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Alkyne and ketone induced novel cleavage of a C–C bond and a C–Si bond in zirconacyclobutene–silacyclobutene fused ring compounds

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Abstract—Novel cleavage patterns of C–C bonds and C–Si bonds were achieved via alkyne- or ketone-induced reactions of zirconacyclobutene–silacyclobutene fused ring compounds; thermodynamically favored six-membered zirconacyclohexadiene derivatives were formed in excellent yields from the four-membered zirconacyclobutenes via this unprecedented alkyne-induced C–C bond and C–Si bond cleavage process. © 2003 Elsevier Science Ltd. All rights reserved.

Selective cleavage of carbon–carbon bonds and carbon–heteroatom bonds such as carbon–silicon bonds is of great interest in the development of synthetically useful methodologies.^{1,2} The chemistry of metallacyclic compounds has attracted much attention because many synthetically important transition metal-assisted reactions proceed via metallacyclic intermediates,³ among which the most often encountered are five-membered metallacycles, including metallacyclo-pentanes, pentenes and pentadienes.^{4,5} In fact, many reports have appeared on the cleavage and synthetic applications of β,β' -C–C bonds in five-membered zirconacycles.^{6–8} However, very few if any investigations into the cleavage and potential synthetic applications of metallacyclobutenes such as zirconacyclobutenes **1** have been undertaken. In this project, we used compounds of

structure **3**, which have both the zirconacyclobutene skeleton **1** and the silacyclobutene skeleton **2**, and investigated their mode of reaction (Fig. 1).

Initially, we expected that the reactive organometallic intermediate **3** would undergo alkyne insertion into the Zr–C bonds to afford six-membered metallacycles **4** and/or **5** (Scheme 1), thus bringing about the formation of six-membered metallacycles from four-membered metallacycles following the concept shown in Eq. (1).

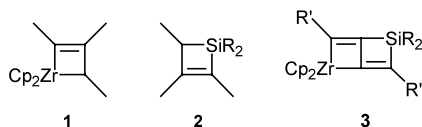
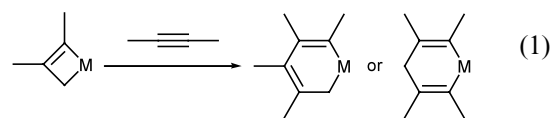
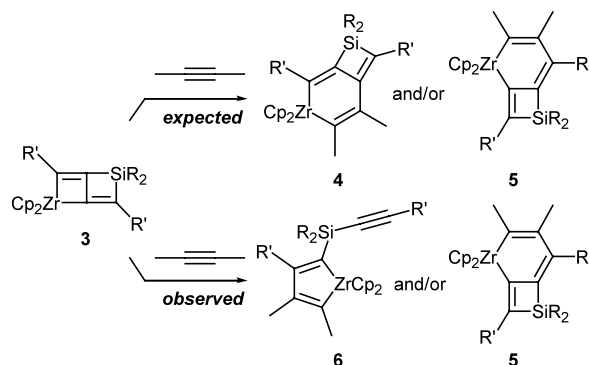


Figure 1.

Keywords: C–C bond cleavage; C–Si bond cleavage; silacyclobutenes; zirconacyclobutenes; zirconacyclopentadienes; zirconacyclohexadienes; alkynes.

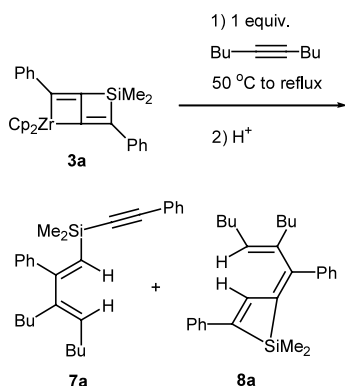
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Scheme 1.

However, surprisingly, preliminary experimental results showed that novel cleavage of a C–C bond in the zirconacyclobutene skeleton and a C–Si bond in the silacyclobutene skeleton were achieved via alkyne or ketone induced reactions. As demonstrated in Scheme 1, although the same product **5** is formed following both the *expected* process and the *observed* process, the reaction mechanisms must be totally different from each other. To the best of our knowledge, the cleavage pattern reported here represents the first example of its kind.

The zirconacyclobutene derivatives **3** are readily formed in situ using Takahashi's method via zirconocene-mediated intramolecular C–C bond formation from the two alkynyl groups of bis(alkynyl)silanes.⁹ A typical experimental procedure for the reaction of **3** with alkynes is as follows. After addition of 1 equiv. of 5-decyne to the THF solution of **3a**, the reaction mixture was warmed to 50°C and stirred at this temperature for 1 h (Scheme 2). Hydrolysis of the reaction mixture with 3% aqueous HCl afforded **7a** in 71% isolated yield (Table 1, run 1),



Scheme 2.

Table 1. Reaction of alkynes with zirconacyclobutene-silacyclobutene fused ring compounds via cleavage of a C–C bond and a C–Si bond

Run	T (°C)	t (h)	Yield of 7a (%) ^a	Yield of 8a (%) ^a
1	50°C	1	72 (71)	<3
2	Reflux	1	58	28
	Reflux	3	24	74
	Reflux	6	Trace	90 (80)

^a GC yields. Isolated yields are given in parentheses.

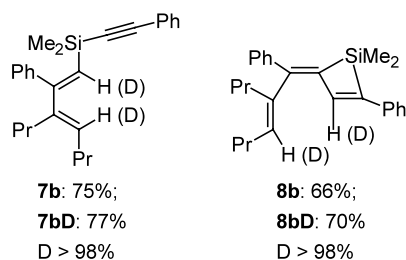


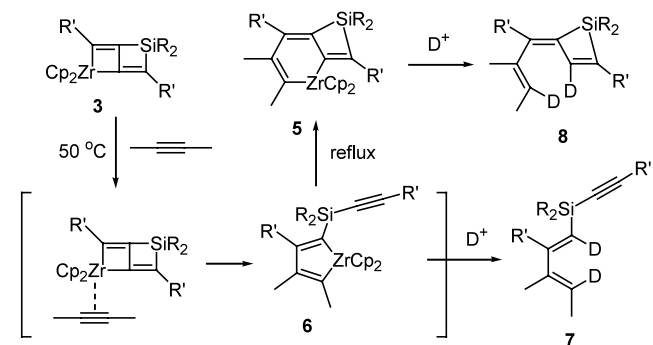
Figure 2.

along with <3% yield of **8a**. With longer reaction time and higher temperature, **7a** decreased while **8a** increased (Table 1, run 2). Finally, on prolonged (more than 6 h) heating at reflux, **7a** disappeared completely and **8a** was formed as the sole product in 80% isolated yield.

In a similar fashion, products **7b** and **8b** were obtained in high yields (Fig. 2). Deuteriolysis of the reaction mixtures instead of hydrolysis afforded the dideuterated products **7bD** and **8bD** in 77% and 70% isolated yields with more than 98% of deuterium incorporation, respectively.

The above results indicate that intermediate **6** is formed and is kinetically favored. On the other hand, intermediate **5** is thermodynamically favored and is presumably generated from **6** (Scheme 3). Takahashi and co-workers reported single crystal structures of compounds of the type **5** and proposed a pathway for their formation from **6**.^{6b} However, although the coordination of alkynes onto the zirconium atom is assumed to be critical for inducing cleavage of the C–C bond and Si–C bond in **3**, it is not clear yet how **6** is formed from **3**.

It is noteworthy that when an unsymmetrical alkyne such as 1-phenyl-1-butyne was used, both **7c** and **8c** were formed respectively in excellent isolated yields with perfect regioselectivity (Fig. 3). The phenyl substituent was always located at the terminal position.^{6a} Interestingly, in the case of 1-trimethylsilyl-1-propyne, only compound **7d** (**6d**) was formed with perfect



Scheme 3.

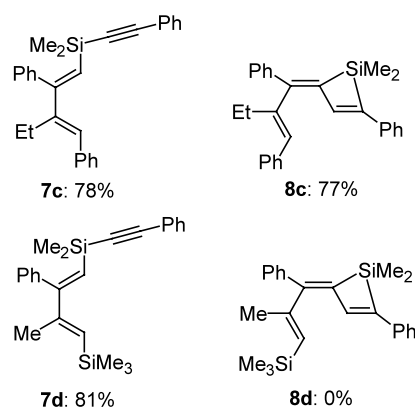
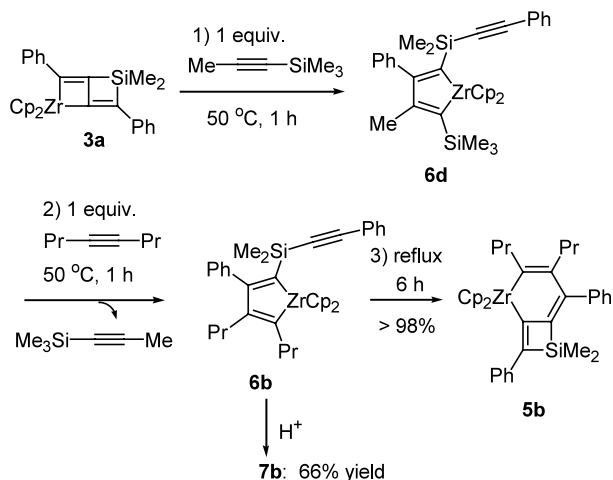
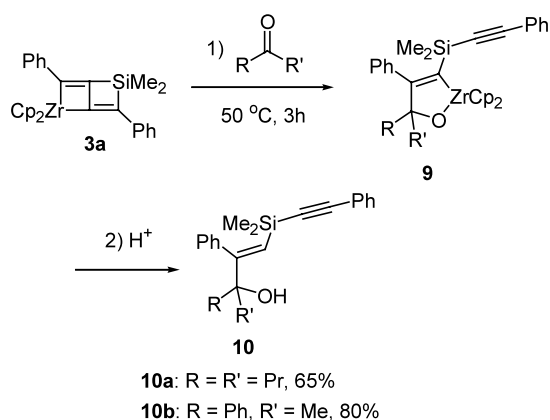


Figure 3.



Scheme 4.



Scheme 5.

regioselectivity, and product **8d** (**5d**) could not be formed even after a prolonged reaction time. However, in the presence of 4-octyne, compound **6d** did undergo the alkyne-exchange process to afford **6b**,⁸ which gave **7b** in 66% isolated yield after hydrolysis (Scheme 4). 1-Trimethylsilyl-1-propyne was regenerated quantitatively. It is interesting to note that the alkyne removed is not the larger silylated one.^{8b} This is probably because the remaining C–C triple bond in **6** is coordinated to the zirconium center.

In addition to alkynes, ketones were also found to be able to induce the novel cleavage of the C–C bond and the C–Si bond. Five-membered oxazirconacyclopentenes **9** were formed as the products. Alcohols **10** were isolated in good yields after hydrolysis of the reaction mixtures (Scheme 5).^{7c}

Further investigation into the reaction mechanism and synthetic applications of the C–C bond and C–Si bond cleavage is in progress.

Acknowledgements

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