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Highlight Review

The Versatile Chemistry of Disilenides: Disila Analogues of Vinyl Anions as Synthons in Low-valent Silicon Chemistry

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Abstract

Since the first isolation of a disila analog to vinyl anion synthons, namely lithium disilenide $Tip_2Si{=}Si(Tip)Li$ (Tip: 2,4,6-triisopropylphenyl), the number of available disilenides and their synthetic applications have rapidly expanded. Derivatives with aryl, silyl, alkyl, and hydrogen substituents have been reported and even one cyclic derivative is available. Disilenides can be used to introduce the Si=Si unit to a variety of organic and inorganic substrates. Depending on whether products feature sufficiently reactive residual functionality, the Si=Si bond is either retained or undergoes further (so far intramolecular) transformations. Heteroatom-substituted disilenes are easily accessible via disilenides. Using $Tip_2Si{=}Si(Tip)Li$ as a starting material, for instance, a variety of otherwise inaccessible compounds can be prepared: conjugated systems with more than one Si=Si unit, η^1-transition-metal complexes, functional homo- and heteronuclear silacycles, and molecular silicon clusters with substituent-free vertices. In this review article, an account on the chemistry of disilenides is given.

◆ Introduction

The report on the first stable compound with a Si=Si double bond, disilene **1** (Chart 1), in the early 1980s by West, Michl, and Fink[1] was a seminal event in main group chemistry. This discovery made the "double bond rule" about the inability of heavier main group elements to engage in multiple bonding redundant, which had been regularly referred to by textbooks of Inorganic Chemistry at the time.[2] The realization that steric protection could be employed to overcome kinetic instability helped kick-start the development of the low-valent chemistry of heavier main group elements in general,[3] and silicon in particular.[4] A vast number of structural motifs has been realized in the meantime, including for example silicon homologs of carbenes, silylenes such as **2**, **3**, and **4**,[5–7] allenes **5**,[8] butadienes **6**,[9] and alkynes **7**[10] to name but a few (Chart 1).

Extensive knowledge has been gathered regarding the considerable reactivity of the low-valent centers of these compounds.[4] In most cases, however, reactions yield products with tetravalent silicon centers, i.e., the low-valent functionality is consumed in the course of the reaction. Among the few exceptions, silylenes such as **2**, **3**, and **4** have proven useful for the syntheses of compounds with heteronuclear double bonds between silicon and e.g., chalcogene.[11] Even though Sekiguchi et al. recently revealed that disilynes **7** smoothly react with amines and boranes to yield otherwise difficult to obtain heteroatom-substituted disilenes,[12] only a limited number of functionalized derivatives with Si–Si double bonds is known.[10b,10c,13]

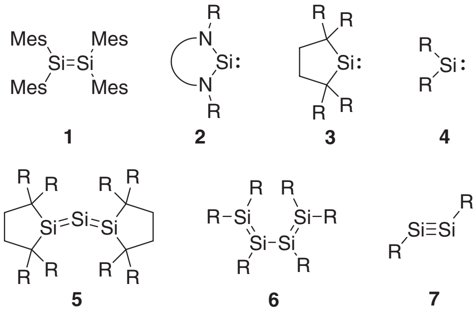

Chart 1. Selected examples of stable low-valent structural motifs (Mes: 2,4,6-$Me_3C_6H_2$; R = silyl, alkyl, and aryl).

After a brief introduction to the unusual properties of the silicon–silicon double bond that account for the ever increasing interest in Si=Si chemistry, this review describes the developments with regards to disila analogs of vinyl alkaline metal compounds that have proven to be very versatile reagents for the introduction of the Si=Si-moiety to organic and inorganic substrates. Anionic synthons with heteroatomic double bonds involving silicon are beyond the scope of the present summary, but were reviewed as part of an earlier account.[4b]

As Power recently pointed out,[14] main group elements in lower oxidation states show a surprising resemblance to transition metals in many ways, e.g., in their ability to activate small molecules such as dihydrogen.[15] The most readily apparent similarity of low-valent silicon compounds to transition-metal complexes, however, is the large variety of colors observed even in the absence of chromophores other than the unsaturated silicon moieties themselves. By way of introduction to this review, we shall focus on this aspect and its underlying reasons and consequences.

As shown by matrix isolation, transient dimesityl silylene, Mes_2Si, is intensely blue ($\lambda_{max} = 580\,nm$, 3-methylpentane),[16] its stable dimerization product, disilene **1**, is yellow[1] ($\lambda_{max} = 420\,nm$) like many other disilenes reported since.[4] Similar to what is textbook knowledge in the case of carbon, the extension of the conjugated silicon scaffold shifts longest wavelength absorptions to the red: tetrasilabutadiene **6a** is deep-red to purple in color (R = Tip: 2,4,6-$^iPr_3C_6H_2$; $\lambda_{max} = 518\,nm$).[9a]

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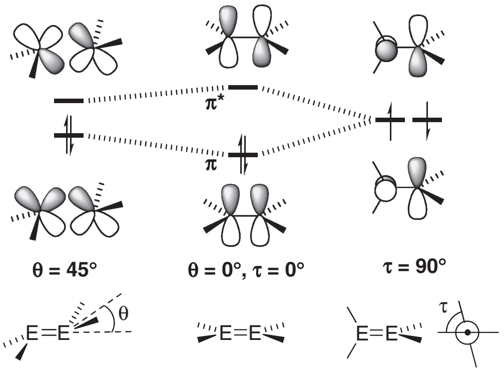
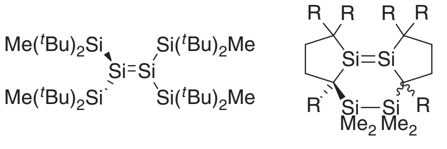


Figure 1. The principal deviations from the coplanar alkene-like structure and their effect on the π(HOMO)–π^*(LUMO) gap (θ = *trans*-bent angle; τ = twist angle).

The absorptions of disilenes in the visible region of the electromagnetic spectrum are usually related to π–π^* transitions representing the relatively narrow HOMO–LUMO gap of low-valent compounds of the heavier main group elements. The most important factor determining this comparatively small energy difference is, however, not an intrinsic property of the heavier main group atoms (despite a slightly smaller energy difference between s and p valence orbitals),[17] but rather the increasingly larger size and hence more diffuse nature of the valence orbitals when going down the group.

Molecular orbital considerations based on orbital overlap and orbital mixing are thus the simplest way to rationalize many distinct electronic features of low-valent silicon compounds: the pronounced preference for the singlet state in silylenes,[18] as well as the relative weakness of Si–Si π-bonding[19] and thus the conformational flexibility of many disilenes.[20] Intriguingly, compounds with Si=Si bond can adopt different conformations of the double bond as a function of relatively weak energetic parameters such as steric requirements of the substituents or crystal packing forces. Disilene **1**, for instance, exhibits three distinctly different solid-state structures depending on the presence and nature of the co-crystallized solvent.[21] Typically, one or both of two types of distortions from the familiar planar alkene structure are observed: 1) *trans*-bending of the substituents, i.e., pyramidalization of the silicon centers, which according to the model proposed by Carter, Goddard, Malrieu, and Trinquier (CGMT) is a function of the singlet–triplet separation of the constituting silylene fragments;[22] 2) twisting of the planes defined by the two silicon atoms and the bonds to their respective substituents to minimize steric repulsion of the substituents (Figure 1).[23,24]

As can easily be rationalized by qualitative orbital overlap arguments the π–π^* separation must decrease with increasing deviation from planarity. Larger angles θ and τ necessarily result in a narrower HOMO–LUMO gap and thus a red shift in the longest wavelength UV–vis absorption. The blue color of tetrasilyldisilene **8** (Chart 2, $\lambda_{\max} = 612$ nm), for instance, has been attributed to the large twisting angle of $\tau = 54.5°$, which is due to the steric repulsion of the bulky substituents (R = $SiMe^tBu_2$).[24] The coordination environments of both silicon atoms are almost planar (sum of bond angles 359.7 and 359.6°) due to the presumably relatively small singlet–triplet gap of the bis(silyl)silylene fragments constituting the double bond. In two isomeric cyclic disilenes, the additional ring strain in *trans*-**9** imposes stronger distortions from planarity compared to an almost planar *cis*-**9** (*cis*-**9**: $\tau = 3.9°$, $\theta = 3.9$ and 12.4°; *trans*-**9**: $\tau = 42.5°$, $\theta = 32.9$ and 30.9°). This results in a large red-shift of the longest wavelength UV–vis absorption for *trans*-**9**, while the UV–vis of *cis*-**9** is very similar to that of **1** (*cis*-**9**: $\lambda_{\max} = 433$ nm; *trans*-**9**: $\lambda_{\max} = 517$ nm).[25]



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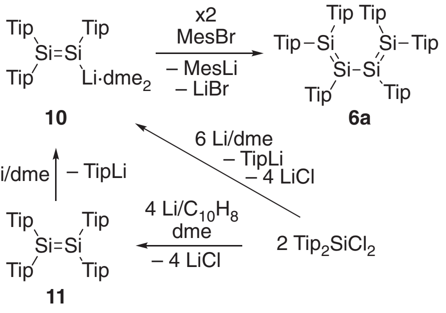
cis/*trans*-**9**

Chart 2. Extremely distorted disilenes (R = silyl, alkyl, and aryl).



Scheme 1. Proposed intermediacy of disilenide **10** in the synthesis of tetrasilabutadiene **6a** (Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$; Mes: 2,4,6-Me$_3$C$_6$H$_2$),[9a] original synthesis of Watanabe's disilene **11**,[26] as well as "direct" synthesis of disilenide **10**.[27]

Apart from the obvious synthetic potential Si=Si bonds bring about, the conformational flexibility and the inherently smaller HOMO–LUMO gap are strong arguments for the incorporation of Si=Si units into both inorganic and organic conjugated materials. As will be summarized in the following, disilenides, i.e., disila analogs of vinyl anion synthons, are suitable as generally applicable Si=Si transfer reagents.

♦ Synthesis of Disilenides

In the report by Weidenbruch et al. on the synthesis of the first tetrasilabutadiene **6a** the authors postulated lithium disilenide **10** as a plausible intermediate, which was then treated with half an equivalent of mesityl bromide to afford **6a** (Scheme 1).[9a] In order to generate **10**, Weidenbruch and co-workers treated Watanabe's disilene **11**[26] with elemental lithium in 1,2-dimethoxyethane (dme) in the expectation that one of the four Tip substituents would be cleaved off reductively in analogy to what had been reported by Masamune et al. for Tip$_2$Ge=GeTip$_2$.[28] The isolation of the final product of this reaction sequence, tetrasilabutadiene **6a**, lent the proposed intermediacy of **10** significant support.

The obvious similarity between the reaction conditions of the originally reported synthesis of **11** by Watanabe[26] and its assumed reduction to **10** as reported by Weidenbruch served as inspiration to try the direct reduction of Tip_2SiCl_2 with an excess of lithium powder in dme. Indeed, this reaction furnished **10** in an acceptable isolated yield of 51%.[27] Disilenide **10** exhibited a rather surprising thermal stability melting at 121 °C with only little decomposition.

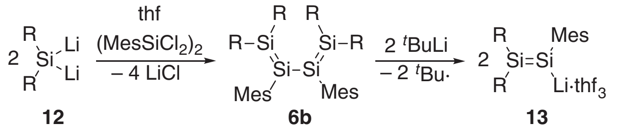
The solid-state structure of **10** revealed an almost planar Si=Si double bond conformation particularly if one disregards the only loosely bound lithium counter cation (Si–Li 2.853(3) Å). The weak Si–Li bond in **10** can be explained by the coordination with two dme molecules leading to an overall coordination number of 5 at the lithium cation (distorted square pyramidal). The most pertinent structural features, however, are an Si–Si bond length, which is with 2.192(1) Å significantly longer than the corresponding bond in neutral **11**,[26] as well as a relatively small Si–Si–C angle (107.6(1)°) at the negatively charged silicon atom, reflecting the high s character of the Si–Li bond.

According to the CGMT model,[22] the structure of a disilene is the more *trans*-bent the larger the singlet–triplet gap of the constituting singlet silylene fragments. Following first principles (Bent's rule) electropositive substituents are one way to favor the triplet state and therefore lithiosilylenes could be expected to exhibit a small singlet–triplet gap if not a triplet ground state. This assertion had been quantified by Apeloig et al.[18] and was experimentally verified by the synthesis of a lithiosilylene that has a thermally accessible triplet state according to EPR.[29] In view of these considerations, the planar structure of **10** is not unsurprising. In fact, a planar structure was predicted for $H_2Si{=}Si(H)Li$ early on by Apeloig and Karni on the basis of theoretical calculations.[30]

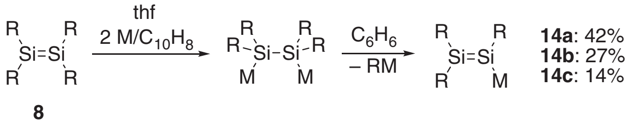
The UV–vis spectrum gives some indications that the HOMO of **10** has indeed a significant contribution to the Si–Li bond. The longest wavelength absorption at 417 nm is with an extinction coefficient of $\varepsilon = 760\,M^{-1}\,cm^{-1}$ too weak for a π–π^* transition and more in line with an n–π^* transition. The presence of a negative charge in the periphery of the Si=Si bond results in a substantial deshielding of both signals in the ^{29}Si NMR spectrum compared to the neutral disilene **11** (**10**: 100.5, 94.5 ppm;[27] **11**: 53.4 ppm[26]). While these low-field shifts may be surprising at first considering the strong shielding observed in sp^3 silyl anions,[31] they are in line with the general trend that more electropositive substituents shift the ^{29}Si NMR resonances of disilenes to lower field.[32]

As will be shown in the following, the structural and spectroscopic observations described above are recurring features of the disilenides reported so far.

A side remark by Weidenbruch in his 2003 review article[4g] referred to the treatment of tetrasilabutadiene **6a** with lithium powder, which had resulted in the cleavage of the central Si–Si single bond to afford **10**. This observation may have prompted Sekiguchi and co-workers to exploit a related strategy for the synthesis of a different disilenide, which was reported only months after **10**. Starting from the dilithiosilane **12**, they initially prepared tetrasilabutadiene **6b** in 11% isolated yield, which was then converted to disilenide **13** by cleavage of the central Si–Si single bond with ^{t}BuLi as the reducing equivalent and isolated in 67% yield (Scheme 2).[9b] The ^{t}Bu-radical necessarily formed in view of the stoichiometry of the reaction presumably underwent disproportionation to isobutene and isobutane as the authors mentioned the detection of the former in the reaction mixture.



Scheme 2. Synthesis of disilenide **13** from dilithiosilane **12** via tetrasilabutadiene **6b** (R = SiMe^{t}Bu$_2$).[9b]



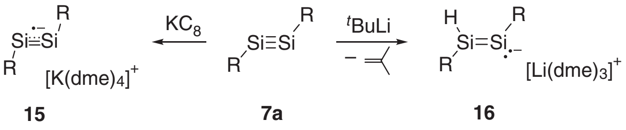
Scheme 3. Synthesis of disilenides **14a**–**14c** from disilene **8** (M = Li (**14a**), Na (**14b**), and K (**14c**); R = SiMe^{t}Bu$_2$).[34]

While direct reduction of **6b** with lithium metal apparently does not proceed cleanly enough to isolate a product, potassium/graphite affords the potassium analog of **13** in 80% isolated yield.[33]

The Si–Li distance of **13** is with 2.702(9) Å much shorter than in **10**, which is presumably due to the decreased coordination number of the lithium cation (three thf molecules, i.e., distorted tetrahedral). The disorder of the lithium cations over two distinct positions, however, renders the interpretation of this value somewhat ambiguous. Otherwise, the structure and spectroscopic analysis of **13** shows similar features to that of **10**: the Si=Si moiety exhibits an almost planar coordination environment with only a small twist between the two silicon bonding planes ($\tau = 15.2°$).[9b] The Si–Si bond length of **13** is with 2.2092(7) Å like that of **10** rather long, but interestingly almost identical with those of the tetrasilabutadiene precursor **6b**. The bond angle of 109.79(6)° at the silicon atom formally carrying the negative charge is acute; in the ^{29}Si NMR this atom is strongly deshielded (267.6 ppm). Even though UV–vis data are not available, the yellow color of **13** suggests a longest wavelength absorption in the area around 400 nm.

A much simpler and higher yielding procedure, reminiscent of the synthesis of **10**, was employed for the synthesis of the tris(silyl)-substituted disilenides **14a**–**14c** by Sekiguchi et al.[34] Notably, reduction of the sterically extremely crowded blue disilene **8** with the appropriate alkaline metal naphthalenes afforded 1,2-dimetallated disilanes, which were stable in THF and thus characterized NMR spectroscopically. Exchange of the solvent for benzene, however, prompted the elimination of MSiMe^{t}Bu$_2$ to yield the corresponding alkaline metal disilenides **14a**–**14c** in acceptable yields (Scheme 3).

The solid-state structure of **14a** features an almost perfectly planar Si=Si bond (sum of angles 359.99 and 359.98°) without any appreciable twisting or *trans*-bending. The Si=Si bond length of **14a** is with 2.1983(18) Å only marginally shorter than that of **13**. Interestingly, the bond angle at the negatively charged Si atom with 125.48(8)° is far larger than the corresponding angle in both **10** and **13**. Though the authors did not specifically address this puzzling finding, it seems to suggest a relatively evenly distributed p character and thus an Si–Li bond approaching an sp^2 hybridization state of consequently highly covalent character. Indeed, the Li counteraction of the contact ion pair is coordinated by only two thf molecules (distorted trigonal



Scheme 4. Synthesis of disilyne radical monoanion **15** and H-substituted disilenide **16** (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$).[35]

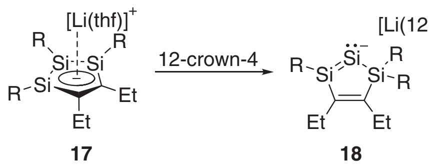
planar); the Si–Li distance is therefore with 2.598(9) Å shorter than those in **10** and **13**.[34] The ^{29}Si NMR signals of the negatively charged silicon atoms of **14a**–**14c** are significantly more low-field shifted than in **13** (δ^{29}Si 323–329).

As part of their investigations regarding the reduction of disilyne **7a**, Sekiguchi et al. showed that the reaction of **7a** with stoichiometric amounts of potassium/graphite yields the disilyne radical monoanion **15** (Scheme 4). Conversely and in marked contrast to the reaction with tetrasilabutadiene **6b**, ^{t}BuLi does not act as a reducing agent toward **7a** but rather as a source of lithium hydride. The thus obtained lithium disilenide **16** consequently features a hydrogen-substituted Si=Si bond (the authors report that the product of LiH elimination from ^{t}BuLi, isobutene, was detected as the only significant side product).[35]

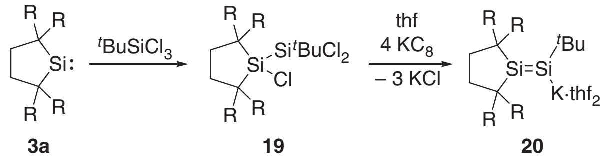
The solid-state structure of **16** is particularly informative since the Li counteraction is spatially well separated from the disilenide moiety by coordination with three dme molecules. A solvent separated ion pair of **10** had been reported but details on the X-ray structure were omitted due to a disorder issue.[27] The two silyl substituents R of **16** were found to be coplanar with the Si=Si bond (2.2034(9) Å) and the bond angle on the formally negatively charged silicon atom is with 102.69(3)° the smallest of all disilenides characterized in the solid state so far, probably due to the high s character of the unperturbed lone pair. The ^{29}Si NMR exhibits shows two signals: the one at 165.0 ppm was assigned to the negatively charged silicon atom and the doublet at 124.7 ppm unambiguously attributed to the H-substituted silicon atom on grounds of the 155 Hz coupling constant. The longest wavelength absorption of the UV–vis spectrum was found at $\lambda_{\max} = 390$ nm showing a surprisingly large extinction coefficient of $\varepsilon = 5400\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, which on these grounds was assigned to the π–π^* transition.

The thermodynamic stability of the disilenide moiety was impressively demonstrated by the facile rearrangement of an aromatic 1,2,3-trisilacyclopentadienide **17** to the isomeric cyclic disilenide **18** via a 1,2-silyl shift. The reaction takes place at room temperature upon removal of the coordinated lithium cation with two equivalents of 12-crown-4 (Scheme 5).[36] Furthermore, this isomerization provided a further example of the unique role of lithium ion pairs for the stability of negatively charged aromatic species involving silicon and therefore their degree of aromaticity.[37] Only a preliminary X-ray structure of **18** was qualitatively discussed in the report mentioning a significantly more acute endocyclic bond angle at the central silicon atom compared to **17**, which again was attributed to the high s character of the lone pair.

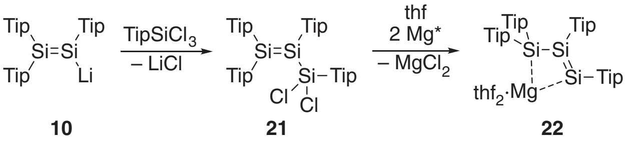
In terms of a more systematic approach to disilenides a contribution by Kira, Iwamoto, et al. is instructive. Insertion of the donor-free silylene **3a** into a Si–Cl bond of SiCl$_4$ had provided the 1,1,1,2-tetrachlorodisilane precursor that was then converted to the trisilaallene **5a** upon reduction (Chart 1; **3a**, **5a**: R = SiMe$_3$).[8] The extension of this prototypical reactivity of silylene **3a** to the analogous reaction of **3a** with ^{t}BuSiCl$_3$ afforded the 1,1,2-trichlorodisilane **19**. Reduction of **19** with the required amount of potassium/graphite furnished the first trialkyldisilenide **20** in acceptable yield (Scheme 6).[38] The interesting dimeric solid-state structure revealed a typical Si=Si bond length of 2.2117(13) Å and a Si–Si–C bond angle at the negatively charged Si atom of 114.73°. The ^{29}Si NMR data are comparable to **10** inasmuch as that both silicon atoms of the double bond show appreciable deshielding at δ^{29}Si 126.4, 144.9.



Scheme 5. Rearrangement of the 1,2,3-trisilacyclopentadienide **17** to the cyclic disilenide **18** (R = SiMe^{t}Bu$_2$).[36]



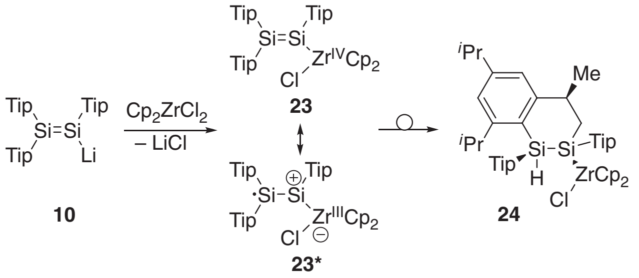
Scheme 6. Synthesis of a trialkyldisilenide **20** (R = SiMe$_3$).[38]



Scheme 7. Synthesis of a magnesium trisilendiide **22** (Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$).[39]

The only disilenide featuring an earth alkaline metal reported so far became accessible through the exploitation of the reactivity of disilenide **10** toward chlorosilanes (see subsequent section: *Reaction with Group 13, 14, and 15 Element Halides*). Reaction of one equivalent of TipSiCl$_3$ with **10** in toluene affords the dichlorosilyldisilene **21** in near quantitative yield (Scheme 7). Reduction of **21** with activated magnesium powder in thf then affords the magnesium trisilendiide **22** as orange crystals in 42% yield.[39]

The ^{29}Si NMR shifts of the Si=Si bond (δ^{29}Si 143.9, 134.5) and UV–vis data ($\lambda_{\max} = 415$ nm, $\varepsilon = 3200\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) suggested a very similar electronic structure to that of **10** despite the presence of an additional negative charge, which was interpreted as an indication for highly localized charges in concert with the significantly differing Si–Si bond lengths (Si–Si 2.362(1); Si=Si 2.198(1) Å). Notably, the Mg–Si distance to the formally sp^2 hybridized Si atom with 2.552(1) Å was found to be significantly shorter than that to the formally sp^3 hybridized one (2.625(1) Å). Though not specifically discussed in the original paper, the Si–Si–C bond angle at the terminal atom of the double bond is with 120.98(7)° not nearly as acute as the corresponding angle of **10**, which may again be taken as an indication for the more covalent character of the Si–Mg bonds of **22**.[39]



Scheme 8. Synthesis of an η^1-disilenide zirconocene complex **23** and its intramolecular CH-insertion reaction to **24** (Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$).[40]

The isolation of the zirconocene complex **23** from the reaction of lithium disilenide **10** (Scheme 8) can be regarded as proof of principle as to the possibility of coordinating a disilenide ligand to a transition metal in η^1-fashion.[40] The complex **23** turned out to be stable at room temperature only for limited periods of time. The most pertinent feature of **23** is its intense green color ($\lambda_{max} = 715\,nm$, $\varepsilon = 7000\,M^{-1}\,cm^{-1}$), which was tentatively attributed to a ligand-to-metal charge transfer transition on grounds of the enormous red shift compared to alkaline metal disilenide **10**. In addition a remarkable deshielding of the ^{29}Si NMR signals suggested a considerable influence of the zirconium center on the electronic ground state (δ^{29}Si 116.8 and 152.5), which was confirmed by an X-ray diffraction study. The Si=Si bond length of 2.2144(7) Å in concert with a significant twisting ($\tau = 20.2°$) of the almost perfectly planar silicon bond planes (sum of angles: 359.68, 359.51°) would be in agreement with some mixing of the ground state **23** with the excited state **23*** corresponding to the aforementioned ligand-to-metal transition.

The thus increased diradical nature of **23** (in other words activation of the Si=Si double bond) was invoked to explain the easy rearrangement to a CH insertion product **24**, which appeared to be catalyzed by oxygen as well as by both acids and bases.[40] While such insertion reactions are actually relatively common in disilene chemistry (albeit at much more elevated temperatures),[41] none had been reported for any of the alkaline metal disilenides.

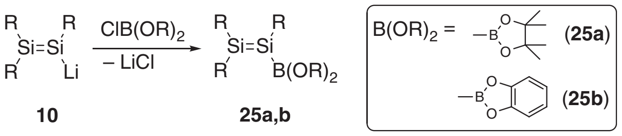
In Table 1 the most important structural and spectroscopic features of disilenides are summarized. It is readily seen that the bond angle at the formally anionic silicon becomes more acute with increasing ionic character of the disilenide. This is in line with theoretical calculations on the anionic parent compound $H_2Si{=}SiH^-$ without counter cation that predicted a value of 90° for this angle.[42] Similarly, the usually slightly longer Si=Si bond is well reproduced by the calculations.[30,42]

The at first sight surprising deshielding of the formally negatively charged silicon atom in the ^{29}Si NMR (in the case of silyl anions usually strongly shielded signals are observed)[31] might be attributed to the increased mixing of σ orbitals with the π^* orbital of the Si=Si bond.[32] The UV–vis data of disilenides remains somewhat inconclusive at this point, but it is safe to say that a substantial difference between aryl-, alkyl-, and silyl-substituted derivatives can be expected such as it is well established for neutral disilenes.[4] The UV–vis spectroscopy of aryl-substituted disilenides at least give a first indication that the HOMO may indeed be the nonbonding orbital.

Table 1. Structural parameters and physical data of disilenides

	Si=Si/pm	Si–Si–R/° [a]	δ^{29}Si [b]	λ_{max}/nm [c]	Ref.
10	2.192(1)	107.6(1)	100.5[d]	417	28
13	2.2092(7)	109.79(6)	267.6	—	9b
14a	2.1983(18)	125.48(8)	328.4	—	34
16	2.2034(9)	102.69(3)	165.0	390	35
20	2.2117(13)	114.73	144.9[d]	—	38
22	2.198(1)	120.98(7)	143.9[d]	415	39
23	2.2144(7)	107.70(6)	152.8	715	40

[a] *ipso*-Atom of substituent at negatively charged Si atom. [b] Chemical shift of negatively charged Si atom. [c] Longest wavelength absorption. [d] Assignment tentative.



Scheme 9. Synthesis boryldisilenes **25a** and **25b** (R = SiMe^{t}Bu$_2$).[43]

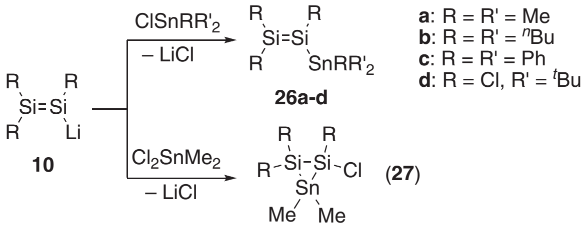
♦ *Reactions with Main Group Element Halides*

The functionalization of the silicon–silicon double bonds is—as mentioned before—of central importance to the further development of low-valent silicon chemistry. In this respect the boryl group may play a prominent role given the extensive use of boronic acid derivatives in organic chemistry. Recently Sekiguchi et al. reported the use of their disilyne as precursor to boryl-substituted disilenes by a hydroboration reaction, i.e., addition of the B–H bond across the Si–Si triple bond.[12] The first boryldisilenes **25a** and **25b**, however, were obtained by the same group through the reaction of disilenide **14a** with the appropriate boronic acid chlorides in good yield (Scheme 9; **25a**: 76%, **25b**: 78%).[43] According to spectroscopic and structural data, the boryl groups adopt a perpendicular conformation with respect to the Si=Si bond and thus do not allow for efficient conjugation of the vacant p_z orbital with the double bond.

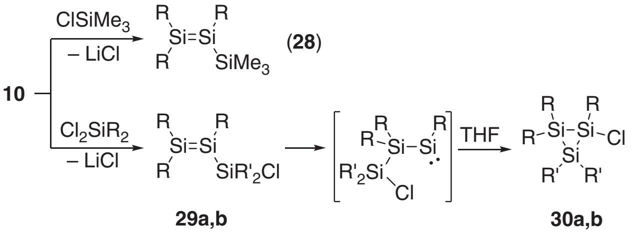
One of the most important reaction classes involving boron reagents in organic chemistry is the (transition-metal-catalyzed) Suzuki–Miyaura coupling of boronic acids and esters.[44] Even though simple cross coupling chemistry with disilenides **10** and **20** was shown to proceed in the absence of catalysts (see section *Reaction with Aryl Halides*) the availability of boryldisilenes may be expected to provide further opportunities in this regard.

Similarly, the reaction of **10** with stannyl chlorides can be viewed as an attempt to access reagents for Stille-type cross coupling[45] of disilenes. The simple yellow to orange stannyl-substituted disilenes **26a**–**26d** were obtained in average to good yields of 55% to 95%, as well as the disilastannirane **27** in the somewhat lower isolated yield of 21% (Scheme 10).[46] Although no intermediate could be observed in the formation of **27**, a chlorostannyl-substituted disilene is the most plausible initial product, which would subsequently cyclize to afford **27**.

Earlier, an additional tin-substituted disilene had been obtained almost quantitatively from the reaction of the magnesium trisilendiide **22** with Me_2SnCl_2 as proof-of-principle for



Scheme 10. Synthesis stannyldisilenes **26a**–**26d** and disilastannirane **27** (R = Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$).[46]



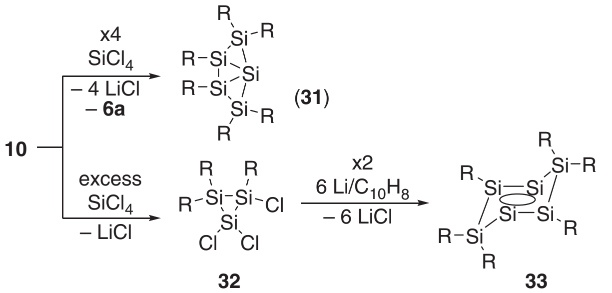
Scheme 11. Synthesis silyldisilenes **28** and **29a** and **29b** and rearrangement of **29a** and **29b** to cyclotrisilanes **30a** and **30b** (R = Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$; **a**: R′ = Me; **b**: R′ = Ph).[47]

the suitability of **22** to transfer the trisilendiide moiety under preservation of the Si=Si double bond. The solution structure of the unsaturated four-membered stannacycle thus formed was unambiguously proven by ^{119}Sn and ^{29}Si NMR.[39]

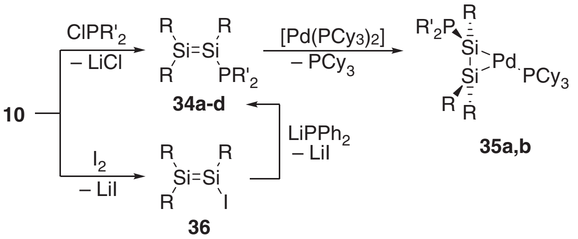
Conversely, disilenes with residual chloro functionalities at the group 14 substituent tend to consume the Si=Si bond and form three-membered rings such as **27** unless prevented by the steric demand of the substituents, e.g., in the case of **26d**. The importance of the steric demand of substituents, the availability of residual functionality, as well as solvent effects had previously been recognized in the reactions of **10** with chlorosilanes. Thus, while the trimethylsilyl-substituted disilene **28** that can be obtained from **10** and Me$_3$SiCl does not seem to undergo rearrangement to the corresponding cyclotrisilane,[27] both chlorosilyldisilenes **29a** and **29b** are more or less stable at room temperature in the absence of n-donors, but rapidly afford cyclotrisilanes **30a** and **30b** in the presence of THF (Scheme 11).[47]

The likely intermediacy of a disilanyl silylene in these rearrangements (Scheme 11) was supported by the thermal rearrangement of **29b**. Unlike in the case of the THF-promoted isomerization the thus occurring insertion into one of the *ortho*-CH bonds of the phenyl groups yields a 1,2,3-trisilaindane derivative.[47]

The reaction of **10** with SiCl$_4$ for the first time provided an entry to the chemistry of silicon clusters with substituent-free vertices. Notably, until the recent reports on NHC-stabilized silicon(II) halides,[48] the absence of low-valent halogenated precursors in silicon chemistry had generally been perceived a major obstacle for the synthesis of such clusters, in sharp contrast to the well-developed chemistry in the cases of germanium, tin, and lead.[49] Upon treatment of four equivalents of **10** with SiCl$_4$ in toluene an equimolar mixture of the orange Si$_5$Tip$_6$ cluster **31** and butadiene **6b** was obtained (Scheme 12).[50] In the solid state all four bonds of the central substituent-free silicon vertex of **31** point into the same hemisphere making it the first example of such a bonding situation in a homonuclear neutral silicon cluster.



Scheme 12. Reactivity of disilenide **10** toward SiCl$_4$: Synthesis of partially substituted cluster **31** and **33** (R = Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$).[50,51]



Scheme 13. Synthesis of phosphino disilenes **34a**–**34d**, complexation of **34a** and **34b** to [Pd(PCy$_3$)$_2$] fragment, and alternate synthesis of **34a** via iododisilene **36**. (R = Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$; **a**: R′ = Ph; **b**: R′ = ^{i}Pr; **c**: R′ = Cy; and **d**: R′ = ^{t}Bu).[53]

On grounds of the required stoichiometry, it was deduced that two equivalents of **10** acted as nucleophiles while the remaining two were oxidized to **6b**, thus removing the remaining chlorine atoms from any intermediate.[50] One likely intermediate of this process was later isolated in 59% yield through inversion of the reaction's stoichiometry at low temperature and characterized as the 1,1,2-trichlorocyclotrisilane **32** (Scheme 12). Through reduction of **32** with Li/C$_{10}$H$_8$ an intensely green ($\lambda_{max} = 623$ nm), tricyclic aromatic isomer of hexasilabenzene **33** was synthesized. The unusually stable **33** (mp 216 °C, dec.) could also be regarded as a silicon-expanded version of **31** and as such features two hemispheroidal silicon vertices.[51] The cyclic delocalization of two nonbonding, two σ- and two π-electrons over four silicon centers in **33** (as opposed to six π-electrons in the hypothetical hexasilabenzene) was put forward as a rational for a new type of aromaticity in intramolecularly dismutated Hückel systems, hence the newly coined term "dismutational aromaticity."[51] A third example of a silicon cluster with unsubstituted vertices had been reported by Wiberg et al. who reduced a pentaiodo cyclotetrasilane affording a Si$_8$R$_6$ derivative with two hemispheroidally coordinated silicon atoms.[52]

Very recently, the reaction of **10** with chlorophosphanes has been reported to cleanly afford the corresponding yellow to orange phosphine disilenes **34a**–**34d** in good isolated yields (Scheme 13).[53] Interestingly, as shown by the preparation of the palladium complexes **35a** and **35b**, the coordination of a [Pd(PCy$_3$)$_2$] fragment occurs to the Si=Si bond rather than to the pending phosphino group. As opposed to Kira's disilene π-complexes[54] involving the same palladium fragment the structure of **35a** exhibits considerable metallacyclopropane character.

Incidentally, the synthesis of **34a** also served as a case study for an umpolung strategy in order to provide an alternative, electrophilic Si=Si-transfer reagent. Disilenide **10** was thus transformed into the corresponding marginally stable iododisilene **36** by treatment with iodine. Treatment of the isolated iododisilene **36** with $LiPPh_2$ indeed produced **34a**[53] as only the second example of nucleophilic substitution at an sp^2 silicon atom of a halo disilene.[10c]

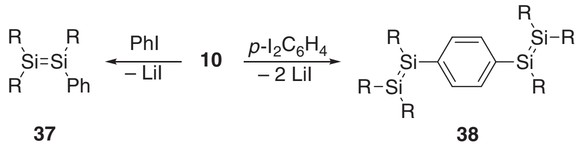
Phosphino-substituted **34c** and iodo-substituted **36** represent a typical case study on the effect of electronegativity on the *trans*-bending in disilenes while the overall sterical requirements of the substituents are left comparable. As predicted by theory, the *trans*-bent angles in **36** ($\theta = 25.7$ and 30.6°) are much larger than those in **34c** ($\theta = 7.7$ and 8.9°) as is the Si=Si bond length (**36**: 2.1914(9) Å; **34c**: 2.1542(11) Å).[53]

Reaction with Aryl Halides

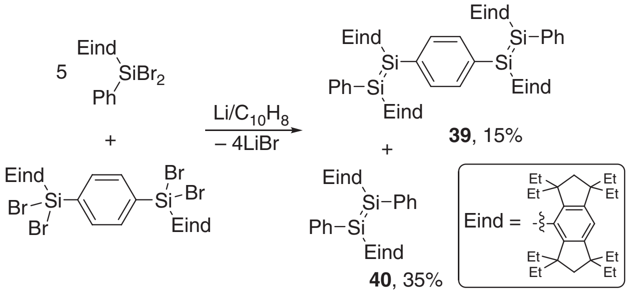
The incorporation of Si=Si bonds into conjugated organic systems has been of considerable interest since the early days of silicon multiple bonding. Weidenbruch was able to show that tetrasilabutadiene **6a** experiences a considerable red shift of the longest wavelength absorption.[9a] In the field of P=C and P=P chemistry, contributions by the groups of Gates, Protasiewicz, and Ott have clearly established that the extension of the π-conjugated system does effectively red-shift the UV–vis absorptions.[55,56] In the light of some precedence regarding the reaction of alkaline metal silyl reagents with aryl halides, in particular bromides and iodides,[57] the use of disilenides as transfer reagents to conjugated systems seemed promising.

The quantitative reactions of disilenide **10** with iodo- and *para*-diiodobenzene, respectively, thus constituted considerable progress as to the study of organic π-conjugated systems incorporating Si=Si bonds (Scheme 14).[58] Compared to the phenyldisilene **37** the *para*-phenylene-bridged tetrasiladiene **38** exhibits a strongly red-shifted longest wavelength absorption in the UV–vis (**37**: $\lambda_{max} = 439$ nm; **38**: $\lambda_{max} = 508$ nm). While this finding in concert with DFT calculations proved the presence of effective conjugation across the organic linking unit, the solid-state structure revealed the shortening of the Si=Si bond in the conjugated system **38** (2.1674(8) Å) relative to **37** (2.1754(11) Å). This counter-intuitive observation was explained by the decreased *trans*-bending of the substituents in **38** due to a more pronounced steric encumbrance (**37**: $\theta =$ 23.6(2)°, 22.3(2)°; **38**: $\theta = 16.5(2)°$, 19.3(2)°).

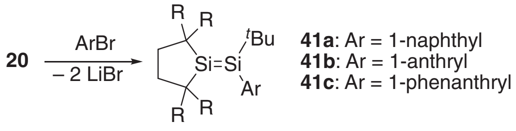
While the apparent conformational flexibility of the Si=Si bond may be desirable for some applications (e.g., of polymers), it is clear that it is probably less than ideal for the emission properties of the materials (radiation-less quenching). Indeed, the phenylene-bridged **37** exhibits fluorescence in neither solution nor the solid state. Conversely, the tetrasiladiene **39** substituted with the extremely bulky and rigid hydrindacenyl groups, which was reported only months after **37** by Tamao et al. (Scheme 15),[59] not only exhibits an even more red-shifted longest wavelength UV–vis absorption at $\lambda_{max} = 543$ nm, but also fluorescence at room temperature with an emission at 612 nm and a quantum yield of $\Phi = 0.10$. It should be noted that disilene **1** only displayed very weak fluorescence ($\Phi = 0.0015$) at 77 K.[60] The synthesis of **39** is, however, intrinsically low-yielding due to the Wurtz-type coupling methodology employed and involves the separation of **39** from the major product, diphenyldisilene **40**.



Scheme 14. Synthesis phenyldisilene **37** and *para*-phenylene-bridged tetrasiladiene **38** (R = Tip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$).[58]



Scheme 15. Synthesis of indacenyl-substituted phenylene-bridged tetrasiladiene **39** and diphenyldisilene **40**.[59]

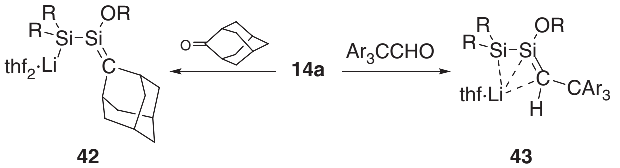


Scheme 16. Synthesis disilenes **41a**–**41c** (R = $SiMe_3$).[58]

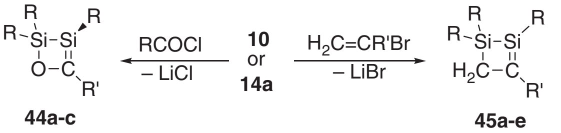
A similar method as the one developed for the synthesis of **37** and **38** was used by Kira, Iwamoto, et al. to prepare disilenes with one extremely bulky aryl substituent. Reaction of potassium disilenide **20** with the appropriate aryl bromide affords **41a**–**41c** in moderate yields (Scheme 16).[38] Unlike in the cases of **37** to **40** the conjugation with the aromatic substituent is deliberately suppressed because the sterically very demanding 1-naphthyl, 9-anthryl, and 9-phenanthryl groups adopt a perpendicular conformation with respect to the Si=Si double bond. This leads to the observation of distinct absorption bands in the UV–vis that result from the charge transfer from the Si=Si π bond to the π^* orbital of the polyaromatic ligand.

Reaction with Organic Carbonyl and Alkene Derivatives

The successful synthetic exploitations of Sila-Peterson rearrangements for the synthesis of silenes by treatment of bulky ketones with silyl anion synthetic equivalents[61] may have prompted Sekiguchi and co-workers to study the reaction of disilenide **14a** with adamantone. Indeed, the rearranged **42** with a Si=C double bond and a lithiated silyl substituent was isolated in good yield (Scheme 17).[62]



Scheme 17. Reactions of disilenide **14a** with adamantone and tris(3,5-di-*tert*-butylphenyl)acetaldehyde ($\mathrm{R} = \mathrm{SiMe}^t\mathrm{Bu}_2$, $\mathrm{Ar} = 3{,}5\text{-}^t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$).[62,63]



Scheme 18. Reactions of disilenides **10** and **14a** with carboxylic acid chlorides (**44a**: R = Tip, R′ = 1-adamantyl; **44b**: R = Tip, $\mathrm{R}' = {}^t\mathrm{Bu}$; **44c**: $\mathrm{R} = \mathrm{SiMe}^t\mathrm{Bu}_2$, R′ = 1-adamantyl; **45a**: R = Tip, R′ = Ph; **45b**: $\mathrm{R} = \mathrm{SiMe}^t\mathrm{Bu}_2$, R′ = Ph; **45c**: R = Tip, $\mathrm{R}' = \mathrm{SiMe}_3$; **45d**: $\mathrm{R} = \mathrm{SiMe}^t\mathrm{Bu}_2$, $\mathrm{R}' = \mathrm{SiMe}_3$; and **45e**: $\mathrm{R} = \mathrm{SiMe}^t\mathrm{Bu}_2$, R′ = H).[64,65]

In the solid-state structure of **42** the lithium counter cation coordinates in η^1-fashion to the silyl group only. A 1,2-disilaallyl anion **43** coordinating to lithium in η^3-fashion was later realized using a less bulky triarylacetaldehyde as a substrate for **14a**.[63]

Toward carboxylic acid chlorides disilenides **10** and **14a** react under elimination of LiCl to yield the cyclic derivatives **44a**–**44c** (Scheme 18).[64] Undetected but plausible intermediates of these reactions are the corresponding acyl disilenes, which would rapidly rearrange to **44a**–**44c** in an intramolecular formal [2 + 2] cycloaddition. Remarkably, the silicon atoms of the double bonds of **44a**–**44c** are strongly pyramidal (**44a** sum of angles 342.2°) in both solution and the solid state as was demonstrated by ^{1}H NMR at variable temperature and X-ray crystallography, respectively. DFT and ab initio calculations proved the pyramidalization to be a general feature of compounds of type **44** independent of the nature of the substituents.[64]

Interestingly, this reactivity of disilenides **10** and **14a** is completely analogous to the reaction of Cummins's isolobal terminal phosphide complex of niobium with carboxylic acid chlorides, which yielded a four-membered niobium cycle with a P=C double bond.[66]

In view of the smooth reactions of **10** with aryl iodides, it was reasonable to expect that disilenides should be compatible with vinyl bromides as electrophiles as well. Indeed, the reaction of **10** and **14a** with various vinyl bromides yielded the donor-free four-membered cyclic silenes **45a**–**45e** in good isolated yields (Scheme 17).[65] Using X-ray crystallography and DFT calculations it was established that unlike **44a**–**44c** the cyclic silenes without endocyclic oxygen atom feature almost perfectly planar Si=C bonds. With **44a**–**44c** and **45a**–**45e** cyclic versions of the archetypical silenes of the Brook[67] and Wiberg[68] type were thus prepared. Since in the acyclic Brook silene no pyramidalization was observed, it must be assumed that the ring strain's subtle influence tips the balance in favor of a pyramidal silicon in the Si=C moiety.

◆ Conclusion and Outlook

Since their first isolation in 2004, disilenides have developed into useful synthetic tools for the introduction of the Si=Si bond into a broad variety of substrates. Occasionally, redox reactions are highly competitive with the desired nucleophilic substitution.[50] While the counter cations of disilenides known to date only cover a small fraction of metals, the available toolbox will be no doubt enriched with further derivatives as the chemistry of disilenide develops. Different counter cations could allow, for instance, a fine tuning of the redox potential of the disilenide reagent. In the case of C=Si, a mercury derivative has been reported.[69] As far as P=Si is concerned, zinc and iron derivatives are known.[70,71]

The ease of synthesis is presumably the major reason why so far reactivity studies of disilenides have been predominantly centered on the derivatives **10** and **14a**. Given the considerable scope of these disilenides for application in synthesis, dimetallated disilenes particularly with lithium cations as counter ions would be a very welcome addition to the synthetic toolbox. Despite considerable progress along these lines in the case of dimetallated digermenes,[72] however, no corresponding silicon derivatives have been reported yet. A possible problem to overcome may be to achieve a subtle balance regarding the steric bulk of the substituents at the silicon centers: they should be large enough to protect the Si=Si bond kinetically, but not too large to avoid dissociation into the silylene fragments constituting the double bond. In fact, a recently reported lithiosilylene,[29] i.e., one half of the desired difunctional disilene, highlights this issue.

In view of the importance of carbon-based vinyl ligands in transition-metal chemistry and the different coordination modes that are realized there,[73] the disilenide transition metal chemistry, which so far was only hinted at, does offer exciting possibilities remaining to be explored.

Given the unusual optoelectronic properties of low-valent silicon compounds and clusters in concert with the conformational flexibility of Si=Si bonds there can be little doubt concerning an imminent rapid development of disilenide chemistry. Both expected and surprising results will continue to hold our fascination.

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