

Review

Synthesis of silacyclobutanes and their catalytic transformations enabled by transition-metal complexes



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ABSTRACT

Silacyclobutanes (SCB), a family of useful organosilicon compounds, have attracted much attention because the highly strained silicon-carbon bond can be activated, as evidenced by transition-metal catalyzed ring-opening and ring expansion reactions. Efforts of extending silicon-carbon bond activation will definitely trigger powerful and privileged catalyst systems capable of unveiling opportunities for highly efficient and valuable transformations of SCB. This review summarized and highlighted representative and important advances for the synthesis of silacyclobutanes and its analogues as well as their catalytic transformations enabled by various transition-metal complexes whose versatility will be demonstrated widely in organosilicon chemistry and transition-metal catalysis. The different contributions in this growing research area summarized in this review could provide inspiration and incentive to make SCB as a precious source of organosilicon compounds.

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1. Introduction

Silicon, as second most abundant element, accounts for approximately 28% of the earth's crust. The proximity suggests chemistry of silicon is similar to that of carbon, which are members of Group 14. However, there are striking differences between silicon and

carbon elements [1]. For example, the chemical dissimilarity between silicon and carbon has arisen from the differences in atomic size (covalent radii: $r_{\text{Si}} = 117$ pm and $r_{\text{C}} = 77$ pm respectively) and electronegativity ($\chi_{\text{Si}} = 1.74$ and $\chi_{\text{C}} = 2.50$ respectively) [1b]. And the *ab initio* calculations for silacyclobutanes showed that its molecular structures and dihedral angles were different from general cyclobutanes [1g–m]. In fact, similarly to metal elements, the chemistry and the coordinated ability of silicon element is affected by the availability of its empty 3d orbitals, which make it easy to form hypervalent silicon-based coordination (5- and 6-coordinated complexes). Although not any organosilicon compound containing a

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silicon-carbon bond has been detected in nature, numerous functional organosilicon compounds are found in a wide variety of applications in chemistry, material science, and electronic or optoelectronic devices [2], and growing attention has been paid to the synthesis of organosilicon compounds as well as the chemistry of silicon-carbon bond activation [2,3]. Meanwhile, organic compounds containing four-membered ring systems are highly reactive molecules because of their broad synthetic utilities for biologically active molecules and functional organic materials [4]. Because of the inherent ring strain of four-membered-ring systems, the ring-opening or ring expansion process through the carbon-carbon bond cleavage has been revealed by chemists for their unique reactivity of small-ring structure [5]. In this context, among cyclic organic molecules and organosilicon compounds bearing four-membered ring systems reported in the past century, silacyclobutane (SCB) is one of the simplest organosilicon molecules. And accordingly, there has been considerable interest in the chemistry of silacyclobutane compounds due to the ring strain and Lewis acidity, including the cleavage chemistry of silicon-carbon bonds and their pyrolytic and photolytic degradation [6]. Especially, the inherent properties and hypervalent coordination of organosilicon compounds bearing four-membered ring systems, provide many exciting possibilities for the investigations of the synthetic chemistry and new transformations of silacyclobutanes [7,8]. Thus, it is necessary to summarize the exciting development on functionalization and applications of silacyclobutanes in the organic synthesis. In this context, both silacyclobutanes and benzosilacyclobutenes were important and air-stable four-membered sila-heterocycles have been widely used in a variety of chemical transformations. Notably, four-membered organosilicon compounds have become an important class of monomers or starting materials in polymer chemistry and modern organic chemistry. For example, they can be used as precursors to undergo facile ring-opening polymerization (ROP) to afford polycarbosilane polymers. Therefore, in this review, we only give a concise overview on the synthesis of silacyclobutanes and benzosilacyclobutenes, and their catalytic transformations enabled by transition-metal complexes. For this purpose, this mini-review will provide an authoritative overview on the recent findings in the transition-metal-catalyzed transformations of various silacyclobutanes.

2. The synthesis of silacyclobutane and its analogues

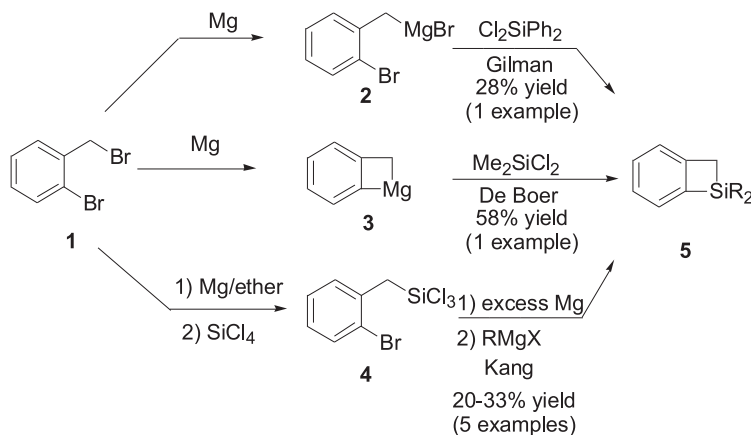
2.1. Catalyst-free synthesis of silacyclobutane and its analogues

The first example of cyclic organosilicon compounds was reported by Hart in 1887 [9]. However, those cyclic organosilicon

compounds were poorly characterized in this work that was obtained by treatment of silicon tetrachloride and organic halides with sodium [10]. Since then, many attempts have been made to prepare the four-membered cyclic organosilicon compounds. In addition, since Kipping reported the pioneering example of the synthesis of SCB in 1920s [11], the synthetic chemistry of four-membered octaphenylcyclotetrasilane has received much attention in the subsequent decades [12]. And notably, Gilman [13], de Boer [14], and Kang [15] contributed greatly to the synthesis of benzosilacyclobutenes by Grignard addition reaction (Scheme 1). However, the synthesis of structurally diverse benzosilacyclobutene and silacyclobutane derivatives still remains sparse [15,16].

In general, a synthetically useful route to silacyclobutanes is completed by one-pot intramolecular silylation with *in situ* formed Grignard reagents (Scheme 2). In 1960s, Vdovin and co-workers [17] reported the first synthesis of 1,1-dichloro-1-silacyclobutane **8a**, and the preparation of silacyclobutane itself and its difluoro derivatives (**9**) were first reported by Laane in 1967 [17]. Both the groups found that the 1,1-dichloro-1-silacyclobutane (**8a**) could be prepared from 3-chloropropyltrichlorosilane or 3-bromopropyltrichlorosilane. Notably, the chloro-substituted silacyclobutane **8a** would be an important intermediate for the further synthesis of structurally diverse silacyclobutanes by subsequent nucleophilic addition [17]. For example, the corresponding derivatives, 1,1-difluorosilane (**9**) and silacyclobutane or silacyclobutane-1,1-d₂ (**10**) could be prepared from the dichloro ring species **8a**. In 1972, Damrauer et al. further demonstrated that magnesium activated by 1,2-dibromoethane could be an effective agent for intramolecular cyclizing 3-chloropropyltrichlorosilane to silacyclobutanes [17]. Notably, 1-chloro-1-methylsilacyclobutane (**8b**), 1,1-dimethylsilacyclobutane (**8c**), and 4-silaspiro[3,3]heptane (**8d**) could be prepared in good yields (75–93.5%). Under optimal reaction conditions modified by Grobe [17], moderate to high yields (50–90%) of silacyclobutane derivatives **11–13** could be obtained by the substitution of SiCl₂-containing silacyclobutane **8** (Scheme 2). Similarly, the SiCl₂-containing silacyclobutane **15** could be obtained by the treatment of 2-(chloromethyl)-3-(trichlorosilyl)propene (**14**) with magnesium in THF at 0 °C, and subsequent Grignard addition reaction by the addition of two equivalents of phenylmagnesium bromide or propylmagnesium bromide to the solution of **15** gave the corresponding silacyclobutane **16** in moderate yields [17,17].

Alternatively, the preparation of silacyclobutanes has been exploited by Jones and Lim [18] through [2+2] cycloaddition reaction of *in situ* formed Me₂Si=CHCH₂-*t*-Bu with butadiene. However, when vinyl dimethylchlorosilane **17** was treated with one equiv of *tert*-butyllithium and 1,3-butadiene under the reported reaction conditions, a mixture of silacyclobutanes and



Scheme 1. Classic methods toward the synthesis of benzosilacyclobutenes [13–15].

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