

Formation of silacycles via metal-mediated or catalyzed Si–C bond cleavage

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Silacycles play a very important role in modern organic chemistry and materials science. Construction of silacyclic skeletons via metal-mediated or catalyzed Si–C bond cleavage has attracted much recent attention. Several interesting and useful synthetic strategies have been reported in the literature. In this review, we have summarized recent developments on metal-mediated or catalyzed Si–C bond cleavage, which lead to the synthesis of silacycles, including silacyclobutenes, silacyclopentanes, silacyclopentadienes (siloles), 6-membered silacycles, and their derivatives.

Si–C bond cleavage, synthesis, silacyclobutenes, siloles, silacycles

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Silacycles, especially silole and related compounds have received growing interest as potential electroluminescent materials [1–9]. Conventional synthesis of silacycles is achieved by silylation of organometallic compounds, such as RLi or RMg, with dihalo or tetrahalosilanes [10–18]. The cleavage of Si–C bond plays an important role in organic synthesis. Various Si–Csp³, Si–Csp² and Si–Csp bond cleavage reactions, such as Brook rearrangement [19] and Hiyama reaction [20,21], have been widely applied in modern organic synthesis. Compared with reactive halosilanes, silanes are more stable and compatible with elaborate systems. Very recently, there is growing interest in using the stable silane derivatives to construct silacycles via Si–C bond cleavage and formation. In this review, we will focus on this topic.

1 Metal-mediated silacycle formation via Si–C bond cleavage

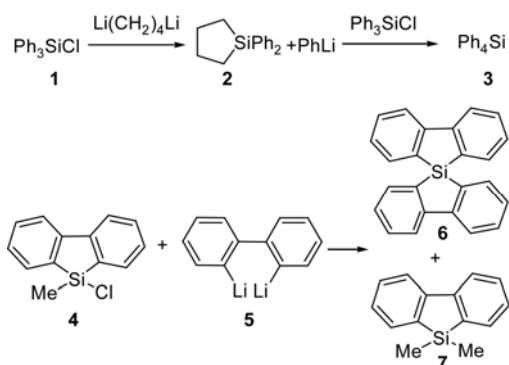
Since the halosilanes play a predominate role in the metal-

mediated Si–C bond formation, the first example of formation of silacycles via Si–C bond cleavage was found with the reaction of dilithio reagent with monhalosilane. More than 50 years ago, Gilman and co-workers [22–24] reported the formation of silacycle via Si–C bond cleavage with 1,4-dilithio reagent. In these researches, silacyclopentane, silacyclohexane and 1,1'-spirobi[dibenzosilole] were obtained. The cleavage of Si–C bond and the formation of a new organolithium reagent were proposed. And the *in situ* formed organolithium was trapped by halosilane (Scheme 1).

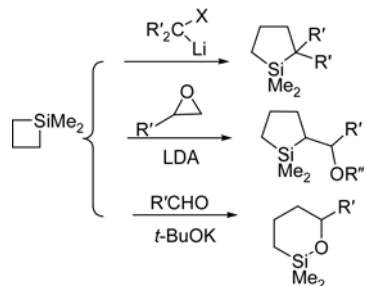
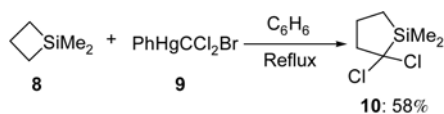
Seyferth et al. [25,26] reported the first carbene insertion into the Si–C bond of siletane with an organomercury compound **9** (eq. (1)). Ando et al. [27] reported carboalkoxycarbenes insertion into Si–C bonds later. Oshima and co-workers [28–30] developed this ring expansion of siletane into an efficient method to synthesize various five- and six-membered silacycles with less toxic alkali metals (Scheme 2). Later, Sakurai and co-workers [31] developed a similar carbene insertion reaction to synthesize silepine **11** (eq. (2)).

In 2002, Van Klink et al. [32] observed a highly efficient intramolecular ring closure reaction of silane derivative to form silafluorene during their research with Grignard reagent (eq. (3)). In 2005, Xi and co-workers [33] reported a

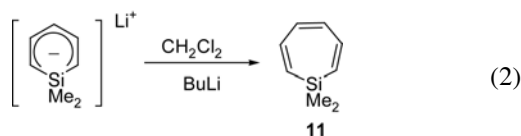
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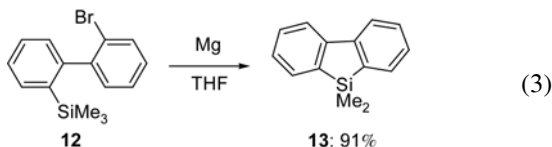
Scheme 1



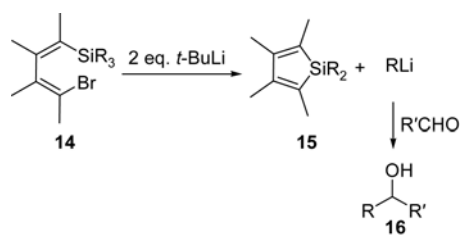
Scheme 2



lithiation-promoted formation of silole from intramolecular Si-C bond activation. Starting with 1-bromo-4-silyl butadienes **14** and $t\text{-BuLi}$, siloles were obtained as the products. Releasing of a new organolithium was proposed, and the proposed organolithium reagent was trapped by an aldehyde. They also found that the Si-C bond can be cleaved selectively in the order of Si-Ph, Si-vinyl > Si-Me >> Si- i -Pr (Scheme 3).

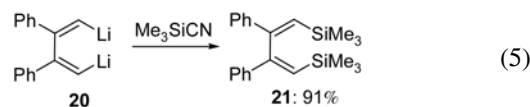


Hudrlik et al. [34] reported an intermolecular type of silole formation from reactions of dilithiobutadienes with monochlorosilanes. Facile loss of organic groups from silicon was also observed (eq. (4)). A similar reaction with Me_3SiCN provided siloles with cleavage of two Si-C bonds: Si-CN and one of the Si-Me bonds. During their research



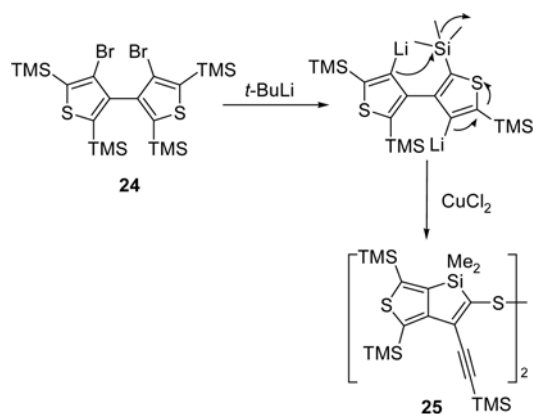
Scheme 3

on the reactions of 1,4-dilithio-1,3-dienes with nitriles, Xi group [35] observed a similar result. They found that the α -substituents played a crucial role in the reaction of dilithio reagents with silicon compound. When 2,3-disubstituted dilithio reagent **20** treated with Me_3SiCN , (Z,Z)-dienylsilane **21** was obtained with high stereoselectivity (eq. (5)). Surprisingly, the reaction of 1,2,3,4-tetrasubstituted dilithio reagent **22** with Me_3SiCN followed a tandem silylation/intramolecular substitution process to yield silole **23** (eq. (6)).

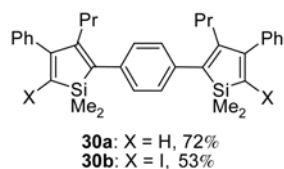
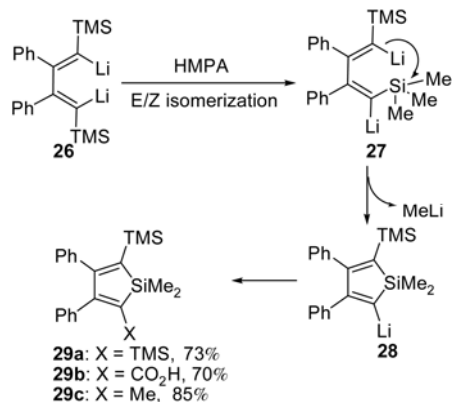


In order to develop a new method to prepare octakis(trimethylsilyl)tetrathienylene, Wang and co-workers [36] found an unexpected siloles formation from intermolecular Si-C and C-S bond activations (Scheme 4). One of the amazing results was the facile synthesis of a new type of lithiosiloles **28** from readily available silyl 1,4-dilithio-1,3-butadiene derivatives **26**. Further experimental investigation proved E/Z isomerization of 1-silyl-1-lithio alkene and nucleophilic attack on silicon as a possible mechanism. This procedure provides a general and simple method to prepare diverse silole derivatives. Even structurally more complex bis-silole compounds **30** can be synthesized by this procedure (Scheme 5) [37-41]. Nucleophilic substitution of the silane to form pentaorganosilicate **31** was proposed as a key step for these reactions, followed by releasing a new organolithium and generation of silacycle (Scheme 6) [42-44].

Compared with main group metals, transition metals bring more exciting results into this area. For example, the platinum-mediated skeletal rearrangement of Si-tethered diynes into alkylidenesilacyclobutene **33** was realized by



Scheme 4



Scheme 5



Scheme 6

Lukehart and co-workers [45] in 1989 (eq. (7)). Organotitanium and organozirconium compounds play important roles in building silacycles via Si–C bond rearrangement. Takahashi and co-workers [46,47] developed an unexpected zirconium-mediated skeletal rearrangement of bisalkynylsilanes **34**, which led to the formation of cyclic Zr/Si organo-bimetallic compounds **35**. This provided an unprecedented method to synthesize silacyclobutene derivatives (eq. (8)). Rosenthal and co-workers [48] applied a similar method to prepare spiro-silacycle systems **37** from the reaction of tetraalkynylsilanes with low valent Ti or Zr complexes (eq. (9)). A

simple method to prepare benzo-zirconacyclo-hexadiene-silacyclobutene fused ring system **38** was also developed by them (Figure 1) [49].

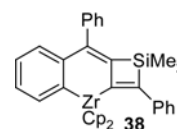
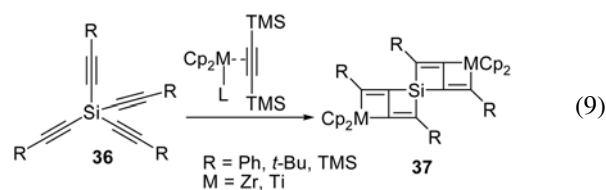
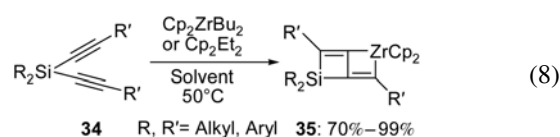
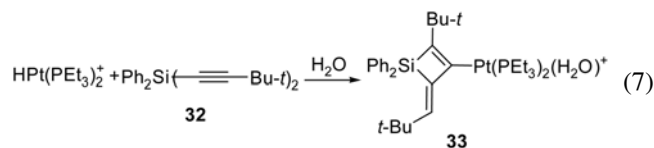
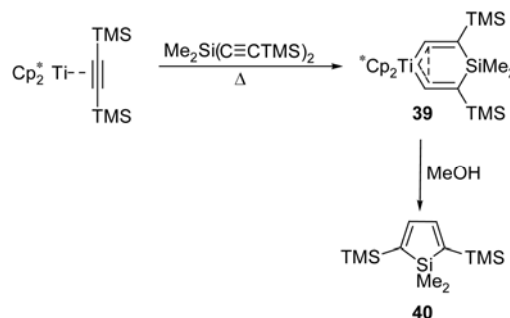


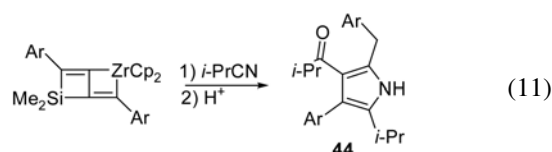
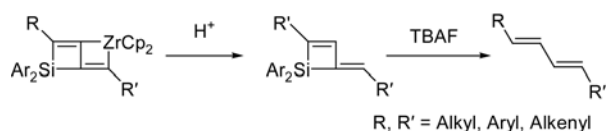
Figure 1 Silacyclobutene.

Mach and co-workers [50] reported an interesting titanium-mediated skeletal rearrangement of Si-tethered diyne into titanasilacycle **39**, which could be transferred into silacyclopentadiene **40** (Scheme 7). The application of this method to prepare silacyclobutene received considerable attention both in organic synthesis and material chemistry. Auner and co-workers [51] reported the spiro-silacycles as potential sensitive sensor materials and optical switches (Figure 2).

Nagao and co-workers [52] developed a highly efficient method to stereoselectively prepare unsymmetrical conjugated (1E,3E)-dienes and -trienes from the zirconium-mediated silacyclobutenes formation (Scheme 8). Xi and co-workers [53] developed the zirconacyclo-butene-silacyclobutene fused



Scheme 7



Scheme 8

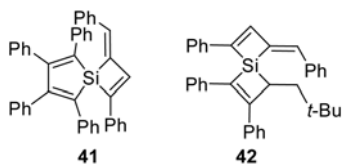
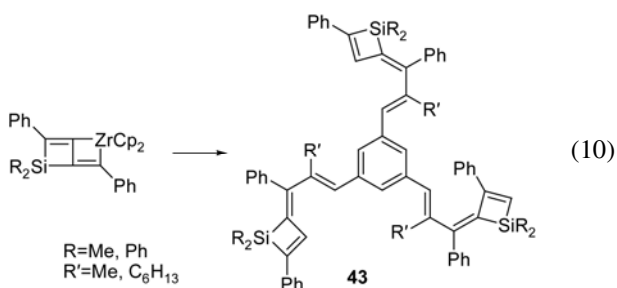


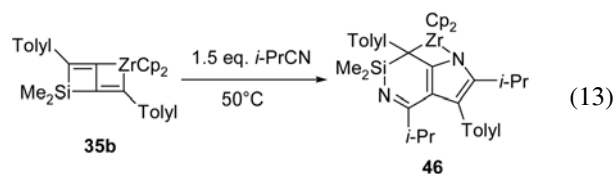
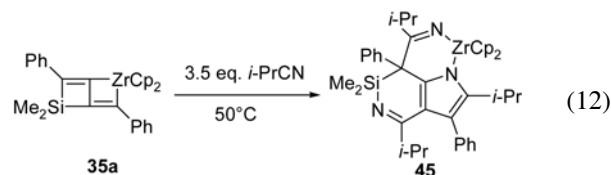
Figure 2 Spirosilacycles.

intermediate into a powerful “chemical transformer” in organic synthesis. A consecutive skeletal rearrangement was observed from the reaction of alkynes with these Zr/Si organo-bimetallic intermediates to produce various silacyclobutenes. Even star-shaped silacyclobutene-containing molecular **43** could be prepared in high yield with high regioselectivity (eq. (10)). Their preliminary optical results suggested that these new silacyclobutenes could be potential candidates for electronic and optoelectronic applications. They also observed that the metal-to-diyne ratio played a key role in this zirconocene-mediated reaction of Si-tethered diynes. Upon increasing the ratio of Cp_2ZrBu_2 :diyne from 2:1 to 1:1, reversible Si–C bond cleavage and formation was observed [54–58].



According to their persistence, Xi and co-workers [59] developed the reaction of zirconacyclobutene-silacyclobutenes with nitriles into a versatile “tool-box” for preparation of various Si and N containing heterocycles. The first report on this topic was the reaction of zirconacyclobutene-silacyclobutene fused ring compound with 3.5 equiv of nitriles. Pyrrolo[3,2-*c*]pyridine derivatives were obtained after hydrolysis, and one of the three $\text{C}\equiv\text{N}$ triple bonds and the two Si–C bonds were cleaved during this five-components coupling process. One important discovery was the steric influence of the substituent. The nitriles with appropriate hindrance, such as *i*-PrCN and 2-methylbutyronitrile, could be applied to stop the reaction in the middle way. This provided an efficient method to prepare multisubstituted pyrrole derivatives **44** (eq. (11)) [60].

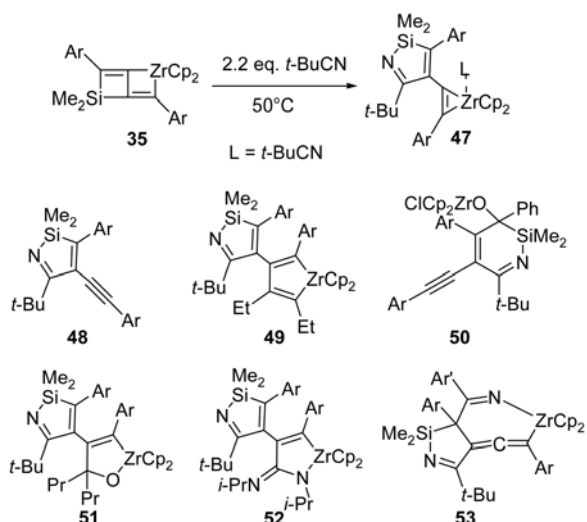
The discovery of the steric influence not only provided a synthetic useful method but also opened the gate to understanding the reaction mechanism. The first break-through was made by the reaction of Zr–Si bicyclic compound **35a** with *i*-PrCN. The X-ray structural analysis of **45** revealed that one *i*-PrCN insert into Si–C bond and the novel three-ring-fused structure composed of one new 6-membered silacycle (eq. (12)). The reaction of **35b** with reduced amount of *i*-PrCN provided another novel silacycle containing tricyclic compound **46** (eq. (13)). The application of this Zr/Si bimetallic compound provided a synthetically useful method to diverse structures of nitrogen-containing heterocycle compounds after reaction with isocyanides, formamides, acid chlorides, and aldehydes. The further application of this Zr/Si bimetallic compound and the understanding of the related reaction mechanism were disclosed very recently [61–63].



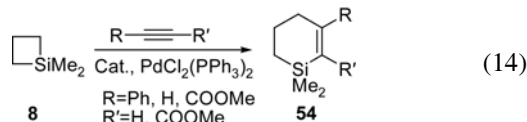
The reactions of **35** with more sterically hindered nitrile, *t*-BuCN, gave the *t*-BuCN stabilized zirconacyclopentene-azasilacyclopentadiene complexes **47** via the coordination-induced Zr–C/Si–C bond cleavage and reorganization. The synthetic application of these intermediates provided various Zr/Si organo-bimetallic compounds and Si/N heterocyclic compounds **48–53** (Scheme 9) [64,65].

2 Metal-catalyzed silacycle formation via Si–C bond cleavage

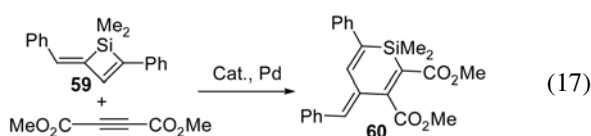
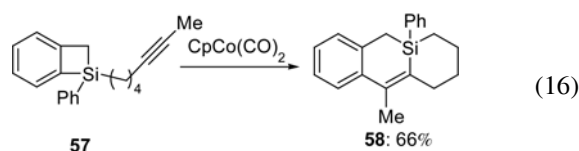
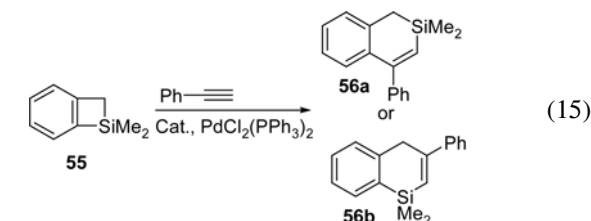
Various metals, such as Ni, Pd, Pt, Cu, Ag, Zn and Mo, have been used to construct silacycle via catalytic Si–C activation. Among these, the catalytic ring expansion reactions of the strained silacycles, such as silacyclobutane, silacyclobutene, silarane and silarene, have been well established. In 1975, Sakurai and Imai [66] reported the first $\text{PdCl}_2(\text{PPh}_3)_2$ -catalyzed alkyne insertion of four-membered silacyclobutane **8** to form silacyclohexenes **54** (eq. (14)).



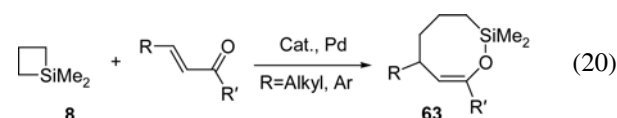
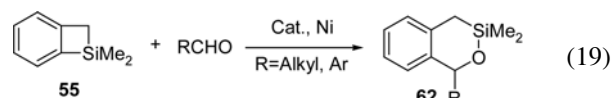
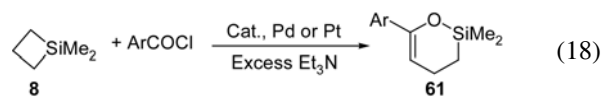
Scheme 9



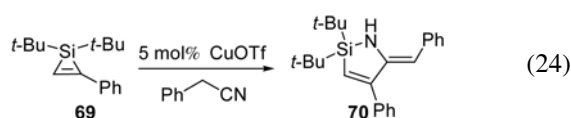
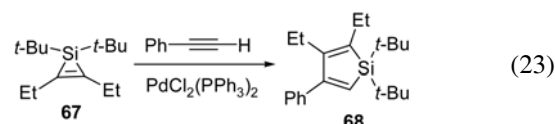
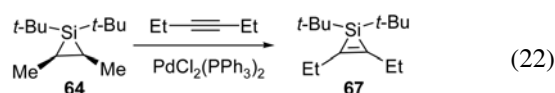
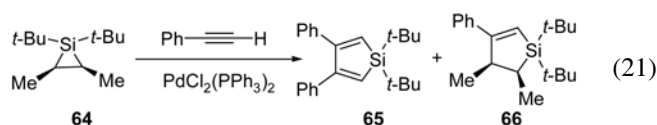
Utimoto, Oshima and co-workers [67] investigated the reaction mechanism for this alkyne insertion, and the insertion of Pd into Si-C bond to form a five-membered pallacycle was proposed as one of the key steps. A similar alkyne insertion with silacyclobutene was reported by them and also by Kende et al. [68]. In some cases, the insertion could proceed with high regioselectivity and the Si-Csp² bond was cleaved selectively (eq. (15)). A cobalt-catalyzed intramolecular ring-expansion of benzosilacyclobutene **57** with alkyne was reported later (eq. (16)) [69]. Based on their continuing research with silacyclobutene, Xi and co-workers [70] reported the first palladium-catalyzed electron-deficient alkyne insertion into silacyclobutene **59** to form silacyclohexadiene **60** (eq. (17)). Both electronic and steric factors played important roles in this insertion reaction.



In 1996, Tanaka et al. [71] reported palladium- and platinum-catalyzed C=O insertion reactions of silacyclobutanes with acid chlorides to give cyclic silyl enol ethers **61**. Excess amount of amine were added to remove the *in situ* formed HCl (eq. (18)). Oshima and co-workers [72,73] reported a nickel-catalyzed ring expansion reaction of benzosilacyclobutene **55** with aldehydes (eq. (19)) and a palladium-catalyzed transformation of silacyclobutane **8** into eight-membered cyclic silyl enolates **63** (eq. (20)).



Woerpel and co-workers [74] reported a series of transition metal-catalyzed ring transformations with strained three-membered silirane and silirene systems. Some of their work are highlighted here. Encouraged by their previous results with palladium-catalyzed silylene transfer reactions of *cis*-silirane **64** (eq. (21)), they developed a new palladium-catalyzed method to synthesize silirene **67** from internal alkyne (eq. (22)). Under the same conditions, this silirene can react with a monosubstituted acetylene further to produce trisubstituted silole **68** in high yield (eq. (23)). The experiment evidence proved that the transformation of silirane into silirene is the most favoured process [75]. They also developed a copper-catalyzed insertion of C≡N bond into the Si-C bond of silacyclopentene to provide azasilacyclopentadiene **70** (eq. (24)) [76]. They found the copper- or zinc-catalyzed reaction of silacyclopropanes with carbonyl compounds being highly stereo-, regio-, and chemoselective.

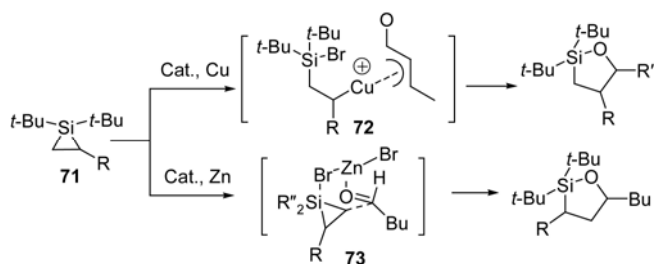


They found in the presence of different metals, this CO insertion reaction proceeded with different activation pathway. Zinc was believed to catalyze insertion of alkyl aldehydes through coordination and activation. While a transmetalation mechanism was proposed in copper-catalyzed α,β -unsaturated aldehydes insertion (Scheme 10) [77].

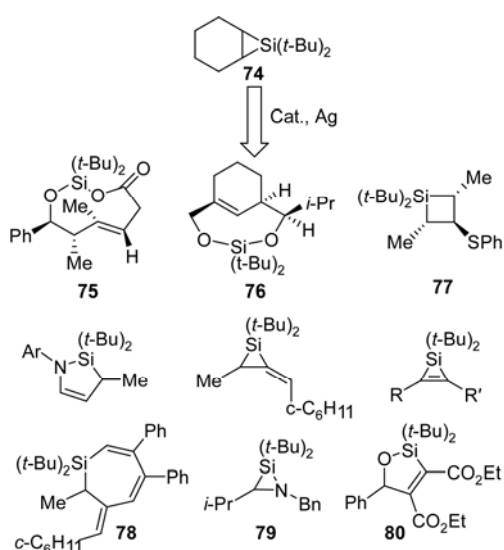
The application of silver-catalyzed silylene transfer reactions of cyclohexene silacyclopropane **74** is an important breakthrough. With this powerful and efficient silylene source, various silacycles (Scheme 11) were prepared with silver catalysts or a combination with zinc, copper, scandium, nickel or palladium catalysts. Silver was found to play a crucial role in the activation of cyclohexene-silacyclopropane. The most recent developments of this area were the formations of *trans*-dioxasilacyclononenes **75** [78] and *trans*-dioxasila-cyclooctenes **76** [79], the transformation of allylic sulfides into silacyclobutanes **77** [80], and the formation of silacycloheptadienes **78** [81].

Very recently, Chatani and co-workers [82] reported a rhodium-catalyzed cleavage of acyclic Si-Csp³ bond of trialkylsilyl group to form benzosiloles under very mild conditions. This is the first example to demonstrate that the robust trialkylsilyl group can be a useful silicon source for new silacycle formations (eq. (25)).

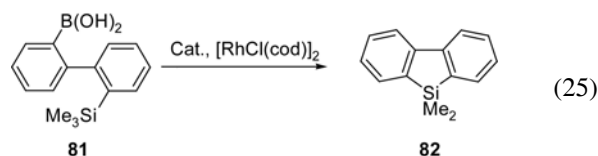
During their research with indole formation [83], Xi and



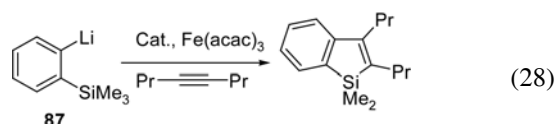
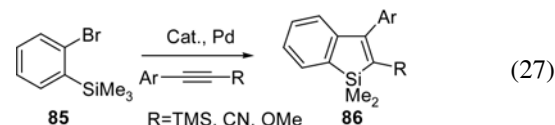
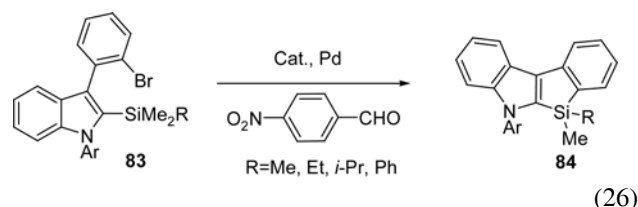
Scheme 10



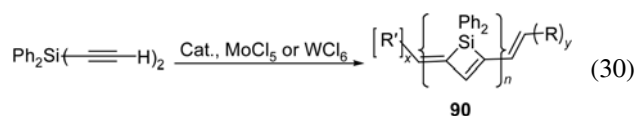
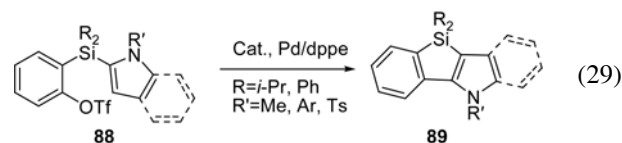
Scheme 11



co-workers [84] found benzosilolo[2,3-*b*]indoles **84** were formed as by-product. After optimization of the reaction conditions, they found the presence of aldehyde can improve the catalytic efficiency dramatically and the Si-Me bond can be cleaved with high chemoselectivity (eq. (26)). Very recently, an intermolecular domino reaction of 2-silylaryl bromides with alkynes to give benzosiloles **86** (eq. (27)) and heteroarene-fused diloles was developed. This provides a facile and efficient method for preparation of various functional siloles for optoelectronic and electronic materials [85,86]. An interesting iron-catalyzed aryllithiation and cyclolization of alkyne with *o*-(trimethylsilyl)phenyllithium **87** could provide benzosiloles as well (eq. (28)) [87].



Shimizu and co-workers [88] reported a novel palladium-catalyzed intramolecular coupling of 2-[(2-pyrrolyl)silyl] aryl triflates **88** through 1,2-Pd migration and 1,2-silicon migration. Most of the Si-bridged 2-phenylindoles exhibit strong and highly efficient blue fluorescence in the solid state (eq. (29)). The metal-catalyzed Si-C reconstruction can also be used to prepare polymers. Barton et al. [89] reported MoCl₅ or WCl₆ catalyzed skeletal rearrangement and polymerization of Si-tethered terminal diynes. One of the core structures of these deep colored polymer **90** is the silacyclobutene moiety (eq. (30)).



3 Summary and outlook

The purpose of this review has been to highlight the new method to synthesize silacycles. Halosilanes have played important roles in this area for long time, as can be seen from the cited examples, the metal catalyzed or mediated Si–C bond activation of stable and easily accessible silanes provide alternative methods to prepare various silacycles. Compared with metal catalyzed Si–C bond transformation of strained silacycles, the catalytic Si–C bond activation of acyclic silanes is less developed, and it is highly desirable to find more efficient catalysts for these transformations. The chemoselectivity between Si–Csp² and Si–Csp³ bonds may provide more interesting applications of Si–C activations in synthetic chemistry. From a mechanistic point of view, the pentaorganosilicate has been proposed as a key intermediate in some reactions, but more efforts are needed to understand these reactions. This fundamental research is often difficult to achieve but indispensable, for example, design more efficient catalytic systems and intermolecular activation of Si–C bonds of acyclic silanes. Exciting novel discoveries with Si–C activation are anticipated and certain to lead to novel applications in the organic synthesis and silicon-based materials.

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