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Reaction of Titanacyclobutene–Silacyclobutene Fused-Ring Complexes with Nitriles via Formal Insertion of the C–N Triple Bond of Nitrile into the Silacyclobutene Ring

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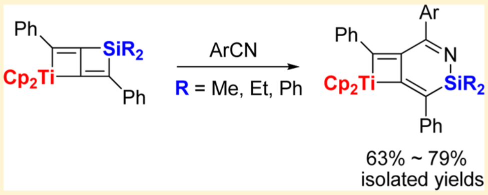
S *Supporting Information*

ABSTRACT: The reaction of titanacyclobutene–silacyclobutene fused-ring complexes with nitriles was investigated. Formal insertion of the C–N triple bond of nitriles into the silacyclobutene ring was observed, affording their corresponding titanacyclobutene and six-membered azasilacycle fused-ring complexes. This reaction pattern with nitriles is totally different from that of their analogous zirconacyclobutene–silacyclobutene fused-ring complexes. The size effect of the central metals (Ti vs Zr) is considered as the major reason for the different reaction patterns.



Titanacycles and zirconacycles are readily available metallacycles.[1] Reaction chemistry studies of these metallacycles with various substrates have proved that they are synthetically very useful.[1−3] Among them, the zirconacyclobutene–silacyclobutene fused-ring complexes **1** and their analogous titanacyclobutene–silacyclobutene fused-ring complexes **5** (Scheme 1) are structurally unique and can be easily generated from the reaction between bis(alkynyl)silanes and low-valent Cp_2Zr^{II} and Cp_2Ti^{II} species, respectively.[4,5] We have systematically investigated the reaction chemistry of the zirconocene complexes **1**.[6,7] The reaction of **1** with nitriles is particularly interesting and useful.[7] As shown in Scheme 1, depending on the nitrile, different reaction patterns of **1** were observed, affording different types of zirconacycles **2**–**4**. In all these reactions, the original zirconacyclobutene ring in **1** is not maintained and is skeletally reorganized. The expected ring-expansion products such as **I**–**III** and their regioisomers were never observed.

Previous reports on group 4 metallocenes in the literature have demonstrated that titanocene complexes, in many cases, behave differently from zirconocene complexes.[1−3] The titanacyclobutene–silacyclobutene fused-ring complexes **5** (Scheme 1) can be readily synthesized by the reaction of bis(alkynyl)silanes with a titanocene–bis(trimethylsilyl)ethyne complex (Rosenthal complex, $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$).[5] We envisioned that a different reaction pattern would result when nitriles were treated with the Cp_2Ti complexes **5**. Herein we discuss a formal insertion of the C≡N triple bond of nitriles into the silacyclobutene ring of **5**. The unprecedented titanacyclobutene and six-membered azasilacycle fused-ring products **6** were obtained in high yields. This reaction pattern of the Cp_2Ti complexes **5** with nitriles is totally different from that of their analogous Cp_2Zr complexes **1**. The size effect of the central metals (Ti vs Zr) is considered to be the major reason for the different reaction patterns.

The complex **5a** could be readily prepared in high yield by the reaction of the Rosenthal complex $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ with bis(alkynylphenyl)dimethylsilane, as reported by Mach and co-workers.[5] When this isolated complex **5a** was treated with 1.5 equiv of PhCN, the titanacyclobutene and six-membered azasilacycle fused-ring product **6a** was obtained as the sole isomer in 67% isolated yield (Scheme 2). Similarly, the formal ring-expansion complexes **6b**,**c** could be also isolated in high yields. In contrast, when **5a** was treated with ^{i}PrCN or ^{t}BuCN, no reaction was observed under the present reaction conditions. None of the types of products **2**–**4** (Scheme 1) were obtained. All of these results are in sharp contrast to the results obtained for the reaction of the zirconocene complexes **1** with nitriles.[7]

Single crystals of complex **6a** suitable for X-ray structural analysis were grown in THF at room temperature, and the ORTEP drawing is presented in Figure 1. X-ray structural analysis of **6a** reveals that it consists of two fused rings: one four-membered titanacyclobutene and one six-membered azasilacycle. The Si1–N1 distance (1.7476(16) Å) is comparable with that found in 5-*tert*-butyl-2,2-dimethyl-3-*p*-tolyl-4-(*p*-tolylethynyl)-2*H*-1,2-azasilole (1.760(3) Å).[7c] The

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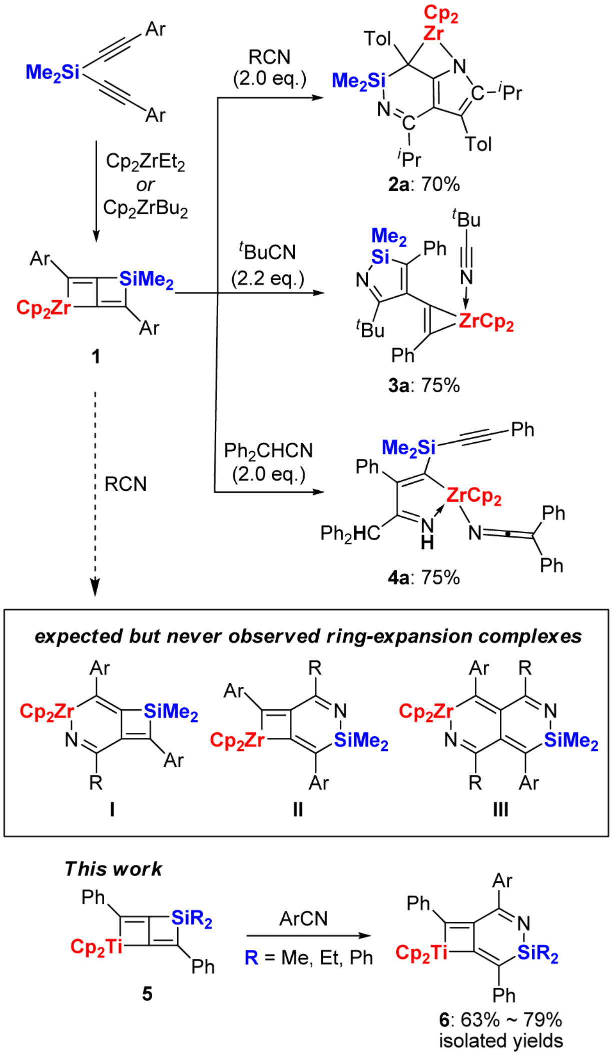
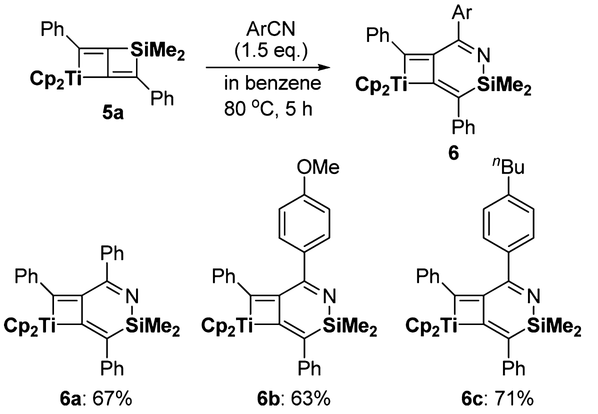
Scheme 1. Totally Different Reactions of Zirconacyclobutene−Silacyclobutene Fused-Ring Complexes 1 and Titanacyclobutene−Silacyclobutene Fused-Ring Complexes 5 with Nitriles



Scheme 2. Formation of Titanacyclobutene and Six-Membered Azasilacycle Fused-Ring Compounds 6a−c from Complex 5a and Nitriles



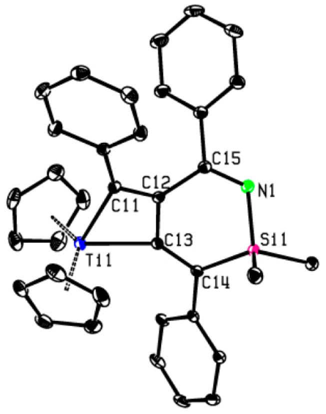
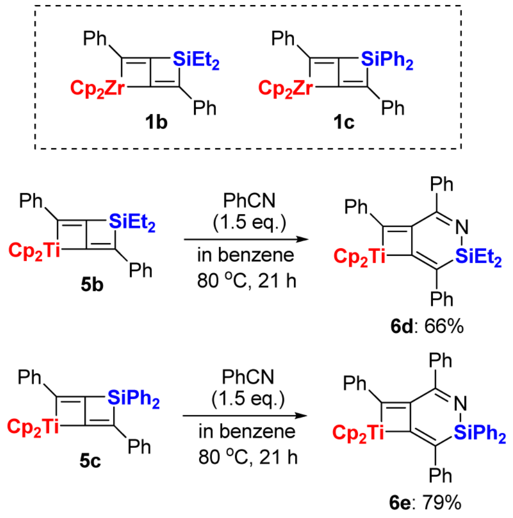


Figure 1. ORTEP drawing of **6a** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1−C11 2.1256(19), Ti1−C13 2.1421(19), C12−C13 1.484(2), C11−C12 1.364(3), C12−C15 1.505(2), C13−C14 1.361(3), Si1−C14 1.8705(19), Si1−N1 1.7476(16), N1−C15 1.283(2); N1−Si1−C14 104.47(8).

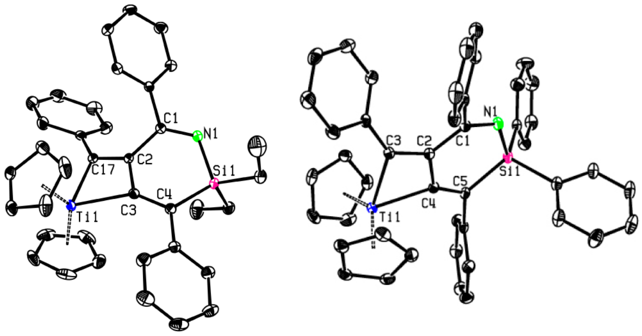
bond lengths of Ti1−C11 (2.1256(19) Å) and Ti1−C13 (2.1421(19) Å) are comparable with the related Ti−C distances in $[Ti(\eta^5\text{-}C_5Me_5)_2\{Ph_2C_4(SiMe_2)\}]$ (2.190(4) and 1.967(8) Å).[6]

Our previous study on the reactivity of the Cp_2Zr complexes has demonstrated that these complexes **1** are very sensitive to the bulkiness of substituents on these complexes and of approaching substrates.[7] For example, the reaction of **1b** (with a $SiEt_2$ moiety; Scheme 3) with PhCN required a much longer reaction time and higher temperature. Notably, when **1c** (with a $SiPh_2$ moiety) was treated with nitriles, only a trace amount of the product was obtained, with most of the complex **1c** being unreacted. This finding indicated that the steric environment around the silicon center has a strong impact on the reactivity of the Cp_2Zr complexes **1**. However, in contrast, their titanocene analogues **5b**,**c** did react with PhCN smoothly and cleanly, affording their corresponding silacyclobutene ring-expansion products **6d**,**e** in 66% and 79% isolated yields, respectively. The structures of products **6d**,**e** were both determined by single-crystal X-ray structural analyses (Figure 2). These results again demonstrate that the reactivity of nitriles

Scheme 3. Formation of Products 6d,e from Complexes 5b,c and PhCN



with the Cp_2Ti complexes **5** is very much different from that of the Cp_2Zr complexes **1**.

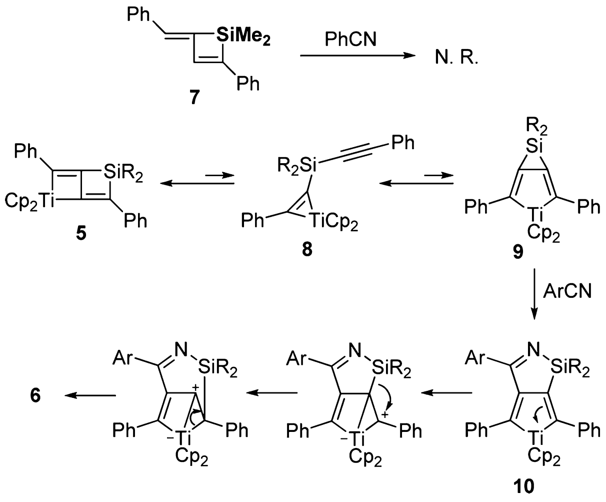


6d **6e**

Figure 2. ORTEP drawings of **6d** (left) and **6e** (right) with 30% probability thermal ellipsoids. Hydrogen atoms and THF in **6e** are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. For **6d**: Ti1−C17 2.131(2), Ti1−C3 2.1724(19), C2−C3 1.481(3), C2−C17 1.363(3), C1−C2 1.500(3), C3−C4 1.364(3), Si1−C4 1.873(2), Si1−N1 1.7484(17), N1−C1 1.281(3); N1−Si1−C4 105.72(9). For **6e**: Ti1−C3 2.133(2), Ti1−C4 2.154(2), C2−C4 1.481(3), C2−C3 1.366(3), C1−C2 1.491(3), C4−C5 1.353(3), Si1−C5 1.859(2), Si1−N1 1.7446(19), N1−C1 1.285(3); N1−Si1−C5 106.80(9).

Although a direct insertion of the C−N triple bond into the silacyclobutene ring of complex **5** cannot be totally excluded, the proposed pathway shown in Scheme 4 for the formation of complex **6** is more likely. No reaction was observed when the silacyclobutene derivative **7** was treated with nitriles in refluxing benzene after 24 h. The existence of the titanacyclopentadiene−silacyclopropane fused-ring complex **9** or its zirconocene analogue has been proposed by Takahashi and Mach.[4−6] The silacyclopropane moiety in **9** is highly strained and should be very reactive.[8] Thus, a C−N triple bond is proposed to insert into the Si−C bond, leading to the formation of the intermediate **10**. Then, skeletal rearrangements via a silyl 1,2-shift would take place to give the final complex **6**.

Scheme 4. Proposed Mechanism for the Formation of 6



In summary, we have demonstrated that the reaction pattern of nitriles with titanacyclobutene−silacyclobutene fused-ring complexes **5** is totally different from the reaction pattern of nitriles with zirconacyclobutene−silacyclobutene fused-ring complexes **1**. The strained fused-ring skeletons, the sterically demanding environments around the metal centers and the silyl groups, and the different sizes of the metals are all considered to contribute to the different reactivities. Further investigation into the reaction mechanism and synthetic applications for the synthesis of silacycles are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving crystallographic data, full experimental procedures, NMR spectra, and details for the preparation of complexes **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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