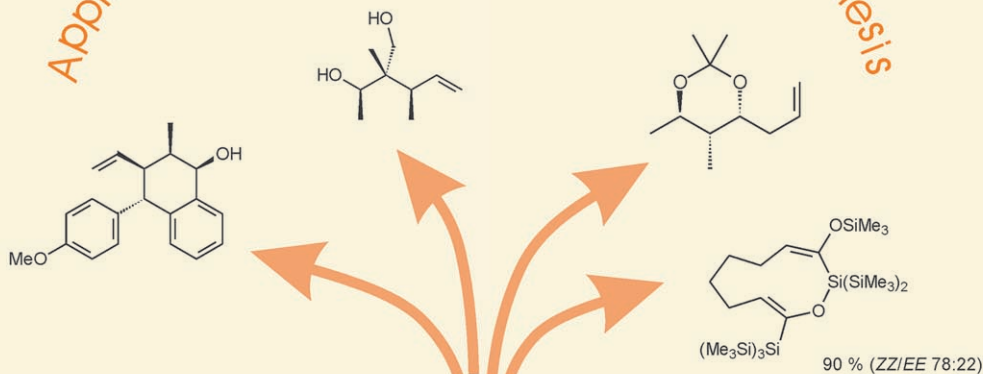


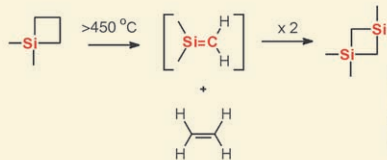
# Applications in stereocontrolled organic synthesis



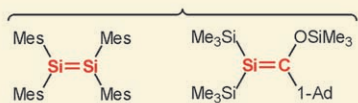
1912: First postulated formation of a Si=C bonded compound

1950s: The double-bond rule: Elements with a principal quantum number greater than 2 do not form  $p\pi-p\pi$  bonds

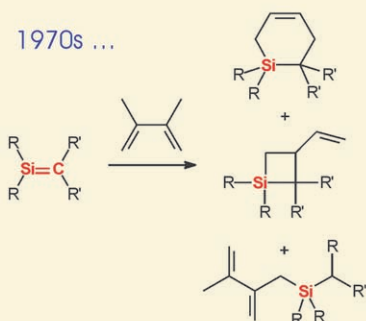
1967



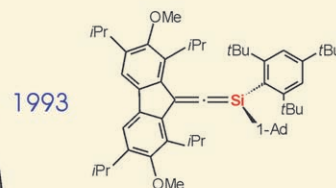
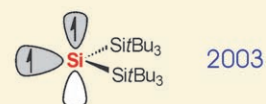
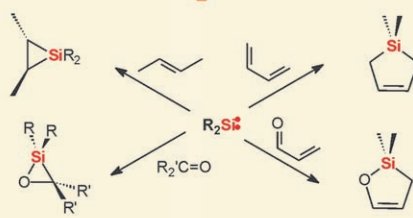
1981



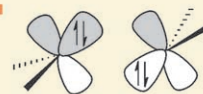
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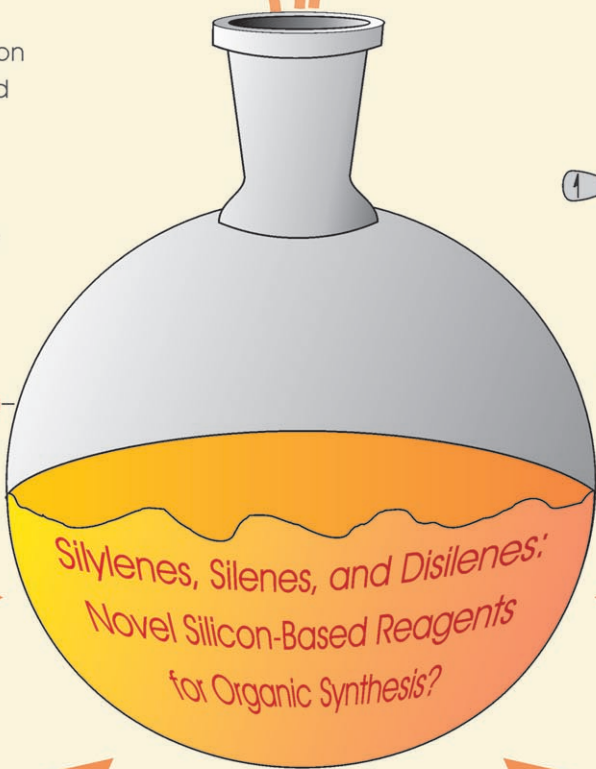
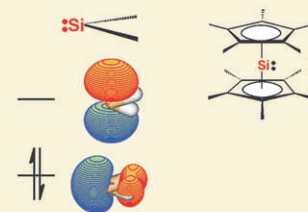


1980s: theory on bonding in heavy alkenes



Nonplanar structures when  $\Sigma\Delta E_{\text{ST}} > 1/2 E_{\sigma+\pi}$

1986



# Silylenes, Silenes, and Disilenes: Novel Silicon-Based Reagents for Organic Synthesis?

Henrik Ottosson\*<sup>[a]</sup> and Patrick G. Steel\*<sup>[b]</sup>

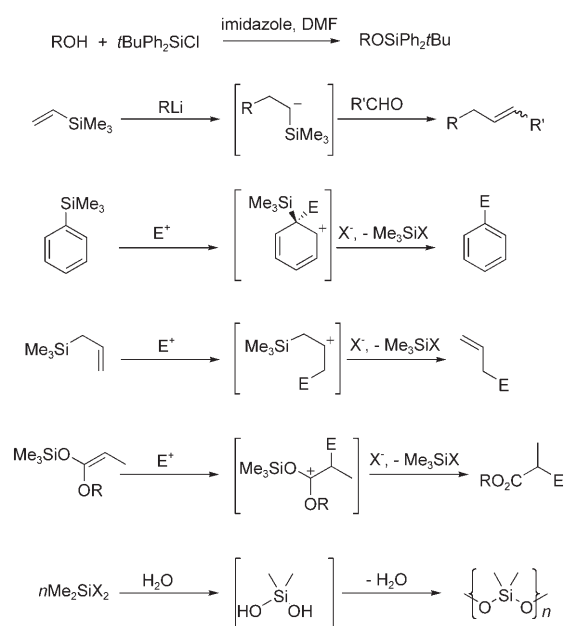
**Abstract:** Silylenes, silenes, and disilenes are silicon analogues of carbenes and alkenes. Since the first detection and isolation of these species a few decades ago, focus has been given to their fundamental structure and reactivity properties. Recent developments show that the time is set to exploit their unique chemistry in applied areas. Emerging applications in catalysis and stereoselective synthesis point to a new field within synthetic organosilicon chemistry.

**Keywords:** alkene homologues • carbene homologues • catalysis • silicon • stereoselectivity

## Introduction

Silicon-based reagents have found widespread use in organic synthesis.<sup>[1]</sup> Invariably these applications involve compounds containing a tetravalent silicon atom and exploit the ability of the silicon atom to undergo facile substitution reactions, enabling easy connections to be established, even between sterically bulky units; stabilise either an  $\alpha$ -carbanion or  $\beta$ -carbocation (allyl silane, silyl enol ether, aryl silane chemistry); and to form multiple silicon–oxygen bonds (polysiloxane chemistry), Scheme 1.

However, recent developments in silicon chemistry have led to the development of synthetic routes to stable or semi-

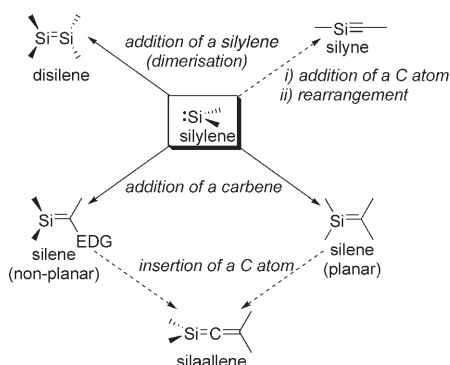


Scheme 1. Classical organosilicon synthesis.

stable low-coordinate silicon compounds, including silylenes, silenes and disilenes.<sup>[2]</sup> One way to display the interconnection of these various low-coordinate silicon compounds is centred on the silylene (Scheme 2), a divalent silicon species. Dimerisation affords a disilene whilst, formally, the addition of a divalent carbon (a carbene) to a silylene yields a silene, in which, depending on the substituents, the properties of the silicon atom range between that of a silyl cation and anion. The hypothetical addition of a carbon atom to a silylene yields a silavinylidene, a species that is isomeric to a silicon–carbon triple-bonded silyne whilst formal insertion of a C atom into a silene affords a sila-allene. Given their unique structure and reactivity, the chemistry of these low-coordinate silicon compounds has been an area of considerable activity. Whilst a detailed account of fundamental silene, disilene, and silylene chemistry is beyond the scope

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Scheme 2. Low-coordinate silicon species.

of a “concepts” paper this has been the subject of a number of recent review articles.<sup>[3–6]</sup>

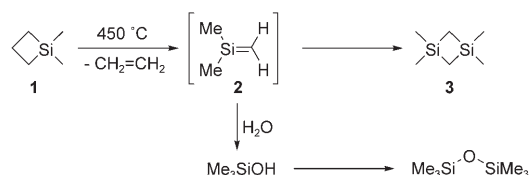
In contrast to classical tetracoordinate silicon compounds, which have relatively low reactivity, all of these species are highly reactive, normally formed only as transient intermediates and offer considerable advances for novel synthetic organic chemistry providing access to compounds that would otherwise be inaccessible. This concepts article will summarise recent developments in the fundamental chemistry of these compounds that demonstrate potential for exploitation in selective organic synthesis.

### Low-Coordinate Silicon—A Historical Overview

Following developments in classical carbon chemistry, organosilicon chemistry had its origins in the late 19th century with the synthesis of tetraethylsilane by Friedel and Crafts.<sup>[7]</sup> Subsequent to this, there was considerable efforts to extend this analogy to generation of multiple-bonded species containing Si=Si or Si=C bonds. The first “successful” attempt was claimed in 1912 when Schlenk and Renning reported the synthesis of a silene by dehydration of a silanol as evidenced by the release of water.<sup>[8]</sup> However, Kipping subsequently showed that the product was a siloxane and later concluded that multiple bonds to silicon were not a realistic objective.<sup>[9]</sup> This view was reinforced by the theoretical work of Pitzer and Mulliken which subsequently led to the formulation of the now discredited double bond rule which stated that elements with a principal quantum number greater than 2 do not form  $p\pi-p\pi$  bonds.<sup>[10,11]</sup>

The first evidence for the existence of silenes was established in 1967 when Gusel'nikov and Flowers reported silene generation as an intermediate during the pyrolysis of dimethylsilacyclobutane **1**.<sup>[12]</sup> The observed production of ethylene and 1,3-disilacyclobutane **3** were explained as arising from retro[2+2] cycloaddition to afford **2**, which then underwent [2+2] silene dimerisation, Scheme 3.

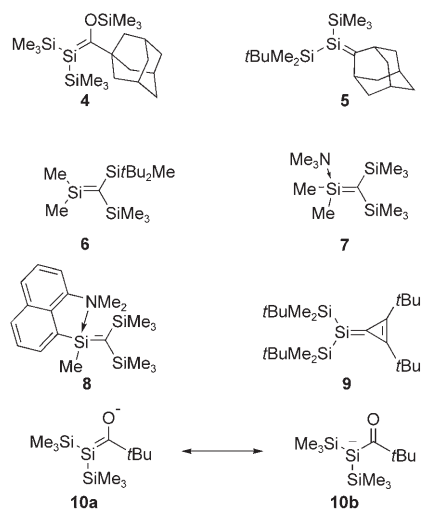
The next major development was the direct detection of silenes in an argon matrix at 8–20 K.<sup>[13–15]</sup> However, it was not until 1981 that Brook, who through investigations into the generation of silenes by photolysis of acylpolysilanes



Scheme 3. The Gusel'nikov and Flowers experiment.

had deduced that the steric bulk of the substituents on the carbon atom was a key factor in moderating their reactivity, ultimately reported the isolation of the stable silene **4** which could be characterised by X-ray diffraction.<sup>[16]</sup> Although, the silene is kinetically stable with regard to dimerisation it is still highly reactive in the presence of other reagents. For example, Brook reports that a sample of silene **4** is “unchanged after several years although if exposed to air disappears in a puff of smoke”.<sup>[17]</sup>

The concept of steric protection has become widely accepted and has been employed to generate a number of other isolable silenes (e.g. **5**,<sup>[18]</sup> **6**,<sup>[19]</sup> Scheme 4). Alternatively, the stability of the silene can be enhanced by providing an electron donor to stabilise the electrophilic silicon atom. This may be achieved either intermolecularly (**7**)<sup>[20,21]</sup> or intramolecularly (**8**).<sup>[22]</sup>

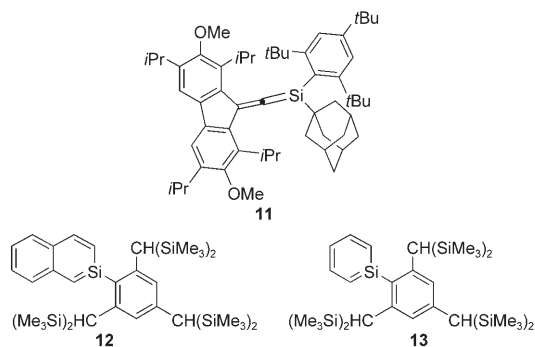


Scheme 4. Selected examples of stable silenes.

Increased stability is also realised with silenes influenced by reversed Si=C bond polarisation, that is, an  $Si^{\delta-}=C^{\delta+}$  instead of  $Si^{\delta+}=C^{\delta-}$  polarisation, effected by  $\pi$ -donor substituents on the carbon atom.<sup>[23]</sup> This leads to a lower release in energy upon dimerisation,<sup>[24]</sup> and slower reaction rates for addition of water and alcohols to the silenes.<sup>[25,26]</sup> Whilst the 2-siloxysilenes of Brook show this reversed Si=C bond polarisation effect, other examples are seen with the silatrifulvene **9**<sup>[27]</sup> and silenolates.<sup>[28,29]</sup> In particular, Ottosson has exemplified this concept in a recent report describing an isolable silenolate **10a** although, having a very long Si–C bond

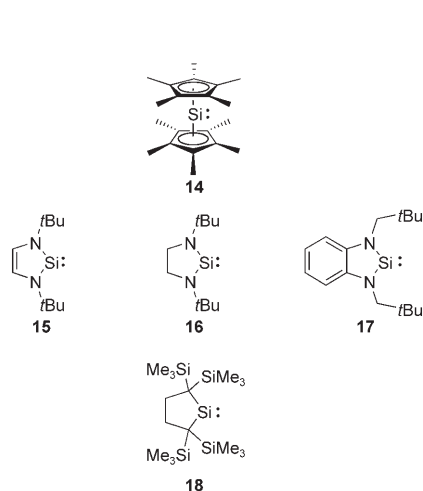
(1.926 Å), this is probably better described by the alternative resonance structure **10b**.<sup>[30]</sup>

Since Brook's first report of a stable silene, efforts have been made to extend this concept to conjugated and cumulated systems. Whilst stable 1-silaallenes **11**, have been known since 1993,<sup>[31]</sup> the first stable silaaromatics **12** and **13**



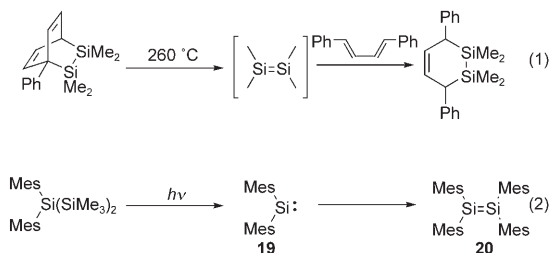
were only reported by Okazaki, Tokitoh and co-workers in 1997 and 2000, respectively.<sup>[32,33]</sup> Despite the increased stability offered by the gain in aromatic resonance energy these compounds still require steric protection, coordination by a transition metal (see Scheme 5), or further stabilisation through electron donation to the silicon atom to inhibit dimerisation.<sup>[34,35]</sup>

The development of "stable" disilene and silylene chemistry parallels that of silenes. In a similar fashion to that described above, silylenes were first identified as transient intermediates by Skell and Goldstein and subsequently spectroscopically characterised in an argon matrix by Michl and West.<sup>[36,37]</sup> The first stable silylenes were the silicocene **14**

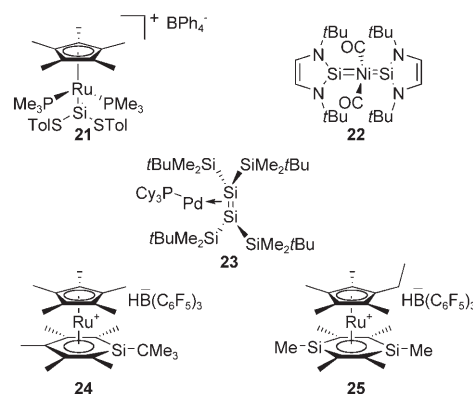


described by Jutzi<sup>[38,39]</sup> and the silicon analogues of N-heterocyclic carbenes (**15–17**) isolated by the West and Lappert/Gehrhuis groups.<sup>[40,41]</sup> More recently, in 1999, a sterically hindered isolable dialkylsilylene **18** was reported Kira.<sup>[42]</sup> As with silenes the stability of these with respect to dimerisation is dependent on steric bulk and to a lesser extent aromaticity for silylenes **15** and **17**.

The initial evidence that disilenes have a finite existence was provided by Peddle et al. through a pyrolysis and trapping experiment [Eq. (1)].<sup>[43]</sup> Although subsequent attempts to obtain matrix-isolated samples were not successful, warming of hydrocarbon matrix isolated dimesitylsilylene **19** allowed West, Fink, and Michl to afford the corresponding disilene **20** which could be structurally characterised by X-ray crystallography [Eq. (2)].<sup>[44]</sup> Subsequently, a significant number of other stable disilenes have been reported.



Whilst the predominant strategy for stabilisation of these low-coordinate silicon species has been based on steric inhibition of dimerisation, enhanced stability has also been realised through coordination to metal centres (see Scheme 5). Although complexes of all three classes of low-coordinate silicon species are known, this strategy is most commonly used for silylenes and it is pertinent to note that the first isolation of a silylene as an uncomplexed species was preceded by the preparation of transition-metal coordinated silylene complexes, first as a base-coordinated silylene complexes<sup>[45–47]</sup> and a few years later as the base-free complex **21**.<sup>[48a]</sup>

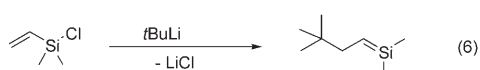
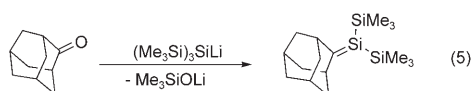
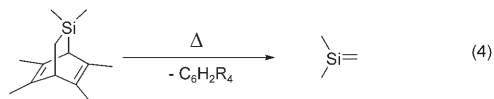
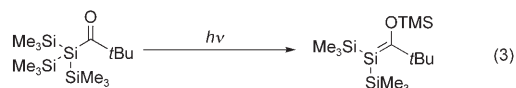


Scheme 5. Selected transition-metal-complexed low-coordinate silicon compounds.<sup>[48]</sup>

### Generation and General Reactivity of Low-Coordinate Silicon Compounds

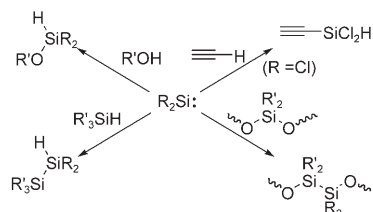
Based on the historical perspective it is not surprising to discover that methods for generation of silenes, disilenes and silylenes are commonly forcing in nature. Many of the earlier methods commonly involved thermolytic or photolytic induced fragmentations or rearrangements, particularly of

strained ring systems or other highly reactive precursors. Alternative methods, which avoid these high energy conditions, have been sought, notably those which involve irreversible elimination of stable salts. Illustrative methods for the generation of silenes are given in Equations (3)–(6).<sup>[49]</sup>



Similarly, as indicated by the efforts required to prepare stable examples of the various low-coordinate silicon species, these are all highly reactive species that commonly only have a transient existence. In the absence of a trapping reagent, unless kinetically stabilised as described in the previous section, these undergo rapid dimerisation. However, in the presence of other reagents these compounds exhibit a rich diversity of chemistry providing access to a range of substituted (cyclic) silanes not easily accessible by more classical methods.

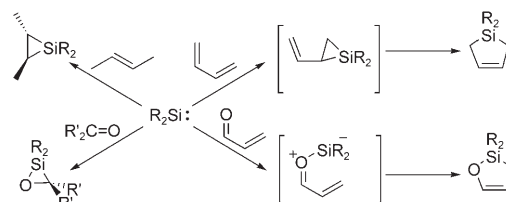
As with their carbon congeners, silylenes tend to react by either insertion into a  $\sigma$ -bond or addition to a  $\pi$ -bond.<sup>[5]</sup> Reflecting the fact that they have singlet ground states,<sup>[50]</sup> silylenes are electrophilic and thus insertion reactions tend to follow a nucleophilic addition–rearrangement pathway, Scheme 6. Insertion occurs readily with O–H, Si–H and O–Si bonds with relative ease but only reluctantly with C–H bonds.



Scheme 6. Insertion reactions of simple silylenes.<sup>[5]</sup>

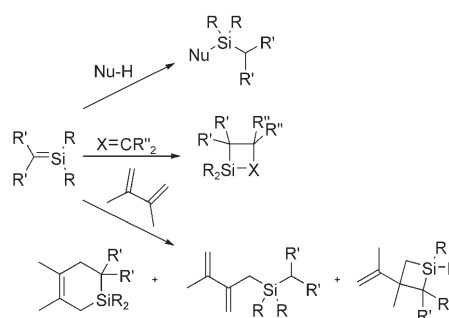
The greatest potential for this class of reagents is in their reactions with multiple bonds. With simple alkenes siliranes are formed whilst dienes afford silacyclopentenes via rearrangement of the initially formed vinylsilirane. In some

cases the initial siliranes are relatively unstable and can be used as a convenient source of silylenes for reactions with other alkenes, a process exploited elegantly by Woerpel (see section on Emerging Applications in Organic Synthesis). Addition to heteronuclear bonds is also known. Ketones initially afford siloxiranes and subsequently silyl enol ethers or siladioxolanes, whilst  $\alpha,\beta$ -unsaturated carbonyl compounds provide access to oxasilacyclopentenes via the intermediacy of an oxysilirane or silyloxy ylide (Scheme 7).



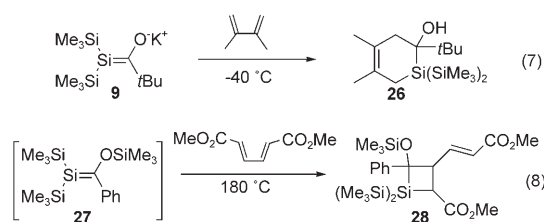
Scheme 7. Common addition reactions of free silylenes.<sup>[5]</sup>

The multiple-bonded species such as silenes and disilenes are particularly susceptible to attack by nucleophiles, particularly oxygen-based species (Scheme 8).<sup>[4]</sup> The exceptions to this observation are found in the highly reversed polarised



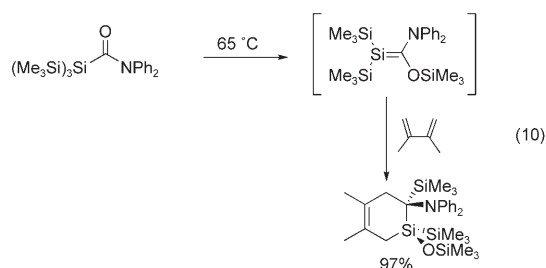
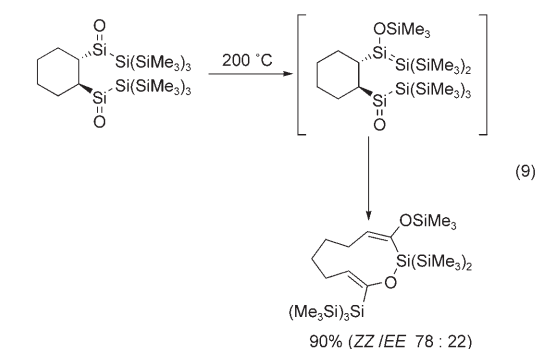
Scheme 8. Typical reactions of silenes.<sup>[3,4]</sup>

silanolates which undergo alkylation reactions with reactive electrophiles.<sup>[29]</sup> Whilst these addition processes can provide access to functionalised silanes and siloxanes they are primarily of fundamental interest and it is the varied cycloaddition chemistry that provides the principal attraction for the synthetic organic chemist. Alkenes, alkynes and ketones/imines undergo a [2+2] cycloaddition whilst dienes and  $\alpha,\beta$ -unsaturated carbonyl compounds normally follow a [4+2] pathway. However, with the latter substrates both ene and [2+2] products can also arise in variable amounts with the exact pathway followed being controlled by the steric and electronic demands of the silene. For example, highly reversed polarised silenes and silanolates undergo exclusive [4+2] cycloadditions [see Eq. (7)]<sup>[30,51]</sup> whilst the Brook-type siloxysilene **27** undergoes preferential [2+2] cycloaddition with the highly electron deficient diene, dimethylhexadienedioate [Eq. (8)].<sup>[52]</sup>



### Recent Developments in Fundamental Aspects of Low-Coordinate Silicon Compounds

In the years since the first isolation of stable low-coordinate silicon species there has been continuing efforts to generate new species. For example, the transient silyne generated by Apeloig and Schwarz,<sup>[53]</sup> and the formation of isolable disilyne, trisilaallene, and tetrasilabutadienes by the groups of Sekiguchi, Wiberg, Kira, and Weidenbruch.<sup>[54–56]</sup> Moreover new reaction pathways for these species continue to be developed including the silene oxy-Cope rearrangement reported by Ohshita [Eq. (9)]<sup>[57]</sup> and the tandem cycloaddition-rearrangement of the 2-amino-2-siloxysilenes of Ottosson [Eq. (10)].<sup>[58]</sup>



In a similar vein, since the first isolation of silylene complexes (section on Low-Coordinate Silicon), a large number of silylene transition-metal complexes have now been reported particularly those based on the stable N-heterocyclic silylenes pioneered by the West and Lappert/Gehrhuis groups.<sup>[59]</sup> The basic reactivity of these silylene complexes have been explored,<sup>[60]</sup> and applications in catalysis are now emerging.

Underpinning these discoveries has been a concomitant growth in the understanding of fundamental electronic

structures of low-coordinate silicon and the implications of these for rationalizing and predicting basic reactivity. For example, with the exception of the recently reported bis(tri-*tert*-butylsilyl)silylene of Sekiguchi and co-workers which by EPR measurements has a triplet ground state,<sup>[61]</sup> and in contrast to carbenes, silylenes have singlet multiplicity ground states. This observation has been examined by Apeloig through a quantum chemical decomposition of the singlet-triplet energy gaps ( $\Delta E_{\text{ST}}$ ) of  $\text{SiH}_2$  and  $\text{CH}_2$ .<sup>[50]</sup> It was found that the major part ( $\sim 60\%$ ) of the difference is attributed to variation in electron–electron repulsion between the two frontier orbital electrons of the two species.<sup>[50]</sup> Dimerisation of silylenes yields disilenes, and the structural features of these species are closely connected to the electronic nature of silylenes. For example, the first disilene formed, tetramesityldisilene, exhibits conformational polymorphism with two of the four possible conformers being nonplanar with pyramidal Si atoms.<sup>[62]</sup> Such nonplanar (nonclassical) alkene structures can be rationalised by the theory of Carter, Goddard, Malrieu, and Trinquier,<sup>[63–66]</sup> which relates the structural features to the sum of the singlet–triplet energy gaps of the two interacting silylenes ( $\Sigma\Delta E_{\text{ST}}$ ). The most favourable orbital interaction between two singlet silylenes occurs at nonclassical bent structures, whereas the most favourable interaction between two triplet silylenes leads to a planar structure. Indeed, disilenes are on the borderline between classical planar and nonclassical nonplanar structures and small structural changes, for example, rotation of the mesityl substituents in tetramesityldisilene, enforce a change in the Si=Si bond. This ability of substituents to influence the structural features of the Si=Si bond has been probed through quantum chemical calculations and an excellent correlation between  $\Sigma\Delta E_{\text{ST}}$  and pyramidalisation angles as well as Si=Si bond length was found.<sup>[67]</sup>

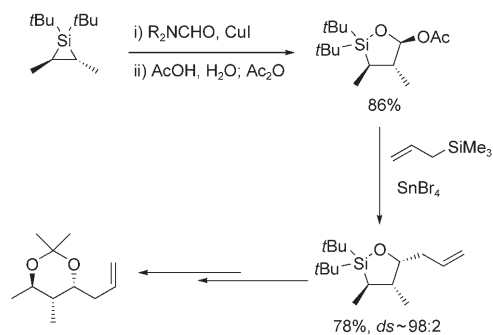
In a related fashion, the bonding in silenes can be related to the singlet multiplicity of silylenes. Ottosson showed that silenes adopt a pyramidal structure at Si when  $\Sigma\Delta E_{\text{ST}}$  exceeds a threshold, and that there is a correlation between the  $\Sigma\Delta E_{\text{ST}}$  and the charge at Si ( $q(\text{Si})$ ). This finding connects the CGMT theory on bonding in heavy alkenes to the reverse Si=C bond polarisation effect of Apeloig and Karni.<sup>[23]</sup> Such reverse Si=C bond polarisation, that is,  $\text{Si}^{\delta-}=\text{C}^{\delta+}$  instead of the natural  $\text{Si}^{\delta+}=\text{C}^{\delta-}$ , is effected through  $\pi$ -donor groups at the C atom ( $\text{OR} < \text{NR}_2 < \text{O}^-$ ) and is suggested to be the single most important electronic factor to influence the reactivity of silenes. Through reverse polarisation negative charge is pushed to Si making this centre less electrophilic and leading to silenes that react more selectively with dienes. Such predictions are supported by observations that transient 2-amino-2-siloxysilenes, 4-silatriafulvenes and lithium silenolates all provide exclusive [4+2] cycloaddition products on reaction with dienes.<sup>[27,51,58]</sup> Furthermore, recent X-ray structural investigation of Ottosson revealed that silenolates are strongly influenced by the resonance structure with negative charge placed at Si.<sup>[30]</sup> Therefore, silenolates are closely related to silyl anions, species with a markedly pyramidal and hence potentially chiral silicon centre.<sup>[68,69]</sup>

Consequently, Ottosson has predicted, based on quantum chemical calculations, that ultimately these silenes may be designed with Si as a chiral centre thereby enabling enantioselective synthetic transformations to be achieved.<sup>[24]</sup>

### Emerging Applications in Organic Synthesis

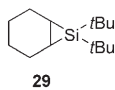
As discussed above, the area of low-coordinate silicon compounds continues to expand. However, this on-going advance in fundamental knowledge has been accompanied neither by a related exploitation of the potential of these reagents in organic synthesis nor for the generation of novel silicon substituted compounds. Such a study is particularly timely as, in recent years, there has been a growing recognition that incorporation of silicon into bioactive molecules can provide distinct advantages in terms of higher activity and better pharmacokinetic profiles.<sup>[70,71]</sup> However, a limitation in exploiting such an approach has been access to complex silicon containing structures with good levels of stereocontrol. Recently these opportunities have begun to be recognised with silylene, metal silylene complexes and silenes all finding applications in synthesis, providing access to novel silanes and siloxanes and enabling new synthetic organic transformations to be realised.

Building on the seminal publications of Seyferth,<sup>[72]</sup> Ando,<sup>[73]</sup> Weidenbruch<sup>[74]</sup> and others, Woerpel has demonstrated that siliranes (silacyclopropanes) formed by addition of silylenes to alkenes undergo a range of synthetically useful transformations, see Scheme 9.<sup>[75]</sup>

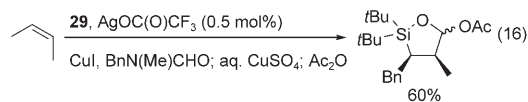
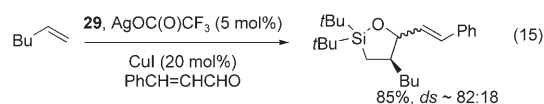
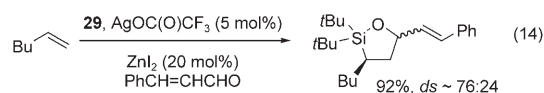
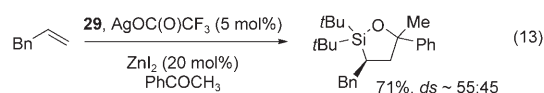
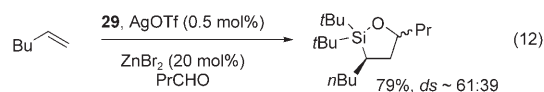
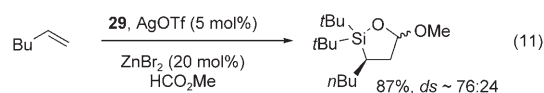


Scheme 9. Applications of siliranes in organic synthesis.

One restriction to this chemistry was the limited methods for the generation of silylenes and hence alternative silirane starting materials. Classically the generation of silylenes requires elevated temperatures, strongly reducing conditions or photolysis which limits the functional groups that can be tolerated. This problem has been recently addressed by Woerpel who has developed an efficient catalytic silylene-transfer process, from readily accessible cyclohexene silirane **29**, promoted by silver salts.<sup>[76,77]</sup> This new reaction is efficient, stereospecific with respect to alkene geometry,



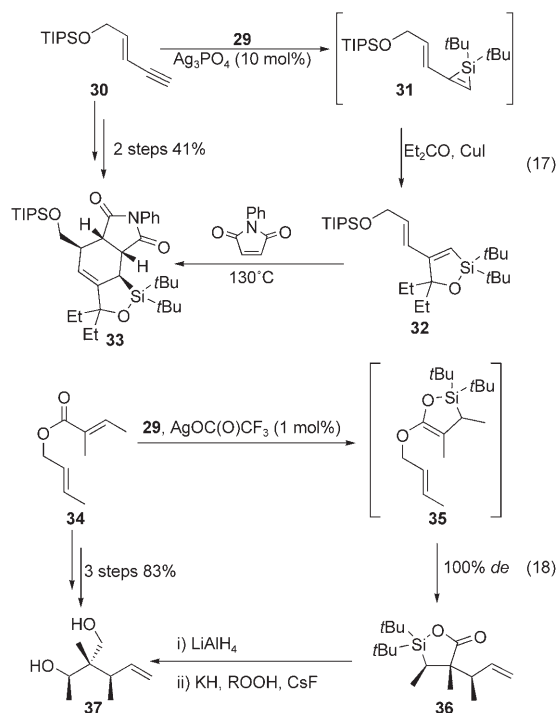
and compatible with aryl, benzyl and silyl ethers and non enolisable esters. Although the silirane products can be isolated in good yields and high diastereoselectivity from unsymmetrical alkenes, their air sensitive nature can complicate handling. This difficulty can be avoided through an in situ metal-catalysed insertion of carbonyl compounds to give oxasilacyclopentanes which represent useful building blocks for further synthetic transformations [Eqs. (11)–(16)].



In contrast to the thermal silylene-transfer reactions involving free silylenes, these silver-catalysed processes [Eqs. (11)–(16)] are postulated to proceed via a silver silylenoid species.<sup>[78]</sup>

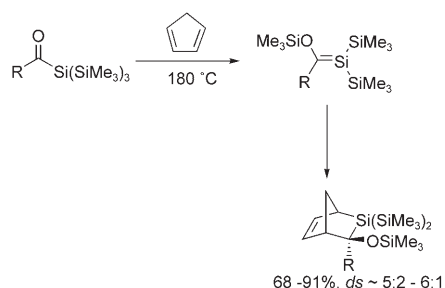
Extension of the silver promoted silylene addition chemistry to alkynes afford silacyclopropenes **31** which undergo carbonyl insertion reactions to provide 1-oxa-2-silacyclopent-3-enes **32**.<sup>[79]</sup> Alternatively, the isomeric 2-oxa-1-silacyclopent-3-enes **35** are generated via additions to  $\alpha,\beta$ -unsaturated carbonyl compounds and silylenol ethers from enolisable carbonyl compounds.<sup>[80]</sup> Both products are versatile intermediates that can be converted into highly functionalised building blocks containing multiple stereocentres in relatively few steps. For example, alkyne addition products lead to the synthesis of allylic alcohols, diols and complex polysilacycles [Eq. (17)] whilst a tandem silylene insertion reaction/Ireland–Claisen rearrangement of allylester **34** provides diol **37** with three contiguous chiral centres including a quaternary centre with high levels of stereocontrol [Eq. (18)].

Transition-metal silylene complexes have been postulated to play roles in a series of catalytic and stoichiometric processes and this has led to the development of new synthetic applications.<sup>[81]</sup> For example, Glaser and Tilley have de-



scribed a new catalytic hydrosilylation of alkenes involving a ruthenium silylene complex,<sup>[82]</sup> and, exploiting the fact that N-heterocyclic silylenes of West and others have similar ligand properties as triarylphosphines and classical NHC, Fürstner has shown that a binuclear Pd<sup>0</sup> complex with bridging N-heterocyclic silylene ligands catalyses Suzuki couplings of aryl boronic acids with bromoarenes in high yields.<sup>[83]</sup>

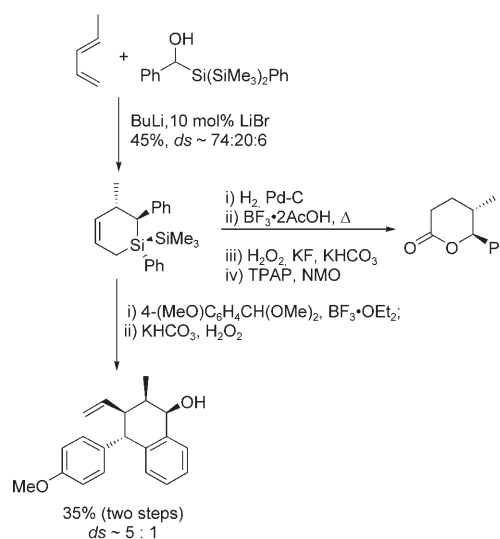
The chemistry of silenes is equally diverse but as yet is much less well explored. Earlier reports have shown that simple siloxysilenes undergo thermal Diels–Alder reactions with electron rich dienes with moderate diastereoselectivity (Scheme 10).<sup>[84]</sup>



Scheme 10. Diastereoselectivity in siloxysilene cycloaddition.

As with the silylene chemistry discussed above, the general applicability of such an approach is limited by the high temperature requirements. More recent studies by Steel have shown that anionic generation of silenes and silenolates avoids these difficulties and enables the cycloadducts

to be generated in good yields and selectivities. As with the silylene adducts, these products are not only structurally complex silanes in their own right but provide access to functionalised molecules in relatively few steps. For example, successive reduction of the alkene and Fleming–Tamao oxidation affords substituted valerolactones, whilst exploiting the latent allylsilane unit in a Lewis acid mediated Sakurai reaction affords molecules with four contiguous chiral centres with good to moderate diastereoselectivity (Scheme 11).<sup>[85,86]</sup>



Scheme 11. Stereoselective synthesis with silenes.

## Conclusions and Future Prospects

Low-coordinate silicon reagents, particularly silylenes and silenes, represent a significantly under-explored class of reagents for alkene, alkyne and carbonyl group functionalisation. Recent work, highlighted above, has illustrated the potential of this methodology for the generation of new organosilanes. Moreover, the selective and efficient cycloaddition chemistry of silylenes and silenes provides facile routes to structurally complex silacyclic compounds that can not only support a growing silapharmaceutical industry but also function as versatile starting materials for the synthesis of polyfunctional molecules. Given the modular nature of the reaction schemes such a strategy represents a particularly powerful method for the generation of diverse structural motifs. The future applications of low-coordinate silicon systems in synthesis will undoubtedly build on these beginnings.

Future drivers of progress in this field will involve the development of new milder (catalytic) methods of silylene and silene generation combined with new stereoselective and enantioselective reactions of both these reagents and the transformations of the initial cycloadducts. Similarly it is reasonable to expect that metal stabilised low-coordinate sil-



icon species will play an increasing role in catalysis and synthesis.

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