we carried out carbonylation of the intermediate **5**, which can be regarded as a zirconacyclopentene, at −23 °C under a slightly positive pressure of CO to obtain cyclopentenone derivative. Therefore, it was expected that the intermediate **5** should have similar reactivity to that of zirconacyclopentenes toward CO. Surprisingly, after isolation we obtained 1,2,3,5-tetrasubstituted benzenes **6** in good yields (Scheme 2) instead of the expected cyclopentenone products.

Some typical examples are given in Table 1. The reaction of CO with alkyl substituted zirconacyclopentadienes **1a**,**b** gave 1,2,3,5-tetrasubstituted benzenes **6a,b**. The reaction of **1d** yielded the corresponding tetrahydronaphthalene **6d**.

After quenching of the reaction mixture with HCl aqueous or iodine, only product **6** was obtained in both cases. Moreover,

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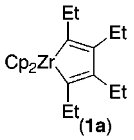
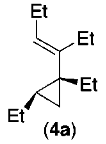
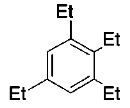
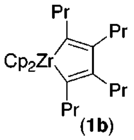
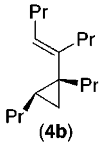
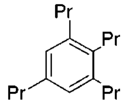
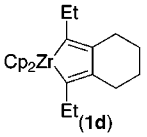
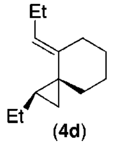
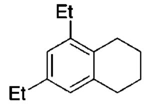
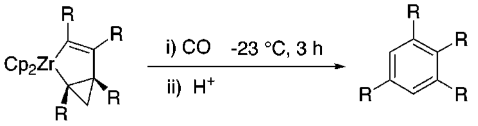
Table 1. Formation of Cyclopropanes and Benzenes from Zirconacylopentadienes

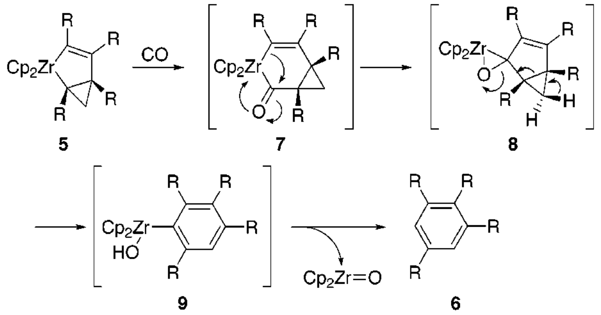
Zirconacyclopentadiene	Cyclopropane^a	Yield(%)^c	Benzene^b	Yield(%)^c
 **(1a)**	 **(4a)**	74 (55)	 **(6a)**	74 (63)
 **(1b)**	 **(4b)**	60 (50)	 **(6b)**	68 (56)
 **(1d)**	 **(4d)**	63 (38)	 **(6d)**	70 (52)

[a] 1. CH_2I_2, Et_2Zn; 2. H^+. [b] 1. CH_2I_2, Et_2Zn; 2. CO. [c] GC yields, isolated yields are given in parentheses.

Scheme 2



Scheme 3



deuteriolysis with DCl/D_2O also did not give deuterated benzenes. Recently, zirconocene-mediated cleavage of vinylcyclopropanes through the formation of a zirconium intermediate with a cyclopropyl moiety has been reported.[15] However, the presented reaction mechanism does not explain our results. Although we must await further investigation to make clear the mechanism, one possible mechanism is shown in Scheme 3.

CO insertion occurs first at zirconium−sp^3 carbon bond of **5** to afford zirconacyclohexenone **7** that undergoes intramolecular nucleophilic addition of the Zr−sp^2 carbon bond to carbonyl group to furnish **8**. Cleavage of metalaoxirane and the C−C bond of the two substituted carbons in the cyclopropane gives rise to the formation phenyl(hydroxy)zirconium species **9**. $Cp_2Zr{=}O$ and the corresponding benzene derivative **6** are liberated from **9**.

It is interesting to note that this method gives 1,2,3,5-tetraalkyl-substituted benzenes. This is in sharp contrast to the conventional benzene formation from 2,3,4,5-tetraalkylmetalacylopentadienes, which affords 1,2,3,4-tetraalkyl-substituted benzenes (Figure 3).[16]

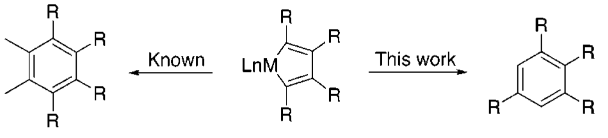


Figure 3. Formation of benzenes from metalacyclopentadienes.

It should be emphasized that the carbon−carbon double bond of the zirconacyclopenadiene was cleaved and that two alkyl groups, which originally came from the same alkyne, were separated by one carbon in the benzene derivatives.

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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