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# Cleavage and Reorganization of Zr–C/Si–C Bonds Leading to Zr/Si–N Organometallic and Heterocyclic Compounds

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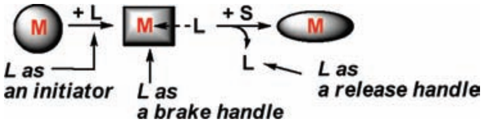
***Abstract:*** The *t*-BuCN-stabilized zirconacyclopropene–azasilacyclopentadiene complexes **2** are generated in situ in high yields from the Si-tethered diynes, $Cp_2Zr(II)$ species, and 2 equiv of *t*-BuCN via a coordination-induced Zr–C/Si–C bond cleavage and reorganization. Complexes **2** have been demonstrated to be synthetically very useful. A variety of novel Zr/Si organo-bimetallic compounds and Si/N heterocyclic compounds, such as azasilacyclopentadienes, azasilacyclohexadienes, and allenylazazirconacycles, are obtained in high yields when complexes **2** are treated with ketones, carbodiimides, alkynes, elemental sulfur ($S_8$), acid chlorides, or nitriles. In this chemistry, *t*-BuCN behaves as both an initiator and a brake/release handle to initiate and control the reaction process.

Among the most fundamental reactions of organometallic compounds, the reaction initiated by the incoming coordinating ligand **L** is central to virtually all organometallic reactions of great significance for organic synthesis.[1] In particular, besides commonly observed ligand substitution, the coordination of ligand **L** may greatly alter the steric and electronic environment around the metal center,[2,3] thus activating the whole compound, resulting in novel skeletal rearrangement or cleavage of chemical bonds (Scheme 1). Depending on its steric or electronic property, **L** may behave as a brake handle to stabilize the **L**-coordinated complexes. When the coordinating **L** is substituted by a different substrate **S**, the whole complex will become reactive again (Scheme 1). Consequently, in this way, reactivity control, synthetic applications, and otherwise unavailable reaction patterns can be expected. The steric and electronic match (or co-operation) between the metal **M** and **L** is essential to realize such a process.[4–6] Herein we report an exciting example following the process model shown in Scheme 1.

***Scheme 1.*** Initiating–Braking–Releasing Process Model[a]

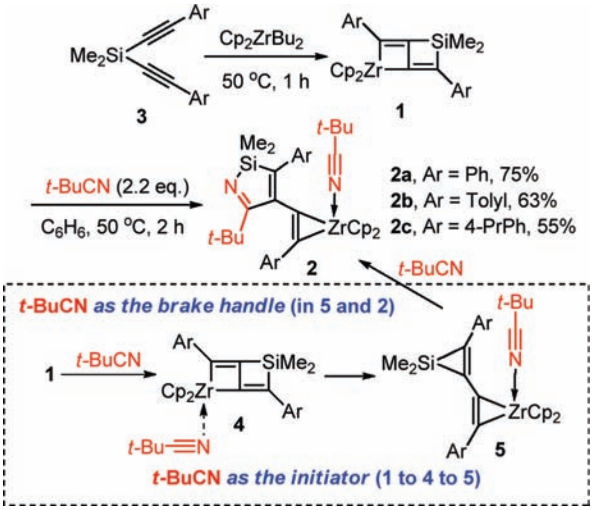


[a] An incoming ligand **L** behaves as both an initiator and a brake/release handle. The different shapes around the metal center indicate different structure and bonding.

The zirconacyclobutene–silacyclobutene fused compound **1**, first reported by Takahashi and co-workers,[7] could be readily generated in high yields from the zirconocene-mediated reaction of its corresponding Si-tethered diyne **3**.[8] Because of the concomitance presence of two Zr–C bonds and two Si–C bonds in the skeleton, this compound **1** is structurally unique and should display novel reaction chemistry and synthetic applications.[6] When we treated **1** with 2 equiv of *t*-BuCN, an unprecedented skeletal rearrangement took place to afford the compounds **2** in 55–75% isolated yields (Scheme 2). An X-ray analysis of **2b** unambiguously revealed the structure of the $C_{sp^2}$–$C_{sp^2}$-linked zirconacyclopropene–azasilacyclopentadiene (Figure 1). The dihedral angle of 88.10° between the two cyclic planes demonstrates a nearly perpendicular conformation. The azasilacyclopentadiene species,[9] though structurally and chemically interesting, are very rare in terms of synthetic methods and reaction chemistry study. This transformation of silacyclobutenes to azasilacyclopentadienes represents an unprecedented and useful reaction pattern of silacycles.[10]

A proposed mechanism involving coordination-induced formation of silacyclopropene–zirconacyclopropene species **5** is given in Scheme 2. Zirconacyclopropene species are known to be very reactive.[11] However, in this case, one *t*-BuCN is coordinated to the zirconium center and thus deactivates the zirconacyclopropene moiety.[11] A second *t*-BuCN is inserted into the C–Si bond of the reactive silacyclopropene moiety in **5** to form the azasilacyclopentadiene moiety in **2**.

***Scheme 2.*** *t*-BuCN-Induced Formation of Zirconacyclopropene-Azasilacyclopentadienes **2**



This successful transformation could be attributed to the strong coordinating ability and the steric effect of *t*-BuCN (as the **L** in

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10.1021/ja1074932

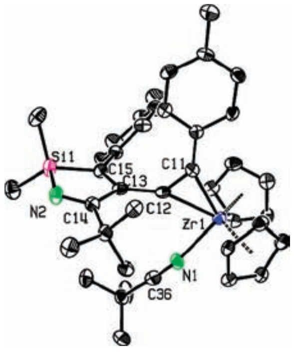
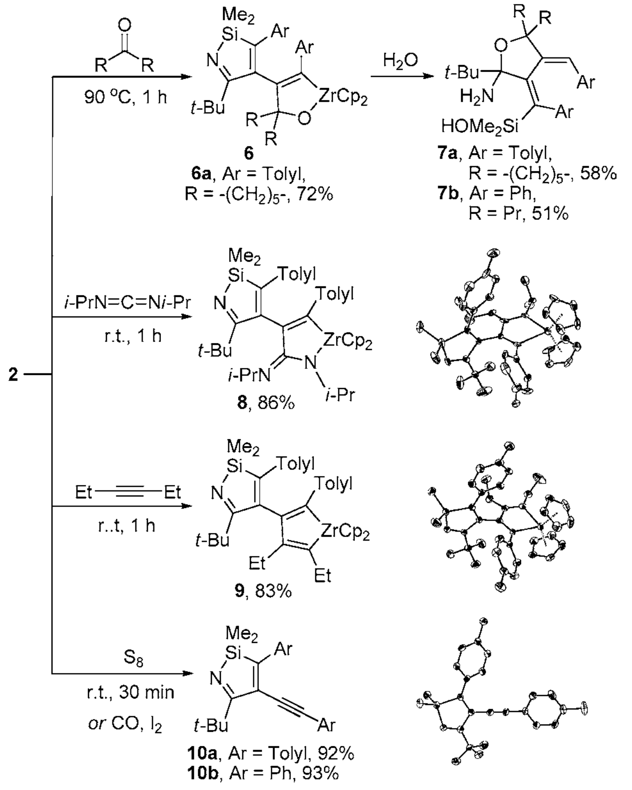


***Figure 1.*** ORTEP drawing of **2b** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Zr1−C11 2.197(6), Zr1−C12 2.289(7), C11−C12 1.322(8), C12−C13 1.480(9), C13−C15 1.358(9), C13−C14 1.547(8), C14−N2 1.281(8), Si1−C15 1.875(7), Si1−N2 1.760(6), C36−N1 1.150(9).

Scheme 1). *t*-BuCN behaved as both an initiator and a brake handle (Scheme 2). The reactivity of the resulting zirconacyclopropene moiety in **2** is controlled (or shut down) by the coordinating *t*-BuCN.

The compound **2** has been demonstrated to be indeed very reactive and synthetically useful. Whenever the coordinating *t*-BuCN, functioning as the brake handle in **2**, is substituted by a different substrate (as the **S** in Scheme 1), the stabilized zirconacyclopropene moiety will become reactive, thus generating diversified zirconacycles (Scheme 3) or even initiating further reactions of the whole molecule, including the azasilacyclopentadiene moiety, generating heterocycles of novel structures (Scheme 4).

***Scheme 3.*** Reactions of the Zirconacyclopropene Moiety of **2**

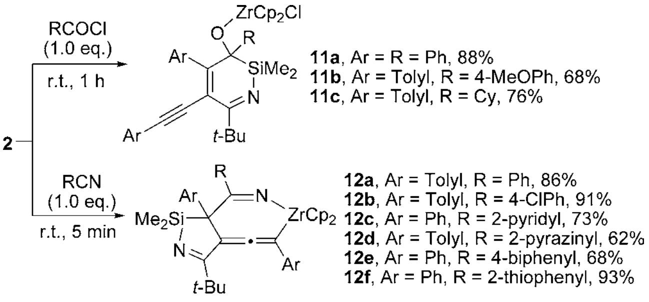


Summarized in Scheme 3 are examples showing independent reactions of the zirconacyclopropene moiety with different substrates. The azasilacyclopentadiene moiety in **2** does not participate in these cases. First, ketones were used to substitute the coordinating *t*-BuCN. Selective insertion of the C═O double bond into the zirconacyclopropene ring afforded the corresponding oxazirconacyclopentene derivative **6**.[11d,12] The compound **6a** was isolated in 72% yield, and its structure was determined by single-crystal X-ray structural analysis (see Supporting Information). Although the azasilacyclopentadiene moiety did not participate in this transformation, the cooperation between the azasilacycle and the zirconacycle resulted in unprecedented cyclization chemistry upon hydrolysis. Hydrolysis of **6** afforded the butadiene-fused aminotetrahydrofuran derivatives **7**, which are useful but not accessible by other means.[13] The single-crystal structure of **7b** and a proposed mechanism for the hydrolysis process of **6** are given in the Supporting Information. Similarly, selective insertion of a C═N double bond of *N*,*N*′-diisopropylcarbodiimide was also observed to afford the complex **8** in 86% isolated yield.[14]

In addition to the above C═O and C═N double bond insertion reactions, the C≡C triple bond of alkynes was also found to react smoothly and selectively with the zirconacyclopropene moiety to afford its corresponding zirconacyclopentadiene derivative **9**.[15]

When **2** was treated with elemental sulfur ($S_8$), demetalation of **2** took place to afford the alkynylazasilacyclopentadienes **10** in excellent yields (Scheme 3).[9] The structure of **10a**, as the first case of azasilacyclopentadiene derivatives,[9] was determined by single-crystal X-ray structural analysis. As far as we know, no other method could efficiently afford alkynylazasilacyclopentadienes. Compound **10** was also obtained when **2** was treated with CO or $I_2$.[16]

***Scheme 4.*** Reactions Initiated by the Release of the Zirconacyclopropene Moiety of **2**



Summarized in Scheme 4 are examples showing the reactions of the whole molecule **2**, including the azasilacyclopentadiene moiety, initiated by the substitution of the coordinating *t*-BuCN with other substrates. The reaction of **2** with acid chloride gave the formally silacycle ring expansion products azasilacyclohexadienes **11** in good to excellent isolated yields. The single-crystal structure of **11a** confirmed its six-membered silacycle bonding with the oxychlorozirconocene moiety (Figure 2). Both aromatic and aliphatic acid chlorides showed high efficiency. To the best of our knowledge, this is the first example of such azasilacyclic skeletons. The isolated azasilacyclopentadienes **10** did not show any reaction with RCOCl. Thus, we assume the RCOCl replaces the coordinating *t*-BuCN and reacts with the zirconacyclopropene moiety as the first step. The azasilacyclopentadiene moiety then takes part (or cooperates) in a further skeletal rearrangement to generate **11** (see Supporting Information for detailed mechanistic discussion).

The cooperative effect between the azasilacyclopentadiene moiety and the zirconacycle showed an unexpected and very interesting impact on the reaction of **2** with nitriles. When **2** was further treated with other nitriles, the incoming nitrile substituted the *t*-BuCN and initiated an unprecedented reaction process. As shown in Scheme 4, the reaction of PhCN with **2b** resulted in the formation of **12a** in 86% isolated yield. The structure of **12a**, unambiguously

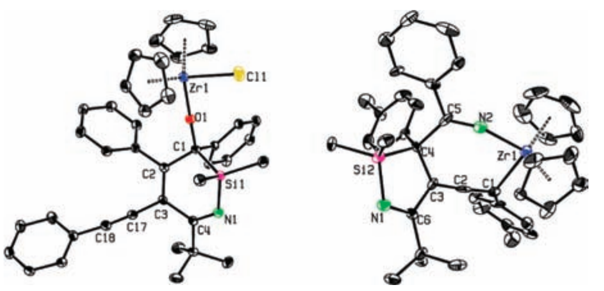
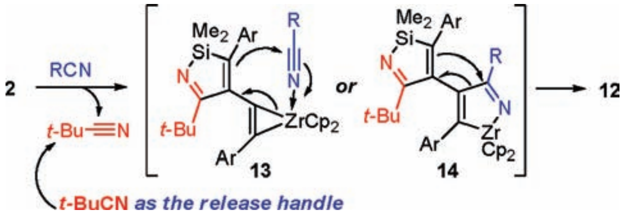


***Figure 2.*** ORTEP drawing of **11a** (left) and **12a** (right) with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **11a**, Zr1−O1 1.938(2), Si1−C1 1.919(4), Si1−N1 1.744(3), C2−C3 1.367(5), C17−C18 1.203(5), C4−N1 1.275(5); **12a**, Zr1−C1 2.379(13), Zr1−N2 2.032(10), C1−C2 1.331(17), C2−C3 1.365(18), C3−C4 1.521(15), C5−N2 1.292(13), C6−N1 1.295(14), C1−C2−C3 175.7(13).

confirmed by single-crystal X-ray structural analysis (Figure 2), features a five-membered azasilacyclopentene-fused seven-membered azazirconacycle incorporating an allenyl moiety.[17,18] This is the first synthesis of a well-defined cyclic allenylazazirconocene complex.[17] The angle C1−C2−C3 was measured as 175.7°, while the bond lengths C1−C2 and C2−C3 were 1.331(17) and 1.365(18) Å, respectively, showing its slightly bent allene nature. The singlet at 193.4 ppm in the $^{13}$C NMR spectrum of **12a** in benzene-$d_6$ confirmed its sp-hybrided allenic carbon character, which is well comparable with reported allenylzirconocene complexes.[17] A variety of aromatic and heteroaromatic nitriles could be used to form complexes **12a**−**f** in high yields. A proposed reaction mechanism is given in Scheme 5.

***Scheme 5.*** Proposed Mechanism for the Formation of Cyclic Allenylzirconocene Complexes **12**



In summary, we have demonstrated a synthetically useful protocol in which *t*-BuCN behaves as both an initiator and a brake/release handle. The *t*-BuCN-stabilized zirconacyclopropene−azasilacyclopentadiene complexes **2**, generated in situ in high yields from their corresponding Si-tethered diynes **3**, a low-valent zirconocene species, and 2 equiv of *t*-BuCN, have been demonstrated to be synthetically very useful and can be readily transformed into a wide variety of novel organometallic compounds and heterocyclic compounds. Among them, the generation and characterization of the azasilacyclopentadienes, azasilacyclohexadienes, and allenylazazirconacycles are fundamentally important and interesting. Further application of this protocol and further investigation into the mechanism and synthetic applications of the reactive organometallic intermediates reported in this Communication are in progress.

**Acknowledgment.** This work was partially supported by the National Natural Science Foundation of China and National High-Tech Research and the Development Program of China (863 Program, 2007AA06A407). Eli Lilly China and BASF are gratefully acknowledged.

**Supporting Information Available:** Details for proposed mechanisms, experimental details, characterization data, and $^{1}$H and $^{13}$C NMR spectra for all isolated compounds; crystallographic data, in CIF format, for **2b**, **6a**, **7b**, **8**, **9**, **10a**, **11a**, and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA1074932