1. INTRODUCTION

1.1 Low-coordinated silicon compounds

1.1.1 Silylenes

Silylenes are divalent neutral silicon species which are the heavier analogues of carbenes. Depending on the substituents, carbenes can be either in a singlet or triplet ground state, while silylenes in general have a singlet ground state. As a representative example, the parent carbene $:CH_2$ exists in a $^3B_1$ triplet ground state with two unpaired electrons (Figure 1) and in comparison, the ground state of the parent silylene $:SiH_2$ is the closed shell $^1A_1$ singlet with both electrons occupying the low energy s orbital. The difference has been attributed to the larger HOMO-LUMO gap for $:SiH_2$ (218 kJ mol^{-1}) than that of $:CH_2$ (113 kJ mol^{-1}).[1] For $:SiH_2$, the energy gained in forming a triplet configuration is not enough to compensate the large HOMO-LUMO separation. The first remarkable example of a triplet silylene is the bis(tri-*tert*-butylsilyl)silylene which was observed in 2003 by Sekiguchi in low-temperature matrix.[2]

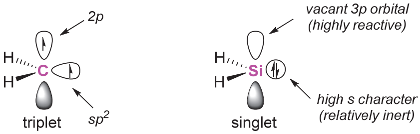


Figure 1. The different electronic ground states of the parent carbene and silylene.

Due to the presence of a lone pair of electrons (HOMO) and a vacant 3p orbital (LUMO), silylenes can behave both as Lewis base and Lewis acid, thus showing ambiphilic character.[3] For a long time, silylenes have been considered as transient intermediates which could be only detected by chemical trapping reactions or in cryogenic matrices ($\leq$ 77 K).[4] At higher temperatures, this reactive species undergoes rapid dimerization or polymerization.

Therefore, to isolate stable silylenes under ambient conditions, sufficient thermodynamic and/or kinetic stabilization are essential (Figure 2).[5] The thermodynamic stabilization relies on the adjacent heteroatom substituents which influence the electronic properties of the silylene. Electron-withdrawing substituents such as N or O can lower the HOMO energy *via* inductive stabilization and as π-donor groups they can donate electrons into the vacant 3p orbital (LUMO) and reduce the electrophilic nature of the Si(II) *via* mesomeric stabilization.

Conversely, electropositive substituents such as silyl, boryl or alkali metals decrease the orbital separations and the triplet ground state is preferred. The kinetic stabilization is achieved by introducing bulky substituents around the silicon atom which can prevent the molecule from self-oligomerization or attack by nucleophiles.

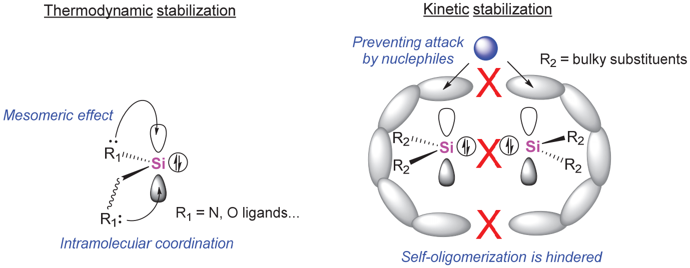
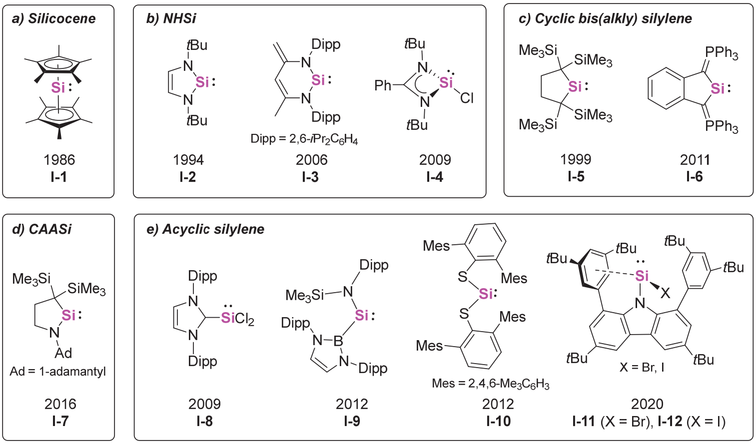


Figure 2. The thermodynamic and kinetic stabilization of silylenes.

By taking advantage of the stabilization strategies, the breakthrough came in 1986 when Jutzi and co-workers isolated the first room temperature stable Si(II) species, decamethylsilicocene (**I-1**, Figure 3), in which the silicon center is stabilized by η^5-coordination of the two Cp* (η^5-C_5Me_5) ligands.[6] However, because of the hypercoodinate nature of the silicon center, it cannot be considered as a dicoordinated silylene species. Following the synthesis of the first N-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991,[7] the group of West isolated the first dicoordinated silylene in 1994, the "*Arduengo-type*" N-heterocyclic silylene (NHSi) **I-2**.[8] This five-membered heterocyclic silylene was synthesized by reduction of the corresponding dichlorosilane with elemental potassium. The silicon atom is stabilized by the two π-donating amino groups and the bulky *tert*-butyl substituents. It has remarkable thermal stability and does not even decompose at 150 °C in toluene. The overall 6π-electron aromatic character of **I-2** offers additional stabilization effect. The isolation of the first NHSi is a milestone in silylene chemistry and since then a large number of stable silylenes have been isolated and structurally characterized.[9] They have been employed in a great variety of chemical processes such as transition metal-mediated catalysis and small molecule activation.[10] Among all isolated silylenes, NHSis are the most studied ones. Beside five membered NHSis with different substitution patterns, four- and six-membered NHSis have also been isolated. In 2006, the group of Driess reported the first six-membered NHSi **I-3** that incorporate a modified β-diketiminato (NacNac) backbone by reduction of the respective dibromosilane with KC_8.[11] The zwitterionic resonance structure indicates that both the Si(II) and the methylene carbon are nucleophilic, therefore **I-3** displays ambivalent reactivity.


a) Silicocene

b) NHSi

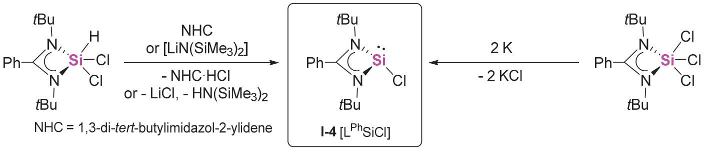
c) Cyclic bis(alkly) silylene

d) CAASi

e) Acyclic silylene

Figure 3. Selected examples of isolable silylenes.

In the same year, the group of H. W. Roesky reported the first example of a four-membered NHSi, the three-coordinated chlorosilylene [$L^{Ph}SiCl$] (L^{Ph} = PhC(N*t*Bu)$_2$, **I-4**), stabilized by an amidinato ligand.[12] It was prepared by reduction of the corresponding trichlorosilane [$L^{Ph}SiCl_3$] with elemental potassium in very low yield (10%) (Scheme 1). In 2010, the same group published an alternative high yield route by dehydrochlorination of [$L^{Ph}SiHCl_2$] with either [LiN(SiMe$_3$)$_2$] or NHC (1,3-di-*tert*-butylimidazol-2-ylidene).[13] This high yield access to [$L^{Ph}SiCl$] in gram-scale enabled further studies of it as ligand in coordination chemistry and other related ligand systems have been designed by easy substitution of the chlorine atom by other monoanionic functional groups.[14]

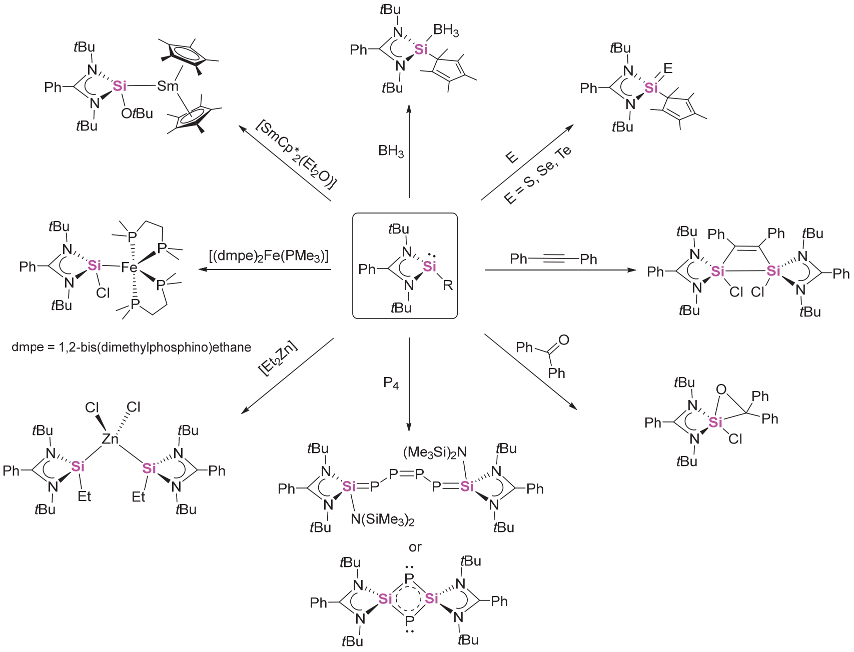


Scheme 1. Different approaches of the four-membered NHSi **I-4**.

Cyclic silylenes are dominated by NHSis, two-coordinated cyclic alkyl silylenes remain relatively scarce. In 1999, the group of Kira reported the first carbocyclic bis(alkyl) silylene **I-5** which is kinetically stabilized by the four bulky trimethylsilyl (TMS) groups on the carbon atom adjusted to the Si(II) center,[15] showing that silylenes can also be stabilized without π-donors. However, this silylene can only be stored at 0 °C in solid state and easily isomerizes in solution *via* 1,2-migration of one TMS group to form the corresponding silene derivate. The thermally unstable nature of the silylene **I-5** has limited further reactivity studies. Another carbocyclic example **I-6** was reported in 2011 by the group of Driess,[16] where the silylene center is stabilized by two phosphorus-ylide moieties with considerable aromatic character. More recently, the silicon analogue **I-7** of Bertrand's cyclic alkyl amino carbenes (CAACs) has been successfully isolated by the group of Iwamoto, in which the silicon is dicoordinated by one amino group and another alkyl group.[17] Compared to the bis(alkyl) analogue **I-5**, **I-7** exhibits a much higher thermal stability and does not decompose at 150 °C for two days, revealing that the π-donor/σ-acceptor character of one amino substituent is sufficient to stabilize the Si(II) center.

Apart from these cyclic silylenes, diverse acyclic silylenes have also appeared in the literature. Already in 2003, the group of West reported the synthesis of the acyclic bis(amido) silylene $[Si\{N(SiMe_3)_2\}_2]$ by reduction of $[Br_2Si\{N(SiMe_3)_2\}_2]$ with KC_8.[18] However, this species is only persistent for about 12 h at –20 °C and no X-ray diffraction analysis could be performed. In 2009, the group of H. W. Roesky reported an NHC-stabilized three-coordinate acyclic dichlorosilylene **I-8**. The real breakthrough came in 2012 when the first examples of two-coordinate acyclic silylenes **I-9** and **I-10** have been isolated and structurally characterized by the group of Aldridge and Power, respectively.[19] The boryl-substituted silylene **I-9** was obtained through the reaction of the respective tribromo(amino)silane with two equivalents of the boryllithium reagent. Due to the presence of the electropositive σ-donating boryl substituent and the relatively widened N–Si–B angle (109.7°), the HOMO-LUMO energy gap is narrower and the silylene is capable of activating H_2 to form the corresponding dihydrosilane. Power's bis(arylthiolato) silylene **I-10** was synthesized by reduction of the dibromo Si(IV) precursor with Jones' Mg(I) dimer. The narrow S–Si–S angle (90.5°) and the high electronegativity of the S substituents increase the HOMO-LUMO energy gap ($\Delta E_{S,T}$ = 4.26 eV), therefore the reaction with H_2 is hampered. In 2020, the base-free bromo- and iodosilylenes **I-11** and **I-12** were isolated,[20] which are stabilized by a bulky carbazole scaffold.[20] Halide abstraction of the iodosilylene **I-12** using a silver salt of a weakly coordinating anion (WCA) led to the formation of the first example of a monocoordinated Si(II) cation.

While a great variety of cyclic and acyclic silylenes have been isolated, considerable attention has been devoted on their reactivity studies. Due to their ambiphilic character, silylenes show diverse reactivity such as insertion, cycloaddition, oxidation and coordination reactions.[5] Representative examples of the reactions of amidinatosilylenes are summarized in Scheme 2. As a Lewis base, they can coordinate to Lewis acids such as metal centers and BH_3.[21] The low-valent Si(II) center can be oxidized by elemental chalcogens forming stable Si=E double bonds,[21] or by P_4 to form exotic polyphosphides. Moreover, reactions with non-saturated organic substrates such as azides, alkynes and carbonyl species, or with polarized C-X bonds are also well established. A variety of transition-metal silylene complexes have been isolated and utilized in catalytic transformations. According to the HSAB (hard and soft Lewis acids and bases) concept,[22] silylenes are considered as soft donors thus preferring to coordinate to soft metal centers, hard Lewis acids such as lanthanides are unfavored and such complexes are relatively rare.



Scheme 2. Different reactivities of the amidinatosilylenes $[L^{Ph}SiR]$ (R = Cl, $N(SiMe_3)_2$, OtBu or C_5Me_5).

Depending on the number and type of donor sites, silylenes can be classified in different categories (Figure 4): a) monodentate silylenes that contain only a Si(II) σ-donor; b) bidentate silylenes which have one Si(II)-donor and another non-silylene donor group (**I-13–I-16**); c) pincer-type bis(NHSis) with two silylenes separated by a spacer (**I-17–I-21**).[14a]

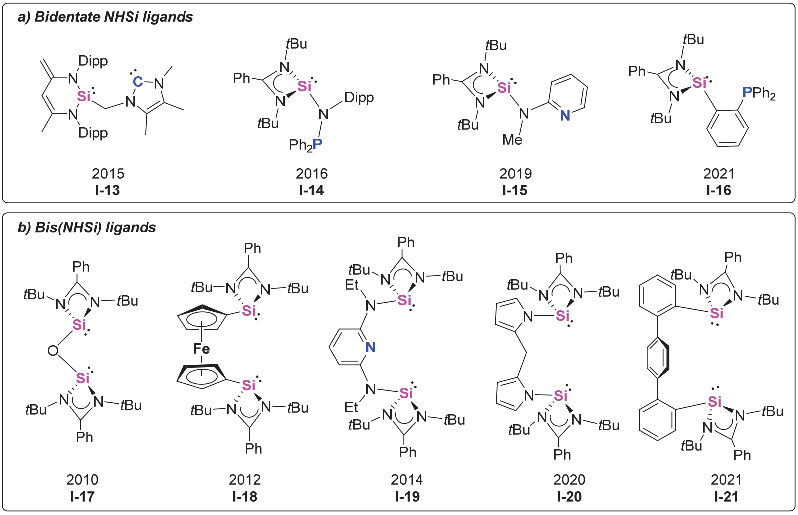
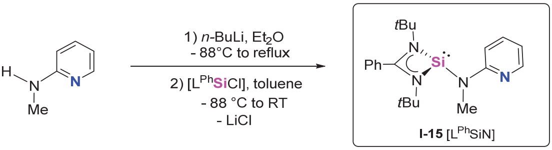


Figure 4. Selected examples of isolable bidentate NHSi ligands and bis(NHSi) ligands.

Bidentate silylene ligands with an additional NHC (**I-13**), phosphine (**I-14**, **I-16**) or pyridine (**1-15**) donor ligand are well established. The largest family of such bidentate silylenes are composed of one amidinatosilylene donor due to the easy metathesis reaction from the chlorosilylene and suitable metalated species. One outstanding example is the pyridyl-amido-silylene **I-15** ([L^{Ph}SiN], N = {(NMe)(2-py)}), which was synthesized by deprotonation of the *N*-methyl-2-pyridinamine with *n*-BuLi and subsequent metathesis reaction with [L^{Ph}SiCl] in relatively high yield (88%).[23] This bidentate ligand was later used as ligand for an iron hydride catalyst for the hydroboration of a series of ketones and aldehydes.

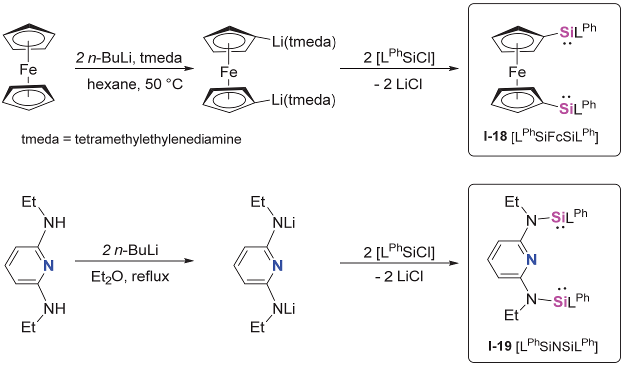


Scheme 3. Synthesis of the bidentate pyridyl-amido-silylene [L^{Ph}SiN] (**I-15**).

In the past few years, the chemistry of multidentate bis(NHSi) ligands with two amidinatosilylenes and a bridging spacer has been developed by the group of Driess (Figure 4). Most of them were synthesized *via* a straightforward salt metathesis from the corresponding doubly lithiated species. Having two Si(II)-donors in a single molecule, such electron-rich systems were initially employed as chelating ligands in metal-mediated catalysis.[10,14a] Furthermore, it was found that those bis(NHSi) ligands stabilize main group elements in extremely low oxidation states such as zero-valent single Si, Ge and Sn atoms.[24] Recent work has extended the use of such bis(NHSis) in the area of small molecule activation.[25] The existence of two silylene moieties in one molecule has allowed the cooperative activation of simple gaseous molecules such as CO and CO_2,[26] leading to unprecedented structural motifs that could not be achieved by using a mono(NHSi).

For example, one of the well-established bis(NHSi) ligands is the ferrocenediyl-bridged **I-18** ([$L^{Ph}SiFcSiL^{Ph}$], Fc = 1,1'-ferrocenediyl).[27] It was synthesized from 1,1'-dilithioferrocene and [$L^{Ph}SiCl$] in 70% yield (Scheme 4) and initially coordinated to a [CoCp] (Cp = η^5-C_5H_5) moiety or reacted with [$CoCp(CO_2)$] forming the Co(I) complexes [$L^{Ph}SiFcSiL^{Ph}$-CoCp] or [$L^{Ph}SiFcSiL^{Ph}$-{$CoCp(CO)$}$_2$]. The former one has been proven to be catalytically active in [2+2+2] cycloaddition reactions of phenylacetylene and acetonitrile. Other Fe(0) η^6-arene complexes stabilized by [$L^{Ph}SiFcSiL^{Ph}$] were isolated and applied in the hydrogenation of unsaturated organic substrates.[28] Furthermore, the reaction of [$L^{Ph}SiFcSiL^{Ph}$] and BPh_3 yielded the corresponding bis(silylene)-borane Lewis adduct that is capable of further activating CO_2.[29] Reductive homocoupling of two CO molecules and further transformation of NH_3 and primary amines to acetamides was also achieved using the same bis(NHSi) **I-18**.[26a,26c]

The bis(amido)pyridine-bridged bis(NHSi) **I-19** ([$L^{Ph}SiNSiL^{Ph}$], N = 2,6-di(ethylamido)pyridine) was synthesized in 2014 by reaction of the doubly lithiated precursor with [$L^{Ph}SiCl$] (Scheme 4) and utilized in the stabilization of an Fe(0) complex for hydrosilylation of ketones.[30] The same ligand was later on employed to support Co- and Mn-mediated catalysis.[31]

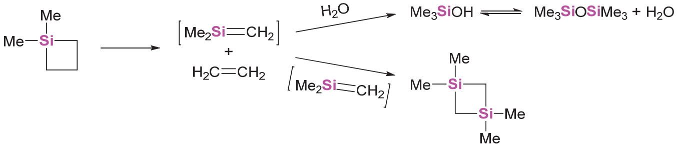


Scheme 4. Synthesis of bis(NHSis) **I-18** and **I-19**.

1.1.2 Silenes

In organic chemistry, stable carbon-containing multiple-bonded species such as alkenes and alkynes contribute greatly to varied reactivity. Those unsaturated organic molecules play an important role as building block and functional moiety in almost all areas in chemistry and material science. In sharp contrast, silicon compounds containing multiple bonds present much lower thermodynamic stability.[32] Already in the late 19th century, the pioneer organosilicon chemist Kipping carried out extensive attempts to synthesize silicon analogues of alkenes. He believed that he isolated [$Ph_2Si{=}SiPh_2$] by reduction of diphenyl dichlorosilane with elemental sodium.[33] However, the isolated products were later proved to be a mixture of singly bonded silicon-containing oligomers and polymers. Meanwhile, similar negative results were obtained by others in the synthesis of multi-bonded compounds with P, Ge, As or Sb. As a consequence, it was concluded that p-block elements with a principal quantum number greater than two could not form stable double bonds with themselves or with other elements.[34] This concept was known as the "double-bond rule" and had been accepted for several decades.

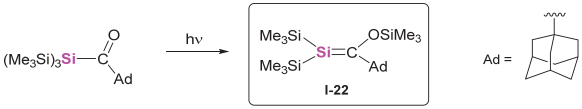
Silenes are compounds with Si=C double bonds. The high reactivity of silenes arises from their strongly polarized $Si^{\delta+}{=}C^{\delta-}$ π-bonds. Based on Pauling electronegativity scale, Si has a considerably lower electronegativity (1.90) than carbon (2.55).[35] Therefore, the Si=C bond is polarized toward the carbon atom and the silicon atom presents the electrophilic side. In 1967, Gusel'nikov and Flowers provided the first convincing evidence of the existence of a “transient silene" by the gas-phase thermal decomposition of 1,1-dimethyl-1-silacyclobutane, giving ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane as products.[36] The latter one arose from the head-to-tail dimerization of the transiently formed 1,1-dimethylsilaethene [$Me_2Si{=}CH_2$] (Scheme 5). In the same work, water was added as trapping reagent in the pyrolysis process affording ethylene, trimethylsilanol and hexamethyldisiloxane. A few years later in a report of Sommer, further convincing evidence of the transient existence of the silene [$Me_2Si{=}CH_2$] was provided by using other suitable trapping reagents.[37] For a long time, silenes have been considered as short-lived intermediates that are impossible to be isolated under normal conditions.



Scheme 5. Formation and trapping reaction of the transiently generated 1,1-dimethylsilene.

This situation was changed in 1981 when the first compounds containing Si=C and Si=Si double bonds were isolated by Brook[38] and West,[39] respectively. From then on, the chemistry of multiple-bonded main group compounds has expanded rapidly and until now a large variety of species with homo- and heteroatomic multiple bonds involving heavy main group elements have been structurally characterized.[40]

Brook's silene, **I-22** (Figure 5) was synthesized by photolysis of the corresponding tris-(trimethylsilyl)acylsilane through 1,3-migration of one $SiMe_3$ group from silicon to oxygen and was characterized by X-ray diffraction analysis (Scheme 6). The very effective kinetic stabilization exerted by the bulky 1-adamantyl substituent and the π-donating siloxy group successfully prevents the silene from dimerization. Due to the π-donor on the silene carbon atom, the silicon carbon double bond has a reduced polarity. This so-called "inversed polarity" significantly changes the electronic and structural features of silenes and increases their stability. The X-ray structure of **I-21** gave a value of 1.764(3) Å for the Si=C bond length, considerably longer than the calculated Si=C bond distances in [$H_2Si{=}CH_2$] or [$Me_2Si{=}CH_2$] (1.69-1.73 Å),[41] the bond lengthening is attributed mainly to the ylidic π-donation from the siloxy group. Both the Si and C centers are in almost perfect planar environment and the Si=C bond is twisted by 14.6°. The isolation of Brook's first stable silene was the crucial breakthrough in silene chemistry and opened an avenue of possibilities for further investigation in the condensed phase. Not long after Brook's first report, the group of Wiberg published the second example of a stable silene (**I-23**) with less bulkier alkyl and silyl substituents and without π-donating substitutents.[42] The Si=C bond is therefore naturally polarized toward the carbon atom and has distance of 1.702(5) Å, which is significantly shorter than in Brook's silene and comparable to the value of the parent silene.



Scheme 6. Synthesis of Brook's first stable silene.

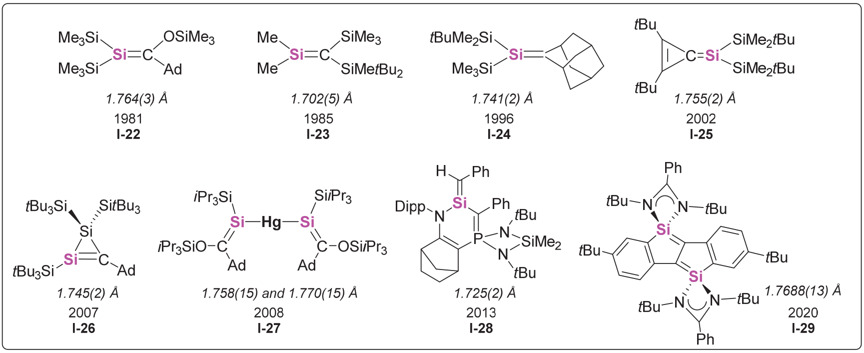


Figure 5. Selected examples of stable silenes.

The concept of kinetic stabilization or thermodynamic stabilization (σ-donor/π-acceptor groups on Si or σ-acceptor/π-donor groups on C) has been widely applied. During the last two decades, many other groups succeeded in the synthesis of different types of compounds comprising Si=C double bonds (Figure 5).[43] In 1996, Apeloig reported the synthesis of silene **I-24** *via* a sila-Peterson-type reaction.[43a] In 2002, Kira isolated 4-silatriafulvene **I-25** and in 2007 the disilacyclopropene **I-26** was reported by Sekiguchi.[43b,43c] The first metal-substituted silene **I-27**, which is also the first example of a bis(silene) was prepared and characterized by Apeloig.[43d]

As the chemistry of silenes matured, significant progress has been made in the application of silene chemistry in different areas. Due to the inherent instability of silenes, it will not replace the dominant role of alkenes in organic chemistry. However, the importance of this class of