

# Zirconocene and Si-Tethered Diynes: A Happy Match Directed toward Organometallic Chemistry and Organic Synthesis

WEN-XIONG ZHANG, SHAO GUANG ZHANG, AND  
ZHENFENG XI\*

*Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of  
Bioorganic Chemistry and Molecular Engineering of Ministry of Education,  
College of Chemistry, Peking University, Beijing 100871, China*

RECEIVED ON MARCH 9, 2011

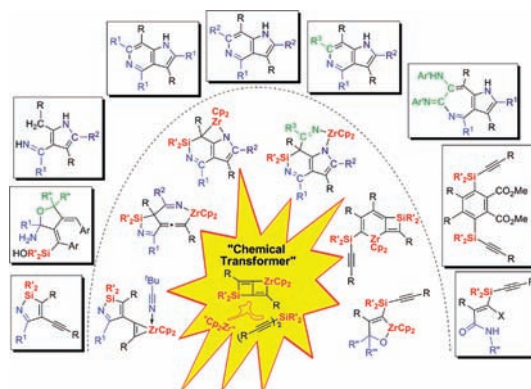
## CONSPECTUS

Characterizing reactive organometallic intermediates is critical for understanding the mechanistic aspects of metal-mediated organic reactions. Moreover, the isolation of reactive organometallic intermediates can often result in the ability to design new synthetic methods. In this Account, we outline synthetic methods that we developed for a variety of diverse Zr/Si organo-bimetallic compounds and Si/N heteroatom–organic compounds through the detailed study of zirconacyclobutene–silacyclobutene fused compounds.

Two basic components are involved in this chemistry. The first is the Si-tethered diyne, which owes its rich reactive palette to the combination of the Si–C bond and the C≡C triple bond. The second is the low-valent zirconocene species Cp<sub>2</sub>Zr(II), which has proven very useful in organic synthesis. The reaction of these two components affords the zirconacyclobutene–silacyclobutene fused compound, which is the key reactive Zr/Si organo-bimetallic intermediate discussed here.

We discuss the three types of reactions that have been developed for the zirconacyclobutene–silacyclobutene fused intermediate. The reaction with nitriles (the C≡N triple bond) is introduced in the first section. In this one-pot reaction, up to four different components can be combined: the Si-tethered diyne can be reacted with three identical nitriles, with differing nitriles, or with a nitrile and other unsaturated organic substrates such as formamides, isocyanides, acid chlorides, aldehydes, carbodiimides, and azides. Several unexpected multiring, fused Zr/Si organo-bimetallic intermediates were isolated and characterized. A wide variety of N-heterocycles, such as 5-azaindole, pyrrole, and pyrroloazepine derivatives, were obtained. We then discuss the reaction with alkynes (the C≡C triple bond). A consecutive skeletal rearrangement, differing from that observed in the reactions with nitriles, takes place in this reaction. Finally, we discuss the reaction with the C=X substrates (where X is O or N), including ketones, aldehydes, and isocyanides. Oxa- and azazirconacycles are formed via a new skeletal rearrangement.

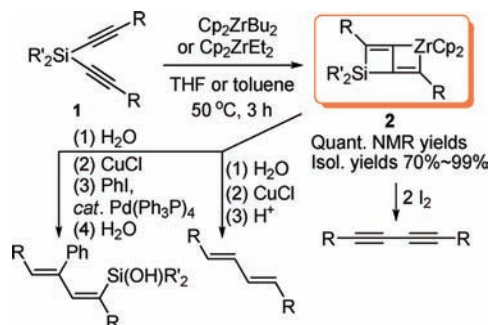
Our results show that the zirconocene and the Si-tethered diyne cooperate as a “chemical transformer” after treatment with various substrates, leading to a diverse range of cyclic Zr/Si organo-bimetallic compounds. This mechanism-derived synthesis of organometallic and organic compounds demonstrates that the investigation of metal-mediated reactions and the isolation of reactive organometallic intermediates not only contribute to the understanding of complex reactions but can also lead to the discovery of synthetically useful methods.



## 1. Introduction

The low-valent Cp<sub>2</sub>Zr(II) species, where Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>, has been proved to be synthetically very useful.<sup>1–6</sup> Several synthetic methods can readily in situ provide such species,

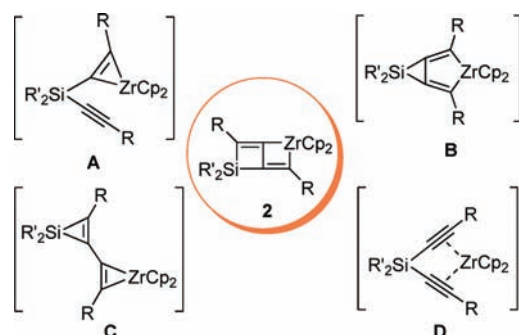
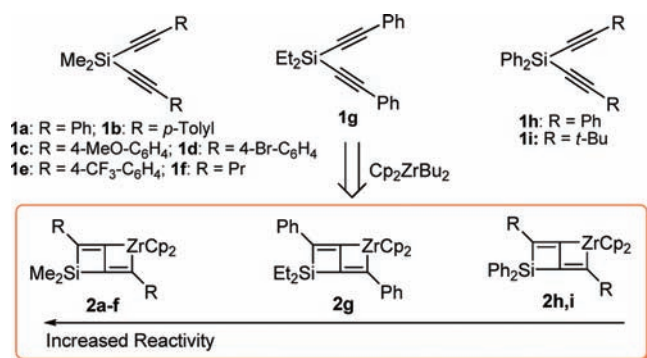
including the Negishi reagent Cp<sub>2</sub>ZrBu<sub>2</sub>,<sup>3</sup> the Takahashi reagent Cp<sub>2</sub>ZrEt<sub>2</sub>,<sup>4</sup> the Rosenthal complexes Cp<sub>2</sub>Zr(L)(η<sup>2</sup>-Me<sub>3</sub>SiCCSiMe<sub>3</sub>), (L = THF,<sup>5a</sup> L = Py<sup>5b</sup>), and the Cp<sub>2</sub>ZrCl<sub>2</sub>/Mg system.<sup>6</sup> The 14-electron Cp<sub>2</sub>Zr(II) species has a d<sup>2</sup>

**SCHEME 1.** Formation of Zirconacyclobutene–Silacyclobutene Complexes **2**

configuration with one lone-electron pair and two vacant valence orbitals. Therefore, it readily coordinates to unsaturated organic substrates and undergoes further reactions including the oxidative addition as the major to form  $\text{Cp}_2\text{Zr(IV)}$  species. Among many reactions mediated by such a low-valent  $\text{Cp}_2\text{Zr(II)}$  species, the reaction with alkynes has been frequently reported and is particularly interesting and synthetically useful.<sup>2–5</sup>

The Si-tethered diyne **1** is of rich reaction chemistry because of the concomitance of the Si–C bond and the  $\text{C}\equiv\text{C}$  triple bond.<sup>7–9</sup> In 1995, Takahashi and co-workers reported an unexpected skeletal rearrangement when the diyne **1** was treated with low-valent  $\text{Cp}_2\text{Zr(II)}$  species (Scheme 1).<sup>8</sup> This rearrangement led to the formation of a zirconacyclobutene–silacyclobutene complex **2**, whose structure was unambiguously confirmed by X-ray single crystal structural analysis. Similarly, Rosenthal and co-workers obtained a spiro-compound when tetraalkynylsilane  $(\text{RC}\equiv\text{C})_4\text{Si}$  was treated with  $\text{Cp}_2\text{M(L)}(\eta^2\text{-Me}_3\text{SiCCSiMe}_3)$  ( $\text{M} = \text{Ti}$ , without L,  $\text{M} = \text{Zr}$ ,  $\text{L} = \text{THF}$ ).<sup>9</sup>

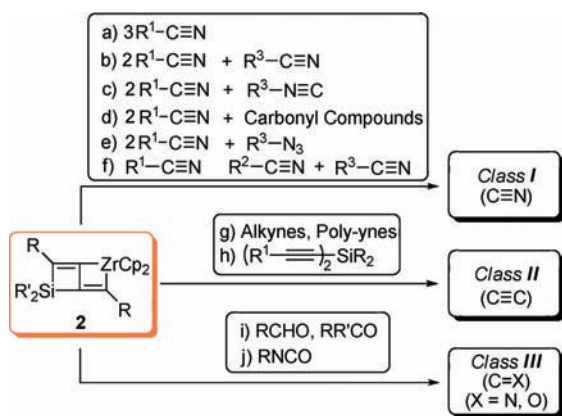
About a decade ago, we initiated a project to develop synthetic methods for six-membered metallacyclic compounds, since compared with the large number of five-membered metallacycles, six-membered metallacycles are very rare.<sup>8a,10</sup> Thus, we applied the zirconacyclobutene–silacyclobutene complex **2**, expecting formation of six-membered zirconacycles via insertion of unsaturated bonds such as C–N and C–C triple bonds into **2**. However, surprisingly, the expected direct insertion reactions never take place. Instead, the readily generated complex **2** behaves always as a “chemical transformer”<sup>11</sup> when treated with various substrates, leading to diversified Zr/Si organo-bimetallic compounds. As shown in Scheme 2, at least four different forms of the complex **2** would be generated in the reaction process, and these will be discussed later in this Account. Different types of reactive organometallic

**SCHEME 2.** Four Different Forms of **2****SCHEME 3.** Representative Types of **2** Used in Our Lab

intermediates are isolated and characterized. Based on understanding of the reaction mechanisms, synthetically useful methods for a wide variety of *N*-heterocycles such as 5-azaindoles and pyrroles have been also successfully developed.

Zirconacyclobutene–silacyclobutene complex **2** features two fused 4-membered metallacycles with the concomitance of two Zr–C bonds and two Si–C bonds. Shown in Scheme 3 are three representative types of **2** used in our lab. We could prepare and isolate all these compounds in excellent yields. Hydrolysis of these compounds with water generally affords their corresponding silacyclobutene derivatives.

Although the complex **2** is an isolable and stable compound, it is in fact highly reactive and is readily transformed when a coordinating ligand (substrate) approaches. Upon the 16e compound **2** being coordinated with a substrate, the space-demanding nature of the  $\text{Cp}_2\text{Zr}$  moiety and the strained four-membered skeleton will initiate skeletal rearrangement to release the high-tension energy. It was found that the reactivity of **2** was very sensitive toward the bulkiness of all components involved. In general, the smaller the substituents on Si, the higher the reactivity of **2**. The steric

SCHEME 4. Three Classes of Unsaturated Substrates toward **2**

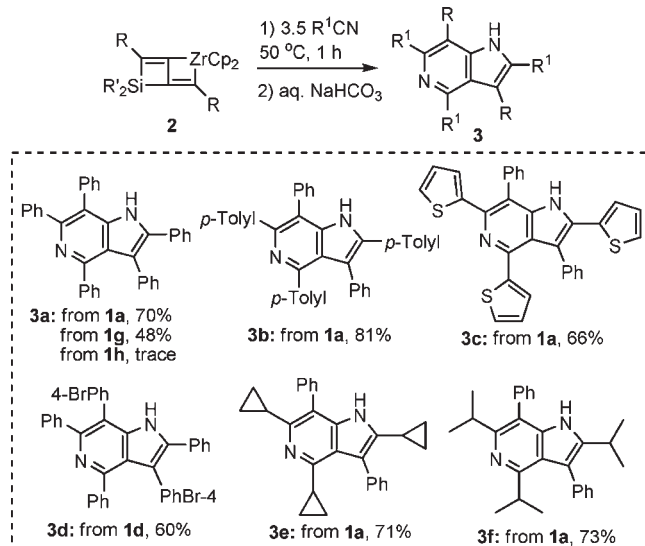
effect of the approaching substrates also remarkably influences the reaction. Noticeably, this steric effect was successfully applied to control the chemo- and regioselectivity of the reaction.

Summarized in Scheme 4 are three major classes of substrates which make the complex **2** transform. Three types of reactions are classified based on these three classes of substrates and will be discussed in this order.

## 2. Reaction of Complex **2** with Nitriles (Class I), Mechanistic Aspects, and Further Synthetic Applications

**2.1. The Reaction (Class I-a,b).** Complex **2** was in situ generated from bis(alkynyl)silane **1** and  $Cp_2ZrBu_2$  in toluene at  $50\text{ }^\circ\text{C}$  for 3 h.<sup>8,12–14</sup> Then 3.5 equiv of nitriles was added and the reaction mixture was stirred at  $50\text{ }^\circ\text{C}$  for 1 h. After quenched with saturated aqueous  $NaHCO_3$ , normal workup procedure afforded 5-azaindoles **3** in good yields (Scheme 5).<sup>12–14</sup> Changing the substituents on the Si center from methyl to ethyl obviously decreased the reaction rate along with the lower yields. Notably, when the  $Ph_2Si$ -tethered diyne **1h** was applied in this reaction, only trace amount of the product was obtained. This finding indicated that the steric environment around the silicon center has a strong impact on the efficiency of this coupling reaction. A wide variety of nitriles, either aliphatic or aromatic with both electron-withdrawing groups and electron-donating groups, could be applied in this reaction. Functional groups such as Br,  $CF_3$ , and OMe on the aromatic nitriles and on the bis(alkynyl)silane **1** were tolerated in this process. When three identical nitriles were used in the present zirconocene-mediated multicomponent intermolecular coupling, the reaction afforded 5-azaindoles **3** with the same substituents ( $R^1$ ) at positions 2,4,6. Azaindoles are a class of heterocycles

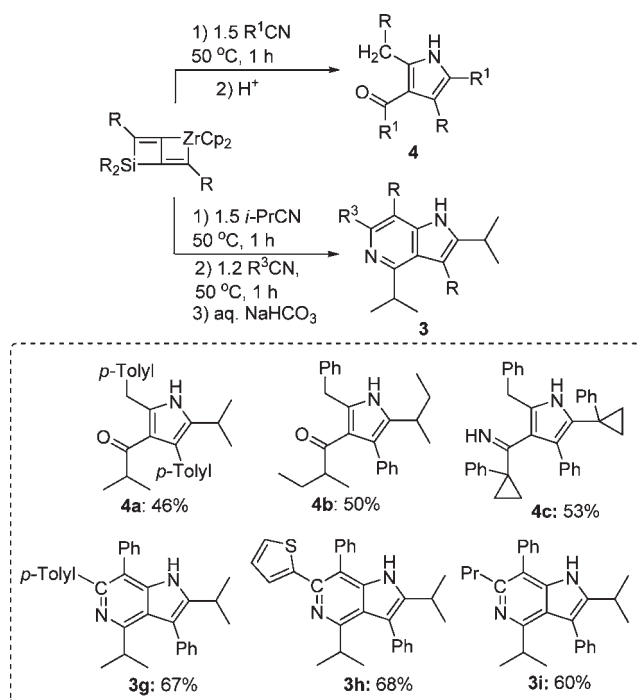
SCHEME 5. Formation of 5-Azaindoles from One Si-Tethered Diyne and Three Identical Nitriles



of considerable biological and pharmaceutical importance.<sup>15</sup> However, synthesis of azaindoles has remained a challenge both in academy and in pharmaceutical industry, since classical methods toward indole analogues do not work well.

The most interesting point of this one-pot reaction is that five components are involved and integrated in a perfect selective manner via an unknown pathway, which tempted us to investigate what is really going on. Thus, a series of experiments were carried out to investigate the reaction mechanism. For example, cross experiments using a 1:1 molar ratio mixture of two different nitriles to react with **2a**, up to six products could be observed. This result indicates that three molecules of nitriles are incorporated into the product via a step-by-step manner. No cross-coupled products were obtained when addition of a nitrile to a 1:1 molar ratio mixture of **2a** and **2b**, indicating that the coupling reaction proceeded intramolecularly.

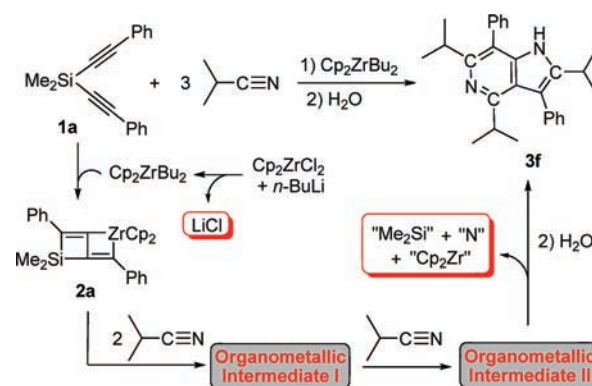
Since it was observed that the steric effect played an important role in this reaction process, we tried to use bulky nitriles in this reaction, aiming at observation of reaction intermediate information.<sup>12</sup> Interestingly, when *i*-PrCN was used, the reaction could be stopped after two molecules of *i*-PrCN were incorporated into the reaction intermediate. When the reaction mixture was hydrolyzed, it gave rise to multisubstituted pyrroles **4** (Scheme 6). Other nitriles with appropriate hindrance, such as 2-methylbutyronitrile could be also applied to stop the reaction in the middle way.<sup>13</sup> The bulkier 1-cyano-1-phenylcyclopropane was utilized in the reaction to afford the sole pyrrole **4c**. These pyrroles having

**SCHEME 6.** Formation of Pyrroles and 5-Azaindoles

four different substituents are difficult to access by other methods.<sup>16</sup>

The above results indicate that a different reactive organometallic intermediate should be generated after the reaction with two molecules of *i*-PrCN or 2-methylbutyronitriles. Further reaction of this in situ generated intermediate would provide an opportunity to construct 5-azaindoles by integrating two different nitriles. Thus, as demonstrated in Scheme 6, a variety of 5-azaindoles **3** assembled from one Si-tethered diene, two molecules of *i*-PrCN, and one molecule of another nitrile can be readily obtained with excellent chemo- and regioselectivity. A wide range of the second nitrile ( $R^3\text{CN}$ ), for example, aromatic and aliphatic ones, could be applied.<sup>13</sup> In these cases, the reaction generated the 5-azaindoles **3** with the same substituents ( $R^1$ ) at positions 2,4 and a different substituent ( $R^3$ ) at position 6. This reaction not only provides a synthetic method for pyrroles with all different substituents and 5-azaindoles with a different substitution pattern but also provides information on the reaction mechanism.

**2.2. Mechanistic Aspects.** The isolation and characterization of reactive organometallic intermediates are of great importance for understanding the mechanistic aspects of metal-mediated organic reactions. In the whole reaction process of this zirconocene-mediated four-component coupling, the first intermediate is the zirconacyclobutene–

**SCHEME 7.** Model of Mechanistic Investigation

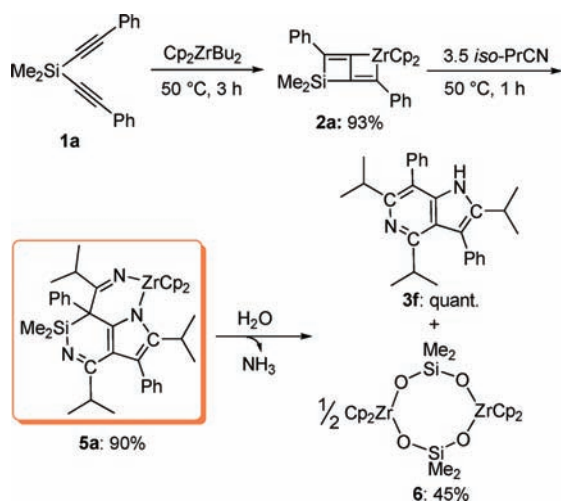
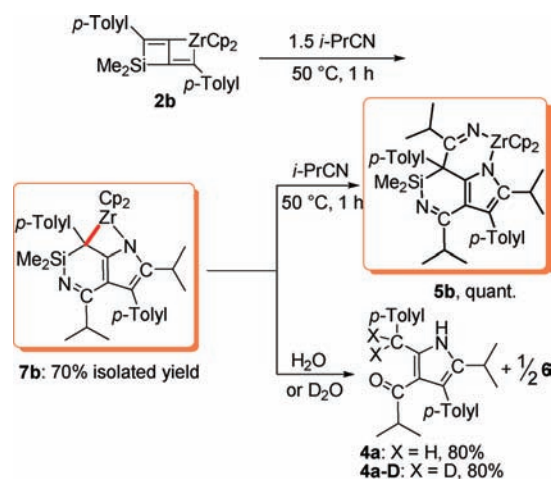
silacyclobutene complex **2**, which was isolated and characterized unambiguously by single crystal X-ray structural analysis.<sup>8a,13,14</sup> The subsequent reaction steps with nitriles are surprising (Scheme 7). This reaction process involved five components including the Si-tethered diene, three *i*-PrCN and the zirconocene “Cp<sub>2</sub>Zr”. Three molecules of *i*-PrCN were used; however, only two nitrogen atoms were integrated into the product **3f**. This information implied the cleavage of one C≡N triple bonds of *i*-PrCN. Further, the “Me<sub>2</sub>Si” moiety from the Si-tethered diene as well as the zirconocene “Cp<sub>2</sub>Zr” were not found in **3f**. The fate of “Me<sub>2</sub>Si” and “Cp<sub>2</sub>Zr” moieties as well as the cleaved nitrogen of nitrile should give a better understanding for the formation of **3f**.

As mentioned above, the reaction process proceeded via a step-by-step manner. Thus, at least it might be possible to isolate the two intermediate organometallic compounds, the one (**I**) containing two molecules of nitriles and the one (**II**) formed from all the five components.

The pure **2a** free of LiCl was first successfully isolated.<sup>14</sup> Then, 3.5 mol equiv of *i*-PrCN was added to a toluene solution of **2a**. After the reaction mixture was stirred at 50 °C for 1 h, a red powder was isolated in 90% yield, which was confirmed to be a very interesting and totally unexpected intermediate **II** (**5a**) (Scheme 8).<sup>14</sup> X-ray structural analysis of **5a** reveals it adopts a three-ring-fused structure composed of one 6-membered ring containing silicon and nitrogen, one 5-membered pyrrole ring, and one 6-membered zirconacycle.

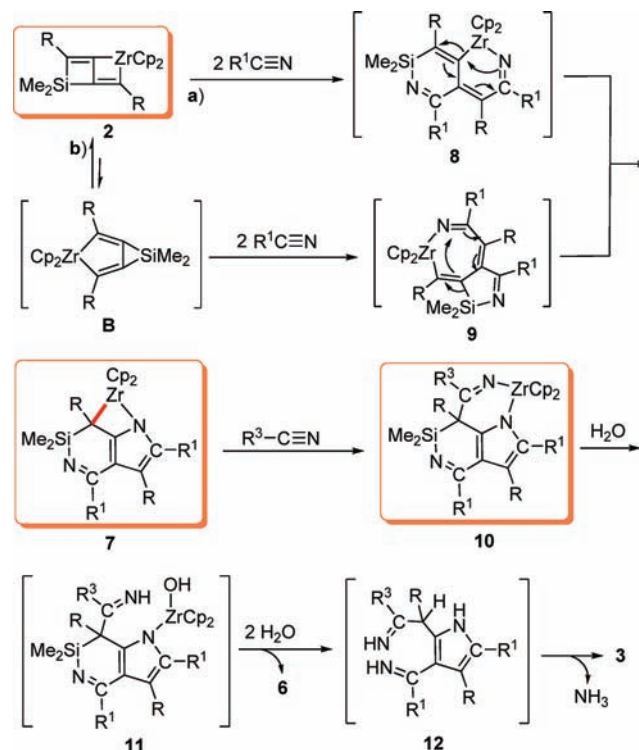
Hydrolysis of this isolated **5a** with a certain amount of H<sub>2</sub>O (1–3 equiv) afforded **3f** quantitatively. In addition to **3f**, formation of NH<sub>3</sub> in the reaction solution was detected using in situ <sup>1</sup>H NMR spectra. Furthermore, the whereabouts of the Cp<sub>2</sub>Zr moiety and the SiMe<sub>2</sub> moiety was determined by successful isolation of the cyclic zirconasiloxane **6**.<sup>14</sup>

In order to isolate the intermediate **I**, we found that the substituent tolyl on the Si-tethered diene was better than

**SCHEME 8.** Isolation of Intermediate **II (5a)** and Its Reaction with Water**SCHEME 9.** Isolation of Intermediate **I (7b)** and Its Reaction with Water

phenyl). Thus, as demonstrated in Scheme 9, a green solid **7b** was obtained in 70% isolated yield by the reaction of **2b** with 1.5 equiv of *i*-PrCN at 50 °C for 1 h.<sup>14</sup> The further reaction of **7b** with *i*-PrCN generated **5b** in a quantitative yield. Complex **7b** was composed of one 6-membered Si/N-containing ring, one 5-membered pyrrole ring, and one 4-membered zirconacycle bearing a reactive quaternary carbon center. Hydrolysis of **7b** with 1–3 equiv of H<sub>2</sub>O or D<sub>2</sub>O gave the compound **4a** and **4a-D**, respectively. The cyclic zirconasiloxane **6** was also obtained.

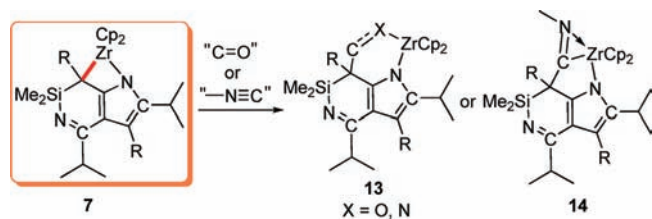
On the basis of all these results, we proposed possible mechanisms for the formation of 5-azaindoles (Scheme 10).<sup>14</sup> Two pathways were proposed for the formation of **7** from **2**. Insertion of the C≡N triple bonds of two R<sup>1</sup>CN into the Zr–C<sup>17</sup> and Si–C<sup>18</sup> bonds of **2** would afford **8** (pathway **a**). The intermediate **8** is thermodynamically unstable and would

**SCHEME 10.** Proposed Reaction Mechanisms Involving One Si-Tethered Diene and Three Nitriles

undergo skeletal rearrangement through 1,2-shift of the Cp<sub>2</sub>Zr moiety in the aza-zirconacyclic ring to afford the key intermediate **7**. An alternative mechanism was proposed for the formation of **7** via a different form (**B**) of the complex **2** (Pathway **b**). Insertion of the C≡N triple bond of two nitriles (R<sup>1</sup>CN) into the Zr–C and Si–C bonds of **B** would afford the intermediate **9**, which might immediately undergo skeletal rearrangement to afford **7**. Insertion of the C≡N triple bond of the third nitrile (R<sup>3</sup>CN) into the Zr–C bond in **7** will lead to the formation of **10**.

A proposed hydrolysis process of **10** rationalizing formation of NH<sub>3</sub>, **3**, and **6** is also shown in Scheme 10.<sup>14</sup> The intermediate **11** might be formed via cleavage of the Zr–N (imine) bond in **10** by the first molecule of water. Further hydrolysis of **11** with two molecules of water would afford the diimine **12**, along with loss of **6**. The cyclic zirconasiloxane **6** was formed through the coupling between the released Me<sub>2</sub>SiOH and Cp<sub>2</sub>ZrOH species. The final product **3** was generated via the cyclization of the diimine **12**, along with loss of NH<sub>3</sub>.<sup>19</sup>

**2.3. Further Synthetic Applications of the Intermediate 7 (Class I-c,d,e).**<sup>14,20,21</sup> As stated above, the isolation and characterization of reactive organometallic intermediates are of great importance for understanding the mechanistic

SCHEME 11. Insertion of Unsaturated Substrates into the Zr–C Bond of **7**

aspects of metal-mediated organic reactions. Even more importantly, based on deep understanding of the reaction mechanism, especially on the isolation of the reactive organometallic intermediates, synthetically useful methods can be designed. During the above mechanistic study, the intermediate compound **7** is successfully isolated. This compound **7**, composed of four components including the  $\text{Cp}_2\text{Zr}$  species, the Si-tethered diyne, and two molecules of nitriles, features one 4-membered azazirconacycle bearing a reactive Zr–C bond. We envisioned that, as shown in Scheme 11, insertion reaction of various substrates into the Zr–C bond of **7** would generate diversified and otherwise unavailable organometallic compounds and organic compounds. The fused 6-membered aza-silacycle moiety is unique and may also take part in the further reaction.

Summarized in Scheme 12 are representative results obtained from the reaction of **7** with various substrates. Each of these reactions provides a selective multicomponent coupling synthesis of interesting structures, including multiring fused Zr/Si organo-bimetallic compounds and *N*-heterocycles such as 5-azaindole, pyrrole, pyrroloazepine, pyrrolo[3,2-*d*]pyridazine, and pyrrole-2,3-dione derivatives.

The zirconocene-mediated multicomponent coupling reaction of a silicon-tethered diyne, *i*-PrCN, and EtCOCl provided the all-substituted 5-azaindole **3j** (Scheme 12a).<sup>14</sup> When a formamide  $\text{Me}_2\text{NCHO}$  was used instead of EtCOCl (Scheme 12b),<sup>14</sup> surprisingly, **3k** was obtained upon hydrolysis with saturated aq.  $\text{NaHCO}_3$ . When hydrolyzed with  $\text{D}_2\text{O}$  instead of saturated aq.  $\text{NaHCO}_3$ , again **3k** was obtained in a similar yield. The deuterium-labeled product **3k-D** was not formed. We then used  $\text{Me}_2\text{NCDO}$  instead of  $\text{Me}_2\text{NCHO}$ ; hydrolysis of the reaction mixture with aq.  $\text{NaHCO}_3$  afforded the deuterated product **3k-D** with  $\text{D} > 98\%$  (Scheme 12c). These results indicate that the CH or CD moiety of the carbonyl groups (–CHO or –CDO) in formamides is incorporated into the product. When an aldehyde such as heptanal was employed, formation of a new type of pyrrole **15** was observed as a mixture of two isomers (Scheme 12d).<sup>14</sup>

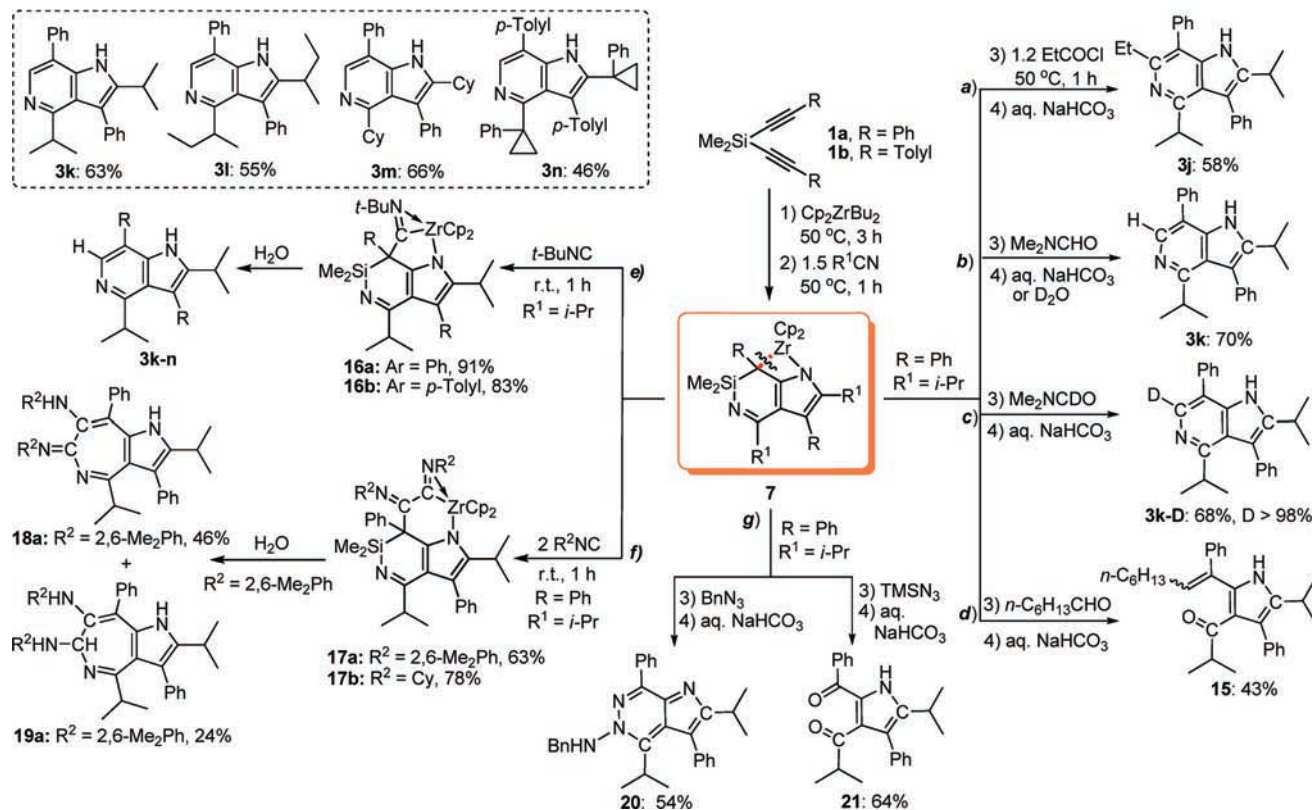
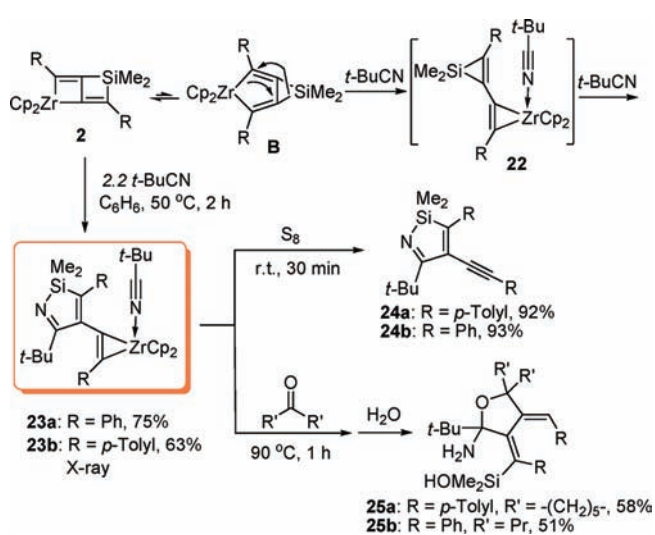
The reaction of isocyanides with **7** is dependent on the steric effect of isocyanides used. When bulky *t*-BuNC was used, reactive intermediates **16a** and **16b** as monoinsertion products were isolated in 91% and 83% yields, respectively.<sup>20</sup> Hydrolysis of **16** gave tetra-substituted 5-azaindoles **3k–n**, which represented a new substitution pattern. On the basis of these results, zirconocene-mediated one-pot synthesis of tetra-substituted 5-azaindoles **3k–n** was developed from Si-tethered diynes, nitriles, and one isocyanide (Scheme 12e).<sup>20</sup> In addition to *i*-PrCN, the scope of nitriles could be expanded to 2-methylbutyronitrile, CyCN, and 1-phenyl cyclopropanecarbonitrile.

When 2.0 equiv of less-bulky 2,6- $\text{Me}_2\text{PhNC}$  or CyNC was used, intermediates **17a** and **17b** as double-insertion products were isolated and structurally characterized. Hydrolysis of intermediates **17a** afforded pyrroloazepine derivatives **18a** and **19a** (Scheme 12f).

Similarly, one-pot synthesis of pyrrolo[3,2-*d*]pyridazine derivatives **20** via the zirconocene-mediated four-component coupling of one Si-tethered diyne, two nitriles, and one azide was also developed.<sup>21</sup> When  $\text{TMSN}_3$  was used, pyrrole-2,3-diones **21** were formed in good yields (Scheme 12g).

**2.4. Reaction of Complex 2 with Three Different Nitriles (Class I-f).** As shown in Scheme 10, we could propose the reaction mechanism for the formation of **11** from **7**. However, the story did not end. The process from **2** to **7** was still mysterious. In fact, we had thought that the right strategy to obtain the information about the first reaction step might be the use of a bulky nitrile such as *t*-BuCN. This strategy would take advantage of the space-demanding nature of the  $\text{Cp}_2\text{Zr}$  moiety, which might stop further reactions. However, when 1 equiv of *t*-BuCN was used to react with various complexes **2**, the reaction generally afforded a messy mixture. Fortunately, when 2.2 equiv of *t*-BuCN was applied, a clean and high-yield reaction was realized. The complex **2** again transformed. As given in Scheme 13, a new type of skeletal rearrangement took place to yield the intermediate compound **23**.<sup>22,23</sup> An X-ray structural analysis of **23b** reveals it adopts an azasilacyclopentadiene–zirconacyclopentene skeleton, in which only one *t*-BuCN is coupled with **2** and another one is coordinated to the zirconium center.<sup>22</sup> The bulky nitrile here initiated the reaction of the 4-membered zirconacycle in **2** but stopped the further transformation of the 3-membered zirconacycle in **23**. The *t*-BuCN behaved as both an initiator and a brake handle to control the reaction process.

The isolated intermediates **23** again gave us an opportunity to explore their synthetic value. Compounds **23**

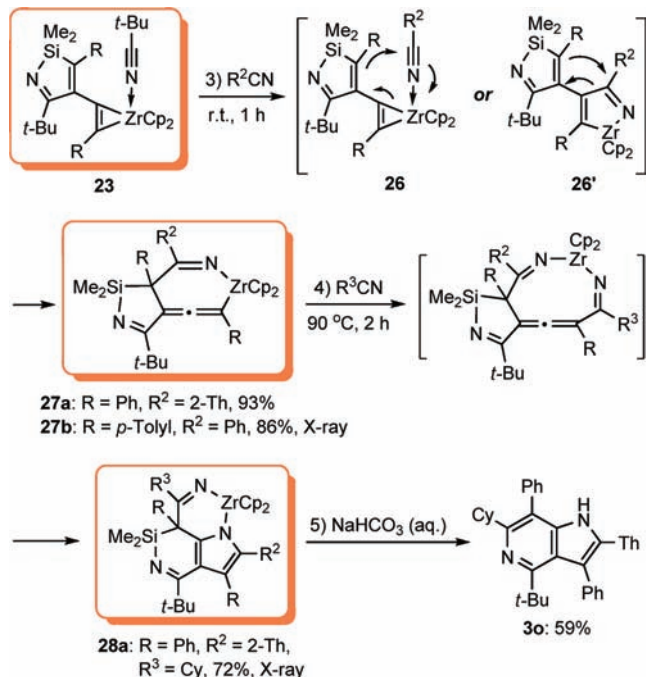
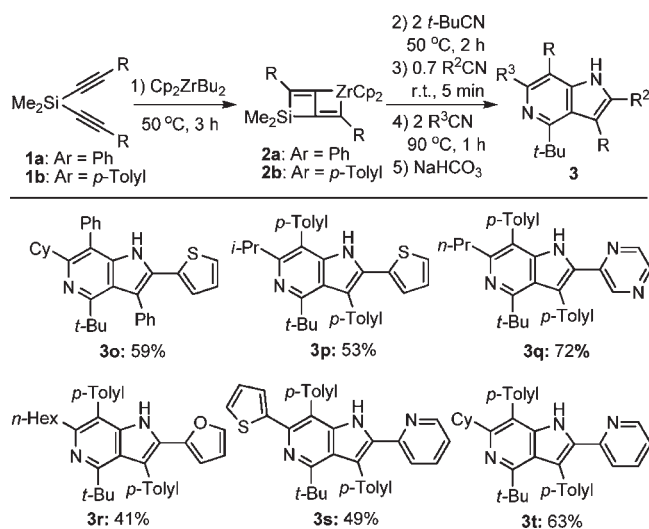
**SCHEME 12.** Formation of 5-Azaindoles, Pyrroles, Pyrroloazepines, Pyrrolo[3,2-*d*]pyridazines, and Pyrrole-2,3-diones from One Si-Tethered Diyne, Two Nitriles, and Carbonyl Compounds, Isocyanide, or Azides**SCHEME 13.** Reaction of Complex **2** with Bulky Nitriles; Formation and Synthetic Application of Azasilacyclopentadiene–zirconacyclopentadiene **23**

demonstrated excellent reactivities toward ketones, elemental sulfur, acid chlorides, and carbodiimides.<sup>22</sup> Thus, a variety of Zr/Si organo-bimetallic compounds and Si/N heterocyclic compounds were obtained. Scheme 13 gave the representative reaction of **23** with ketones, and elemental sulfur.

The reaction of **23** with the second nitrile gave the allenyl-aza-zirconacycle **27** (Scheme 14). The compound **27** featured a fused 5-membered azasilacycle and a 7-membered allenyl azazirconacycle.<sup>24</sup> Even interestingly, the reaction of **27a** with the third nitrile afforded the three-ring fused intermediate **28a**. Hydrolysis of **28a** afforded the 5-azaindole derivative **3o** bearing three different substituents (R<sup>1</sup> = *t*-Bu, R<sup>2</sup> = Th, R<sup>3</sup> = Cy). This finding prompted us to realize a one-pot synthesis of 5-azaindoles integrated with three different nitriles.<sup>23</sup> Listed in Scheme 15 are representative results of 5-azaindoles **3o–t** with all three different substituents at positions 2, 4, 6.

### 3. Reaction of Complex **2** with Alkynes (Class II)

Compared with the large number of five-membered metallacycles, six-membered metallacycles are very rare.<sup>10</sup> Initially, we applied the zirconacyclobutene–silacyclobutene complex **2** to react with alkynes and nitriles, expecting formation of six-membered zirconacycles via direct insertion reaction. However, surprisingly, as discussed above for the reaction with nitriles, the expected direct insertion reactions never take place. It is true also for their reactions with alkynes. Complex **2** also behaves as a “chemical transformer” when treated with alkynes (Scheme 16).<sup>25–28</sup>

**SCHEME 14.** Selective Reaction of the Intermediate Compound **23** with Two Different Nitriles**SCHEME 15.** One-Pot Selective Synthesis of 5-Azaindoles via Zirconocene-Mediated Multicomponent Coupling of Three Different Nitriles and One Alkyne

A consecutive skeletal rearrangement, different from those observed in the reaction with nitriles, takes place in this reaction.

**3.1. Monoalkynes (Class II-g).** Insertion of an alkyne into one of the Zr–C bonds of **2a** was expected to generate the six-membered zirconacycle **30** (Scheme 16). The reaction did afford **30** selectively in excellent yields under reflux

conditions.<sup>25,26</sup> However, experimental results demonstrated that **30** was not formed through a direct insertion pathway. When the reaction of **2a** with an alkyne was monitored at 50 °C, zirconacyclopentadiene **29** was formed. Results indicate that **29** is kinetically favored, while **30** is thermodynamically favored. We assume that two pathways might be considered for the formation of **29** from **2** (Scheme 17): the associative path (path a, and the dissociative path (path b).<sup>26</sup>

Unsymmetrical alkynes such as 1-phenyl-1-butyne would afford **31a** and **32a** as sole regioisomers. Interestingly, in the case of 1-trimethylsilyl-1-propyne, only compound **31b** was formed with perfect regioselectivity. Trapping **29** using DMAD in the presence of CuCl gave fully substituted benzene derivatives **33**.<sup>27</sup>

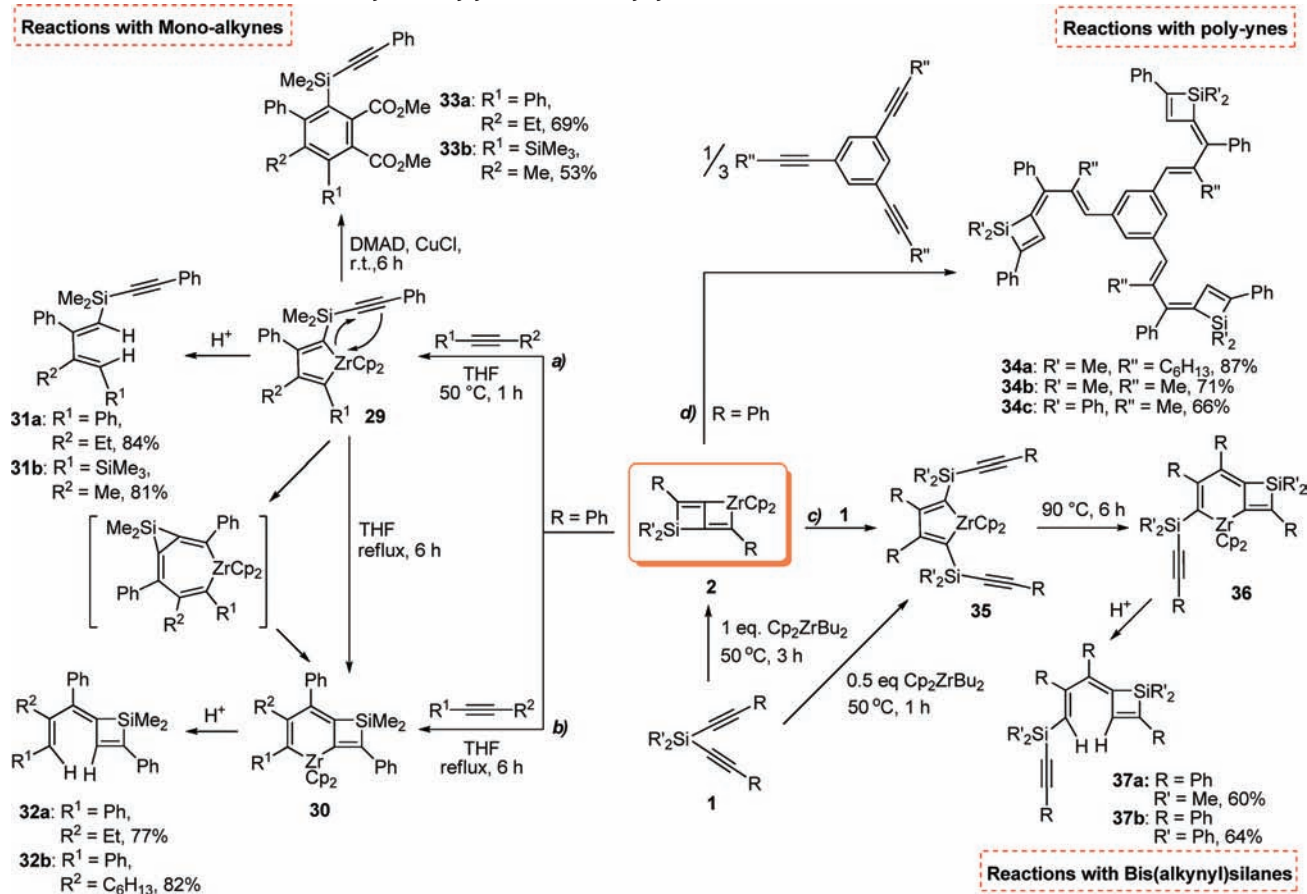
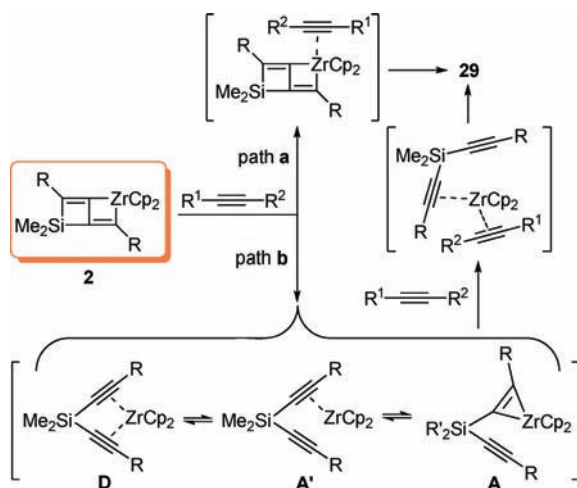
In a pioneer work by Takahashi and co-workers,<sup>8a</sup> similar types of compounds **29–32** were formed starting from zirconacyclopentenes and the Si-tethered diynes. X-ray structural determination of one complex **2** [R = R' = Ph, ZrCp<sub>2</sub> = Zr(*η*5-*t*BuC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] and one complex **30** [R<sup>1</sup> = R<sup>2</sup> = Et, SiPh<sub>2</sub>, ZrCp<sub>2</sub> = Zr(*η*5-*t*BuC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] was also reported in this work.<sup>8a</sup>

**3.2. Polyalkynylbenzenes (Class II-g).** Following the method described in section 3.1, we developed an efficient synthetic method for well-defined benzene-based  $\pi$ -conjugated systems containing two or three silacyclobutene units (Scheme 16d).<sup>28</sup> Preliminary optical properties show the increase of silacyclobutene units brings about an increase of the extinction coefficient.

**3.3. Bis(alkynyl)silanes (Class II-h).** During our continued study on the zirconocene-mediated reaction of Si-tethered diynes, we realized that the metal-to-diyne ratio also played a key role in this case.<sup>29–31</sup> When the amount of the Si-tethered diyne **1** was increased from 1 to 2 equiv relative to Cp<sub>2</sub>ZrBu<sub>2</sub>, the 2,5-bis(alkynylsilyl)zirconacyclopentadiene **35** was isolated with high regio- and chemoselectivity (Scheme 16).<sup>29,30</sup> Both aromatic and aliphatic substituents on the Si and the terminal alkynyl carbon atoms could be used. These results clearly showed that the metal-to-diyne ratio of “Cp<sub>2</sub>Zr” to Si-tethered diynes determined formation of either **2** or **35**.

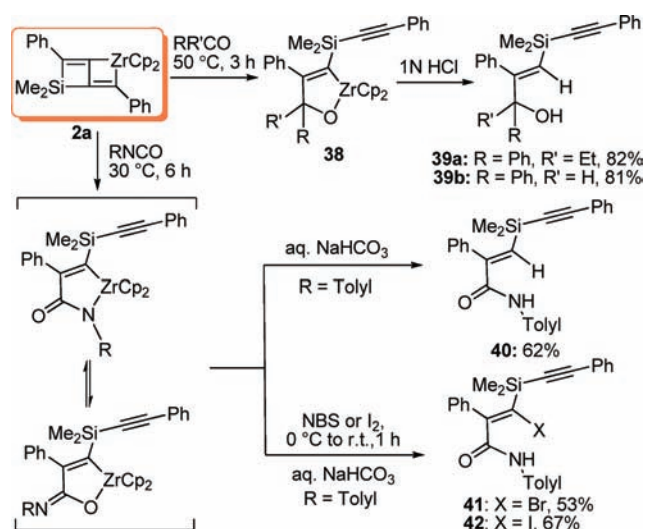
Interestingly, when **35** was further heated at elevated temperatures, it changed completely to the zirconacyclohexadiene–silacyclobutene fused compound **36**. Further skeletal rearrangement of **36** via insertion of the remaining triple bond into the Zr–C bond was not detected even after prolonged reaction time at even higher temperatures.



SCHEME 16. Reactions of **2** with Monoalkynes, Polyynes, and Bis(alkynyl)silanesSCHEME 17. Proposed Reaction Mechanisms from **2** to **29**

#### 4. Reaction of Complex **2** with Ketones, Aldehydes, and Isocyanides (Class III)

In addition to alkynes and nitriles, the C=O and C=N unsaturated substrates, such as ketones, aldehydes, and isocyanides, were also found to be able to induce the

SCHEME 18. Reaction of Complex **2** with Ketones, Aldehydes, and Isocyanides

transformation of **2** via cleavage of its C–C and C–Si bonds (Scheme 18).<sup>26</sup> The five-membered oxazirconacyclopentene **38** was formed as the intermediate when the complex

**2** was treated with ketones or aldehydes.<sup>32</sup> The reaction probably preceded via similar reaction paths as shown in Scheme 17. Allylic alcohols **39** were isolated in good yields after hydrolysis of **38**. When the complex **2** was treated with isocyanides, alkynylsilyl amides **40–42** were obtained upon hydrolysis or halogenation of the reaction mixture with I<sub>2</sub> or NBS.

## 5. Summary and Outlook

Our research demonstrates that the combination of the Si-tethered diynes and the low-valent zirconocene species is a happy match directed toward organometallic chemistry and organic synthesis. The combination not only leads to the formation of the seemingly stable but actually highly transformative zirconacyclobutene–silacyclobutene ring-fused compounds **2**, but also gives rise to a wide variety of unique Zr/Si-containing organometallic compounds and Si/N hetero-organic compounds. Once the complex **2** is excited by external stimuli, both the shape and the function of the whole molecule would change and initiate further reaction processes. Thus, we believe that the complex **2** behaves like a “chemical transformer”.

It remains difficult to answer unpredictable and surprising reactivities of the complex **2**. Its surprising chemistry is ascribed to the concomitance of two Zr–C bonds and two Si–C bonds in zirconacyclobutene–silacyclobutenes as well as at least four different resonance skeletons. The chemistry described here again demonstrates that studies of reactive organometallic intermediates not only play an important role in the in-depth understanding of seemingly complicated reaction mechanisms, but can also lead to discovery of synthetically useful reactions.

## BIOGRAPHICAL INFORMATION

**Wen-Xiong Zhang** received his B.Sc. from Hunan Normal University in 1996, M.Sc. from Guangxi Normal University in 1999, and Ph.D. from Nankai University with Professor Li-Cheng Song in 2003. He carried out postdoctoral research at Peking University with Professor Xi in 2002, and at Riken in Japan with Chief Scientist Zhaomin Hou in 2004. In 2007, he joined the College of Chemistry at Peking University, where he is now an associate professor. His research focuses on characterization and application of organometallic intermediates in metal-mediated organic synthesis, and small molecule activation using rare earth metal compounds.

**Shaoguang Zhang** was born in 1988 in Henan Province. He received his B.En. degree from Beijing Institute of Technology in 2008. In the same year, he joined Professor Zhenfeng Xi's group at Peking University as a Ph.D. candidate. His research interests

include the synthetic organometallic chemistry and development of new methodologies for functional molecules.

**Zhenfeng Xi** received his B.S. degree from Xiamen University in 1983, M.S. degree from Nanjing University, Zhengzhou University and the Henan Institute of Chemistry in 1989, and Ph.D. degree from the Institute for Molecular Sciences, Japan in 1996 with Prof. Tamotsu Takahashi. He took an Assistant Professor position at Hokkaido University in 1997. In 1998, he joined the College of Chemistry at Peking University, where he is now a Professor. His research interests include development of organometallic reagents, study on mechanisms of reactions involving reactive organometallic intermediates, and synthesis of functional structures.

*We thank past and present co-workers and students involved in this research group's long-term study on metallacyclic reagents and mechanism-based organometallic chemistry. Financial support from the Natural Science Foundation of China, the 973 Program, the State Key Laboratory of Organometallic Chemistry, and Peking University is gratefully acknowledged.*

## FOOTNOTES

\*To whom correspondence should be addressed. E-mail: zfxi@pku.edu.cn.

## REFERENCES

- Selected reviews on zirconocene-mediated organic reactions: (a) Suzuki, N.; Hashizume, D. Five-membered Metallacycloalkynes Formed from Group 4 Metals and [n]Cumulene (n = 3,5) Ligands. *Coord. Chem. Rev.* **2010**, *254*, 1307–1326. (b) Chen, C.; Xi, C. Zirconacycle-mediated Synthesis of Carbocycles. *Chin. Sci. Bull.* **2010**, *55*, 3235–3247. (c) Barluenga, J.; Rodríguez, F.; Álvarez-Rodrigo, L.; Fañanás, F. J. Coupling reactions of Zirconocene Complexes and Heterosubstituted Alkenes. *Chem. Soc. Rev.* **2005**, *34*, 762–768. (d) Negishi, E. A Quarter of a Century of Explorations in Organozirconium Chemistry. *Dalton Trans.* **2005**, 827–848. (e) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. Five-Membered Titana- and Zirconacyclocumulenes: Stable 1-Metallacyclopenta-2,3,4-trienes. *Organometallics* **2005**, *24*, 456–471. (f) Rosenthal, U.; Burlakov, V. V.; Bach, M. A.; Beweries, T. Five-membered Metallacycles of Titanium and Zirconium—Attractive Compounds for Organometallic Chemistry and Catalysis. *Chem. Soc. Rev.* **2007**, *36*, 719–728. (g) Yamazaki, S. Rearrangements of Alkyne and 1,3-Diyne in Transition Metal Center Forming Small Ring Complexes. *Inorg. Chim. Acta* **2011**, *366*, 1–18. (h) Erker, G.; Kehr, G.; Fröhlich, R. Some Selected Chapters from the (Butadiene)-zirconocene Story. *J. Organomet. Chem.* **2004**, *689*, 4305–4318. (i) *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; VCH: Weinheim, 2002. (j) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. What Do Titano- and Zirconocenes Do with Dienes and Polyynes? *Acc. Chem. Res.* **2000**, *33*, 119–129. (k) Negishi, E.; Takahashi, T. Alkene and Alkyne Complexes of Zirconocene. Their Preparation, Structure, and Novel Transformations. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755–769. (l) Fillery, S. F.; Gordon, G. J.; Luker, T.; Whitby, R. J. Tandem Reactions on a Zirconocene Template. *Pure Appl. Chem.* **1997**, *69*, 633–638. (m) Broene, R. D.; Buchwald, S. L. Zirconocene Complexes of Unsaturated Organic Molecules: New Vehicles for Organic Synthesis. *Science* **1993**, *261*, 1696–1701.
- Recent examples on zirconocene-mediated organic synthesis: (a) Suzuki, N.; Hashizume, D.; Yoshida, H.; Tezuka, M.; Iida, K.; Nagashima, S.; Chihara, T. Reversible Haptotropic Shift in Zirconocene-Hexapentaene Complexes. *J. Am. Chem. Soc.* **2009**, *131*, 2050–2051. (b) Ren, S.; Chan, H.-S.; Xie, Z. Synthesis, Structure, and Reactivity of Zirconacyclopentene Incorporating a Carboranyl Unit. *J. Am. Chem. Soc.* **2009**, *131*, 3862–3863. (c) Xi, C.; Yan, X.; You, W.; Takahashi, T. Coupling Reactions of Zirconate Complexes Induced by Carbonyl Compounds. *Angew. Chem., Int. Ed.* **2009**, *48*, 8120–8123. (d) Nishihara, Y.; Saito, D.; Tanemura, K.; Noyori, S.; Takagi, K. Regio- and Stereoselective Synthesis of Multi-Substituted Vinylsilanes via Zirconacycles. *Org. Lett.* **2009**, *11*, 3546–3549. (e) Miller, A. D.; McBee, J. L.; Tilley, T. D. Mechanism of Reversible Alkyne Coupling at Zirconocene: Ancillary Ligand Effects. *J. Am. Chem. Soc.* **2008**, *130*, 4992–4999. (f) Nishihara, Y.; Miyasaka, M.; Okamoto, M.; Takahashi, H.; Inoue, E.; Tanemura, K.; Takagi, K. Zirconocene-Mediated Highly Regio- and Stereoselective Synthesis of Multisubstituted Olefins Starting from 1-Alkynylboronates. *J. Am. Chem. Soc.* **2007**, *129*, 12634–12635.

- 3 Negishi, E.; Cederbaum, F. E.; Takahashi, T. Reaction of Zirconocene Dichloride with Alkylolithiums or Alkyl Grignard Reagents as a Convenient Method for Generating a "Zirconocene" Equivalent and its Use in Zirconium-promoted Cyclization of Alkenes, Alkynes, Dienes, Enynes, and Diynes. *Tetrahedron Lett.* **1986**, *27*, 2829–2832.
- 4 Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. I.; Negishi, E. Remarkably "Pair"-Selective and Regioselective Carbon-Carbon Bond Forming Reaction of Zirconacyclopentane Derivatives with Grignard Reagents. *J. Am. Chem. Soc.* **1991**, *113*, 6266–6268.
- 5 (a) Rosenthal, U.; Ohff, A.; Michalik, M.; Goerts, H.; Burlakov, V. V.; Shur, V. B. Transformation of the First Zirconocene Alkyne Complex without an Additional Phosphane Ligand into a Dinuclear  $\sigma$ -Alkenyl Complex by Hydrogen Transfer from  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> to the Alkyne Ligand. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193–1195. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Goerts, H.; Burlakov, V. V.; Shur, V. B. Struktur, Eigenschaften und NMR-spektroskopische Charakterisierung von Cp<sub>2</sub>Zr(Pyridin)( $\eta^2$ -Me<sub>2</sub>SiCCSiMe<sub>2</sub>). *Z. Anorg. Allg. Chem.* **1995**, *621*, 77–83.
- 6 (a) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Honold, B.; Thewalt, U. Preparation, Characterization and Reactivity of Cp<sub>2</sub>M(PMe<sub>3</sub>)<sub>2</sub> Complexes (M = Ti, Zr): the Molecular Structure of Cp<sub>2</sub>Zr(PMe<sub>3</sub>)<sub>2</sub>. *J. Organomet. Chem.* **1987**, *320*, 37–45. (b) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. Cyclization of Diacetylenes to E, E Exocyclic Dienes. Complementary Procedures based on Titanium and Zirconium Reagents. *J. Am. Chem. Soc.* **1987**, *109*, 2788–2796.
- 7 (a) Dierker, G.; Ugolotti, J.; Kehr, G.; Fröhlich, R.; Erker, G. Reaction of Bis(alkynyl)silanes with Tris(pentafluorophenyl)borane: Synthesis of Bulky Silole Derivatives by Means of 1,1-Carbaboration under Mild Reaction Conditions. *Adv. Synth. Catal.* **2009**, *351*, 1080–1088. (b) Jin, C. K.; Yamada, T.; Sano, S.; Shiro, M.; Nagao, Y. Stereoselective Synthesis of Unsymmetrical Conjugated Dienes and Trienes Utilizing Silacyclobutenes. *Tetrahedron Lett.* **2007**, *48*, 3671–3675. (c) Tamao, K.; Yamaguchi, S.; Shiro, M. Oligosiloles: First Synthesis Based on a Novel Endo-Endo Mode Intramolecular Reductive Cyclization of Diethynylsilanes. *J. Am. Chem. Soc.* **1994**, *116*, 11715–11722.
- 8 (a) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.-H.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, T. Zirconocene-Mediated Intramolecular Carbon-Carbon Bond Formation of Two Alkynyl Groups of Bis(alkynyl)silanes. *J. Am. Chem. Soc.* **1997**, *119*, 12842–12848. (b) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. Intramolecular Coupling of Alkynyl Groups of Bis(alkynyl)silanes Mediated by Zirconocene Compounds: Formation of Silacyclobutene Derivatives. *J. Am. Chem. Soc.* **1995**, *117*, 2665–2666.
- 9 Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. Reactions of Tetraalkynylsilanes (RC≡C)<sub>4</sub>Si (R = Ph, <sup>t</sup>Bu, SiMe<sub>3</sub>) with Titanocene and Zirconocene Complexes. *Organometallics* **2000**, *19*, 1198–1200.
- 10 (a) Xi, Z.; Huo, S.; Noguchi, Y.; Takahashi, T. Formation of Zirconacyclohexadienes from Zirconacyclopentadienes and LiCHClSiR<sub>3</sub>. *Chem. Lett.* **2000**, 218–219. (b) Cadierno, V.; Zabolocka, M.; Donnadiou, B.; Igau, A.; Majoral, J. P.; Skowronska, A. Unexpected Formal [1 + 3] Cycloadditions between Azides and  $\alpha$ -Zirconated Phosphanes: A Route to Unprecedented Phosphazide and Iminophosphorane Complexes. *Chem.—Eur. J.* **2000**, *6*, 345–352. (c) Norton, D.; Whitby, R. J.; Griffen, E. Insertion of (E)-(1,2-Dihalovinyl)lithium and (2-Haloethynyl)lithium into Zirconacycles. *Chem. Commun.* **2004**, 1214–1215. (d) Wang, Q.; Fan, H.; Xi, Z. 1-Zircona-2-cyclohexenes: Novel Synthesis and Preliminary Reactions. *Organometallics* **2007**, *26*, 775–777.
- 11 The term "Chemical Transformer" was noticed after we finished writing this manuscript on the cover page of the following paper: Peitz, S.; Peulecke, N.; Aluri, B. R.; Mueller, B. H.; Spannenberg, A.; Rosenthal, U.; Al-Hazmi, M. H.; Mosa, F. M.; Woehl, A.; Mueller, W. Activation and Deactivation by Temperature: Behavior of Ph<sub>2</sub>PN(iPr)(Ph)N(iPr)H in the Presence of Alkylaluminum Compounds Relevant to Catalytic Selective Ethene Trimerization. *Chem.—Eur. J.* **2010**, *16*, 12127–12132.
- 12 Sun, X.; Wang, C. Y.; Li, Z.; Zhang, S.; Xi, Z. Zirconocene-Mediated Intermolecular Coupling of One Molecule of Si-Tethered Diene with Three Molecules of Organonitriles: One-Pot Formation of Pyrrolo[3,2-c]pyridine Derivatives via Cleavage of C≡N Triple Bonds of Organonitriles. *J. Am. Chem. Soc.* **2004**, *126*, 7172–7173.
- 13 Zhang, S.; Sun, X.; Zhang, W.-X.; Xi, Z. One-pot Multi-Component Synthesis of Azaindoles and Pyrroles from One Molecule of a Si-Tethered Diene and Three or Two Molecules of Organonitriles Mediated by Zirconocene. *Chem.—Eur. J.* **2009**, *15*, 12608–12617.
- 14 Zhang, W.-X.; Zhang, S.; Sun, X.; Nishiura, M.; Hou, Z.; Xi, Z. Zirconium- and Silicon-Containing Intermediates with Three Fused Rings in a Zirconocene-Mediated Intermolecular Coupling Reaction. *Angew. Chem., Int. Ed.* **2009**, *121*, 7363–7367.
- 15 For recent reviews on azaindoles, see: (a) Song, J. J.; Reeves, J. T.; Gallou, F.; Tan, Z.; Yee, N. K.; Senanayake, C. H. Organometallic Methods for the Synthesis and Functionalization of Azaindoles. *Chem. Soc. Rev.* **2007**, *36*, 1120–1132. (b) Popowycz, F.; Mérour, J.-Y.; Joseph, B. Synthesis and Reactivity of 4-, 5- and 6-Azaindoles. *Tetrahedron* **2007**, *63*, 8689–8707. See also: (c) Moustafa, M. M. A.; Pagenkopf, B. L. Synthesis of 5-Azaindoles via a Cycloaddition Reaction between Nitriles and Donor–Acceptor Cyclopropanes. *Org. Lett.* **2010**, *12*, 3168–3171.
- 16 For a recent review on pyrrole synthesis: Estevez, V.; Villacampa, M.; Menendez, J. C. Multicomponent Reactions for the Synthesis of Pyrroles. *Chem. Soc. Rev.* **2010**, *39*, 4402–4421.
- 17 For reviews on insertion of nitriles into metal–carbon bonds, see: (a) Ferreira, M. J.; Martins, A. M. Group 4 Ketimide Complexes: Synthesis, Reactivity and Catalytic Applications. *Coord. Chem. Rev.* **2006**, *250*, 118–132. (b) Michelin, R. A.; Mozzon, M.; Bertani, R. Reactions of Transition Metal-Coordinated Nitriles. *Coord. Chem. Rev.* **1996**, *147*, 299–338.
- 18 Anderson, L. L.; Woerpel, K. A. Formation and Utility of Azasilacyclopentadienes Derived from Silacycloprenes and Nitriles. *Org. Lett.* **2009**, *11*, 425–428.
- 19 Doxsee, K. M.; Mouser, J. K. M. Metal-Vinyl vs Metal-Alkyl Insertion Reactions of Titanacyclobutenes with Nitriles. *Organometallics* **1990**, *9*, 3012–3014.
- 20 Zhang, S.; Zhang, W.-X.; Xi, Z. Efficient One-pot Synthesis of N-Containing Heterocycles by Multicomponent Coupling of Silicon-tethered Dienes, Nitriles and Isocyanides through Intramolecular Cyclization of Iminoacyl-Zr Intermediates. *Chem.—Eur. J.* **2010**, *16*, 8419–8426.
- 21 Zhang, S.; Zhao, J.; Zhang, W.-X.; Xi, Z. One-pot Synthesis of Pyrrolo[3,2-d]pyridazines and Pyrrole-2,3-diones via Zirconocene-mediated Four-component Coupling of Si-tethered Diene, Nitriles and Azide. *Org. Lett.* **2011**, *13*, 1626–1629.
- 22 Zhang, S.; Zhang, W.-X.; Zhao, J.; Xi, Z. Cleavage and Re-organization of Zr-C/Si-C Bonds Leading to Zr/Si-N Organometallic and Heterocyclic Compounds. *J. Am. Chem. Soc.* **2010**, *132*, 14042–14045.
- 23 Zhang, S.; Zhang, W.-X.; Zhao, J.; Xi, Z. One-Pot Selective Syntheses of 5-Azaindoles through Zirconocene-Mediated Multicomponent Reactions with Three Different Nitrile Components and One Alkyne Component. *Chem.—Eur. J.* **2011**, *17*, 2442–2449.
- 24 (a) Fu, X.; Chen, J.; Li, G.; Liu, Y. Diverse Reactivity of Zirconacyclocumulenes Derived from Coupling of Benzylzirconocenes with 1,3-Butadiynes towards Acyl Cyanides: Synthesis of Indeno[2,1-b]pyrroles or [3]Cumulenones. *Angew. Chem., Int. Ed.* **2009**, *48*, 5500–5504. (b) Bredeau, S.; Ortega, E.; Delmas, G.; Richard, P.; Fröhlich, R.; Donnadiou, B.; Kehr, G.; Pirio, N.; Erker, G.; Meunier, P. Versatile Behavior of Conjugated Dienes with Zirconocene Reactive Species. *Organometallics* **2009**, *28*, 181–187. (c) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. Reactions of Five-Membered Zirconacyclocumulenes with Tris(pentafluorophenyl)borane: Carbon–Carbon Double Bond Cleavage and Formation of Novel Zwitterionic Complexes. *Organometallics* **2004**, *23*, 5188–5192.
- 25 Yu, T.; Deng, L.; Zhao, C.; Li, Z.; Xi, Z. Alkyne and Ketone Induced Novel Cleavage of a C–C Bond and a C–Si Bond in Zirconacyclobutene–silacyclobutene Fused Ring Compounds. *Tetrahedron Lett.* **2003**, *44*, 677–679.
- 26 Yu, T.; Sun, X.; Wang, C.; Deng, L.; Xi, Z. Zirconocene-Mediated Intermolecular Coupling of Si-tethered Dienes with Alkynes, Ketones, Aldehydes, and Isocyanates by Means of Novel Skeletal Rearrangement of Zirconacyclobutene–Silacyclobutene and Zirconacyclohexadiene–Silacyclobutene Fused-Ring Intermediates. *Chem.—Eur. J.* **2005**, *11*, 1895–1902.
- 27 Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. Cycloaddition Reaction of Zirconacyclopentadienes to Alkynes: Highly Selective Formation of Benzene Derivatives from Three Different Alkynes. *J. Am. Chem. Soc.* **1998**, *120*, 1672–1680.
- 28 Liu, J.; Zhang, S.; Zhang, W.-X.; Xi, Z. Star-Shaped Silacyclobutene-Containing  $\pi$ -Systems: Synthesis and Optical Properties. *Organometallics* **2009**, *28*, 413–417.
- 29 Liu, J.; Zhang, W.-X.; Guo, X.; Hou, Z.; Xi, Z. Isolation and Synthetic Application of 2,5-Bis(alkynylsilyl) Zirconacyclopentadienes. *Organometallics* **2007**, *26*, 6812–6820.
- 30 Luo, Q.; Wang, C.; Gu, L.; Zhang, W.-X.; Xi, Z. Formation of  $\alpha$ -Lithio Siloles from Silylated 1,4-Dilithio-1,3-Butadienes: Mechanism and Applications. *Chem.—Asian J.* **2010**, *5*, 1120–1128.
- 31 Horacek, M.; Stepnicka, P.; Gyepes, R.; Cisarova, I.; Kubista, J.; Lukesova, L.; Meunier, P.; Mach, K. Nonclassical Bonding in Titanasilacyclohexadiene Compounds Resulting from Highly Methyl-Substituted Titanocene–Bis(trimethylsilyl)ethyne Complexes and Bis(trimethylsilyl)ethynyl)silanes. *Organometallics* **2005**, *24*, 6094–6103.
- 32 For recent examples on oxazirconacyclopentene and azazirconacyclopentene formation, see: (a) Guo, S.; Liu, Y. A Facile Zr-mediated Multicomponent Approach to Arylated Allylic Alcohols and its Application to the Synthesis of Highly Substituted Indenes and Spiroindenes. *Org. Biomol. Chem.* **2008**, *6*, 2064–2070. (b) Liu, Y.; Yan, B. Direct Reaction of Aroyl Cyanides with Azazirconacyclopentadienes: Synthesis and Structural Characterization of Stabilized Azazirconacyclopentenones. *Organometallics* **2006**, *25*, 544–547.