

Stable Silylenes

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ABSTRACT

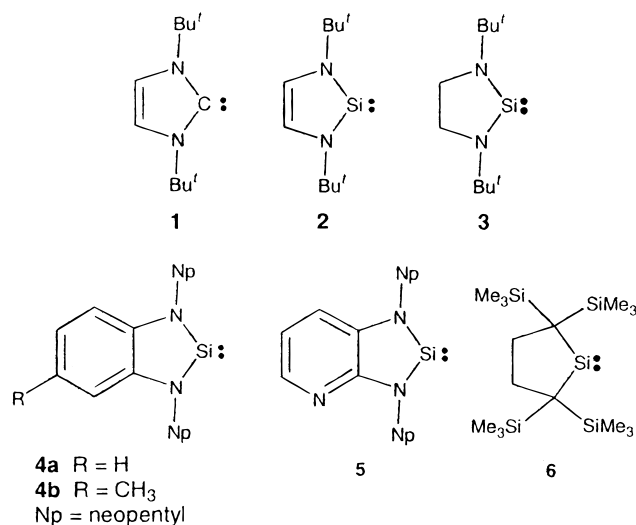
The field of stable silylene research has grown dramatically since the first isolation of a stable silylene in 1994. Prior to 1994, silylenes existed only as reactive intermediates, isolable only in low-temperature matrixes. Since then, several stable silylenes have been synthesized, some in fact showing remarkable thermal stability. This Account highlights the developments in stable silylene chemistry, including theoretical and experimental studies attempting to explain the remarkable stability of the silylenes as well as the rapidly expanding reaction chemistry of the stable silylenes.

Introduction

Silylenes are divalent, dicoordinate silicon species. As reaction intermediates, the silylenes are even more important in silicon chemistry than their counterparts, the carbenes, are in organic chemistry.¹ Like carbenes, most silylenes are intensely reactive. During the 1980s several organosilylenes were isolated and studied in argon or hydrocarbon matrixes, at temperatures of 77 K or below;² above this temperature they react rapidly with themselves or with solvents. It is safe to say that no one thought that silylenes could be stable at room temperature.

The situation changed in 1991, when Arduengo and co-workers at the du Pont Co. reported the isolation of the first stable carbene, **1**.³ This remarkable discovery left silicon as the only element in periodic group 14 with no stable dicoordinate compound,⁴ since stable germynes (R_2Ge) and stannylenes (R_2Sn) had long been known.⁵ Shortly afterward, Michael Denk came to Wisconsin and undertook the synthesis of **2**, the silicon analogue to **1**. The successful isolation of **2** completed for the silylenes

a classic progression, from transient intermediate to matrix-isolated molecule to stable compound.⁶ Silylene **2** is a colorless crystalline substance, with truly astounding thermal stability. Not only is **2** indefinitely persistent at room temperature, but it also survived unchanged after heating to 150 °C in toluene for 4 months. Solid **2** finally decomposes at its melting point, 220 °C.⁶



Compound **1** and many similar stable carbenes have been extensively studied since 1991, and a great deal is now known about their reactions and behavior.⁷ The chemistry of stable silylenes, the subject of this Account, is in a much earlier state of development. The preparation of **2** was followed by the synthesis of its saturated analogue, **3**, also at Wisconsin,⁸ the preparation of the benzo-fused silylenes **4a** and **4b** by the Lappert–Gehrhus team,⁹ and the isolation of the pyrido-fused analogue **5** by Heinicke and co-workers.¹⁰ All of these molecules are stabilized by two nitrogen atoms bonded to the divalent silicon. Most recently, Kira and co-workers have isolated a silylene, **6**, with no such nitrogen stabilization.¹¹ Of these known isolable silylenes, **2**, **4a,b**, and **5** are indefinitely stable, but **3** and **6** are only marginally stable.¹²

Syntheses

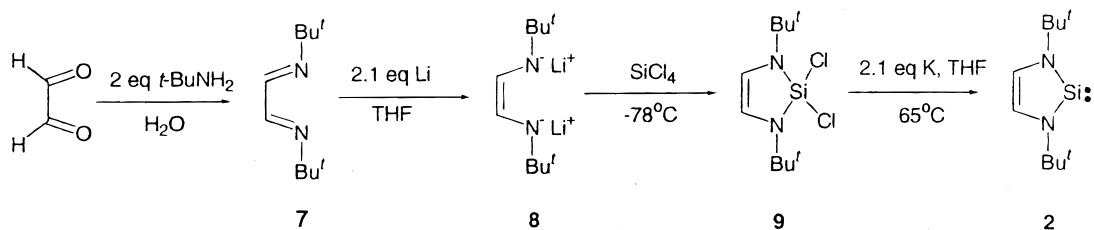
The preparation of a precursor to **2** was straightforward, as shown in Scheme 1. Reaction of glyoxal with *tert*-butylamine yielded diimine **7**, which was reduced with lithium metal to the lithiated diamine **8**. The latter reacted with silicon tetrachloride to give the dichloro compound **9**, bringing us to the difficult step in the synthesis. Many gentle reduction conditions were employed, all producing mixtures which proved impossible to separate. After several frustrating months, in desperation, we heated **9** with liquid potassium metal in refluxing THF. Under these vigorous conditions, **9** was converted to **2** in 80% yield.⁶ The reaction should be carefully monitored to avoid overreduction, and air and moisture must be strictly

Michael Haaf, born in upstate New York in 1972, received his undergraduate degree at Ithaca College and his Ph.D. in chemistry at University of Wisconsin—Madison under the supervision of Robert West. His research interests lie in low-valent silicon-containing compounds and in metal-catalyzed cross-coupling reactions. He taught chemistry at the University of Wisconsin—Baraboo for two years and recently joined the chemistry faculty at Elizabethtown College in Pennsylvania.

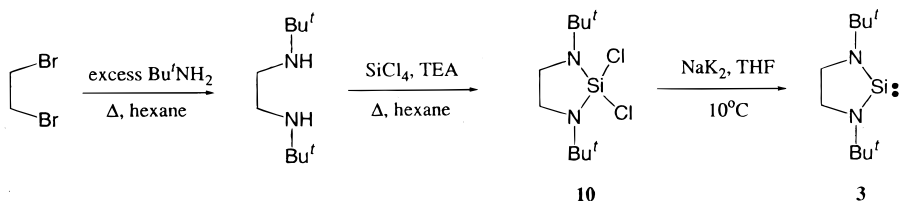
Tom Schmedake was born in Illinois in 1972. He received his B.A. from Knox College in Galesburg, IL, in 1994. Currently he is completing his Ph.D. under the supervision of Robert West at the University of Wisconsin—Madison. His research focus is on the chemistry of the saturated silylene. He will begin a post-doc in the lab of Mike Sailor at the University of California—San Diego starting August 2000.

Robert West, born in New Jersey in 1928, received his undergraduate and graduate degrees from Cornell and Harvard Universities. He is E. G. Rochow professor of chemistry at the University of Wisconsin—Madison, where he has served on the faculty for more than 40 years, with research on oxocarbons, polylithium compounds, and polyquinoid compounds as well as silicon chemistry. He is also the Director of the Organosilicon Research Center, founded in 1999.

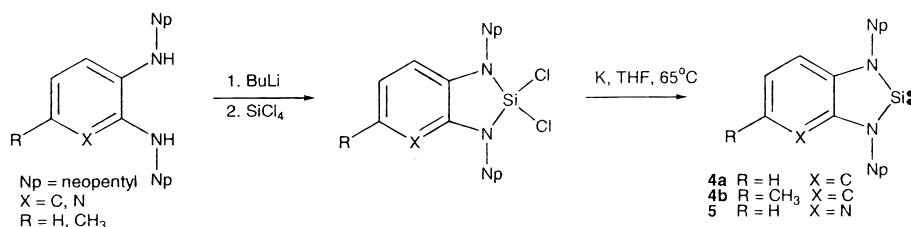
Scheme 1



Scheme 2



Scheme 3



excluded. Silylene **2** can be purified by distillation at 90 °C (1 Torr).

Synthesis of **3** proceeds according to Scheme 2. *N,N'*-Di-*tert*-butylethylenediamine, formed from the treatment of dibromoethane with excess quantities of *tert*-butylamine, is treated with triethylamine (TEA) and silicon tetrachloride, yielding dichloride **10**. Various reducing conditions have been employed to convert **10** (or its dibromo analogue) to **3**, but good results are obtained with Na/K alloy at 10 °C.¹³ It is again important to follow the course of the reaction to prevent overreduction.

The syntheses of **4a,b**⁹ and **5**,¹⁰ outlined in Scheme 3, are similar: dilithiation of the corresponding diamine, condensation with SiCl₄ to yield the dichlorides, followed by reaction with potassium in refluxing THF, a final step which has become somewhat standard for those stable silylenes which can withstand these conditions.

Spectroscopy, Structure, and Bonding

Structures have been determined by gas-phase electron diffraction for **2**,⁶ and by X-ray crystallography for **3**⁸ and **4a**.⁹ Structural diagrams for **2** and **3** are shown in Figure 1, and significant molecular parameters for the three compounds are given in Table 1.

The bond distances and angles within the five-membered rings are quite similar in **2** and **4a**. The five-membered rings in **2** and **4a** are planar, but the ring in **3** is necessarily puckered. As expected, the N–C distances within the ring are shorter in **2** and **4a** than in **3**, by about 10 pm. The Si–N bond lengths are similar to normal Si–N single bond distances, ~172–174 pm. However, bonds to

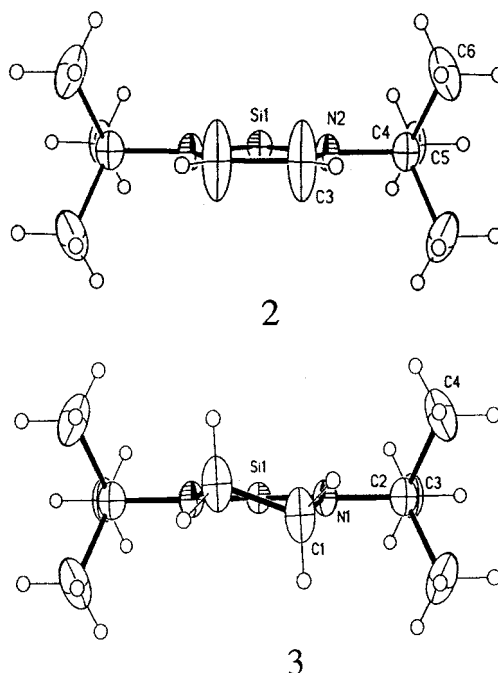


FIGURE 1. Structural diagrams for silylenes **2** and **3**.

divalent silicon are predicted to be longer, by about 8 pm, than bonds to tetravalent Si.¹⁴ The bond lengths in the silylenes are therefore consistent with some multiple bond character in the Si–N bonds.

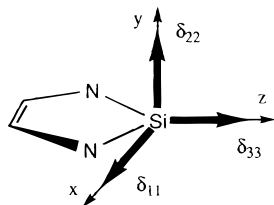
The NMR spectra, and especially the ²⁹Si resonance, are of obvious interest. The isotropic silicon atom resonance appears at low field, as shown in the data in Table 2.

Table 1. Bond Distances (pm) and Angles (deg) in Stable Silylenes

silylene	$r_{\text{N-Si}}$	$r_{\text{N-C}}$	$r_{\text{C-C}}$	angle N-Si-N
2	175.3	140.0	134.7	90.5
3	171.9	148.9	152.1	92.0
4a	174.7 175.2	138.0 138.5	141.7	88.2

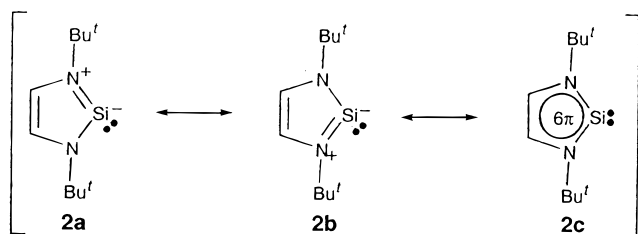
Table 2. Observed Chemical Shift Tensors for Silylenes

silylene	δ_{11}	δ_{22}	δ_{33}	δ_{iso}
2	284.9	-16.1	-43.3	75.2
3	350.7	-2.1	-4.5	114.7
4a	316.4	21.1	-60.0	92.5

**FIGURE 2.**

For silylenes **2**, **3**, and **4a**, the shielding tensors were determined by slow-spinning CPMAS NMR.¹⁵ Only *one component* of the tensor is deshielded, very strongly, resulting in the downfield shift in solution. DFT calculations established that the deshielded axis is the one in the ring plane, perpendicular to the lone pair orbital (Figure 2). A magnetic field along this axis mixes the lone pair with the vacant p orbital, leading to a very large paramagnetic effect.

The properties of silylenes **2–6** raise fascinating questions in chemical bonding theory. Why is **2** so stable, and why is it so much more inert than **3**? Steric hindrance may play a part in the stabilization, but is unlikely to be a major factor, except for silylene **6**. Inspection of models for **2–5** indicates that the silicon atom is not strongly protected sterically in any of these molecules. Undoubtedly, π -electron donation from the nitrogen lone pairs into the vacant p orbital on silicon is a strong stabilizing factor in these silylenes, as illustrated for **2** in the resonance structures **2a** and **2b**. Greater electron donation from nitrogen would be expected for **3** than for **2** and **4a**, since the nitrogen atoms in **3** are more basic, and indeed the Si–N distance in **3** is shorter than in **2** and **4a** (Table 1).



What then accounts for the much greater stability of **2** than **3**? In **2**, and likewise in **4a,b** and **5**, but not in the saturated molecule **3**, stabilization may be gained by aromatic delocalization over the 6- π -electron ring (see

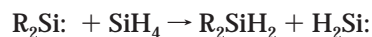
structure **2c**). The extent and importance of such aromaticity in **2**, and in the stable carbenes such as **1**,⁷ has been a matter of considerable controversy.

Several kinds of experimental evidence might bear on the question of aromatic delocalization. One simple test is the ¹H NMR chemical shift of the ring C–H protons. In **2**, these lie about 0.75 ppm downfield from the resonances of protons in model compounds, such as the dichloro precursor **9** or the dihydro analogue **11**.⁶ This shift is consistent with a moderate diamagnetic ring current in **2**, resulting from aromatic delocalization.

The photoelectron spectra for **2** may also shed light on the question of delocalization. Data for **2**, **3**, and **11**, the dihydride corresponding to **2**, are shown in Figure 3.¹⁶ Comparison of the orbitals for **2** and **11** is instructive. Both compounds have an analogous ring orbital with 1a₂ symmetry. The silicon can make no contribution to either orbital, and the two orbitals lie at almost identical energies. The HOMO for both molecules is also a ring orbital, of 2b₂ symmetry, and here the silicon p-orbital can contribute in **2** but not in **11**. The result is to increase the energy of this orbital in **2** by almost 0.5 eV, compared to **11**. This result is consistent with Si–N π -bonding, and with cyclic delocalization. Similar experiments, with analogous results, have been obtained for **4a**.¹⁷ However, the photoelectron results have also been interpreted in terms of a localized model, without delocalization.¹⁸

Recently, core excitation spectra have been determined for the C, Si, and Ge molecules analogous to **2**, as well as their corresponding dihydrides. The results strongly indicate N–Si π -bonding, and are also consistent with cyclic, aromatic delocalization.¹⁹ Also, Raman spectra have been recorded for **2** and related molecules containing tetra-coordinate silicon, such as **9**. Raman lines for the C=C stretching mode, near 1600 cm⁻¹ in the tetravalent molecules, are shifted by 60 cm⁻¹ to lower energy in **2**, and are strongly enhanced in intensity.²⁰ These results also suggest aromatic delocalization in **2**.

Several groups have carried out ab initio molecular orbital calculations to examine the nature of chemical bonding in **2**. Particularly useful are the results of Heineemann and co-workers,²¹ who studied the isodesmic reaction:



For (H₂N)₂Si, with the nitrogen lone pairs held perpendicular to the silicon p orbital, the reaction is exothermic by -5.6 kcal mol⁻¹. Twisting the nitrogen lone pairs so that they are parallel to the Si p orbital provides 36 kcal mol⁻¹ of stabilization, attributed to Si–N π -bonding. This amount is half as great as that for the similar change in the analogous carbenes, as expected since Si–N π -bonding should be much weaker than C–N.

Introduction of a bridging -CH₂-CH₂- group, to give silylene **3**, stabilizes the molecule by an additional 9 kcal mol⁻¹, perhaps due to electrostatic effects. Now, substituting the saturated bridge by a -CH=CH- group, to give **2**, further stabilizes the molecule by 12 kcal mol⁻¹. This

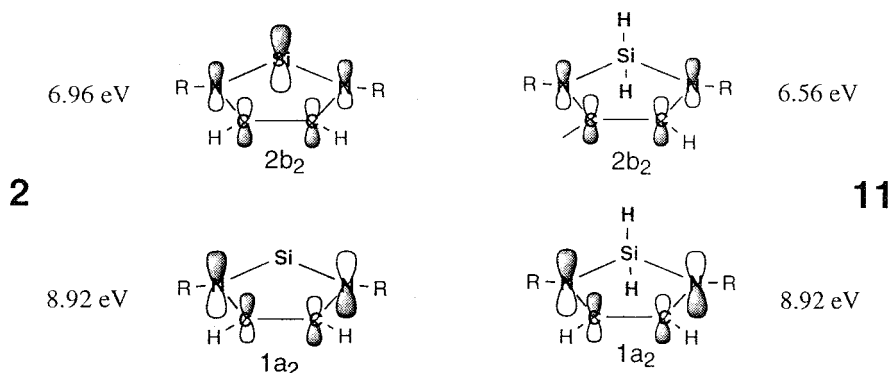
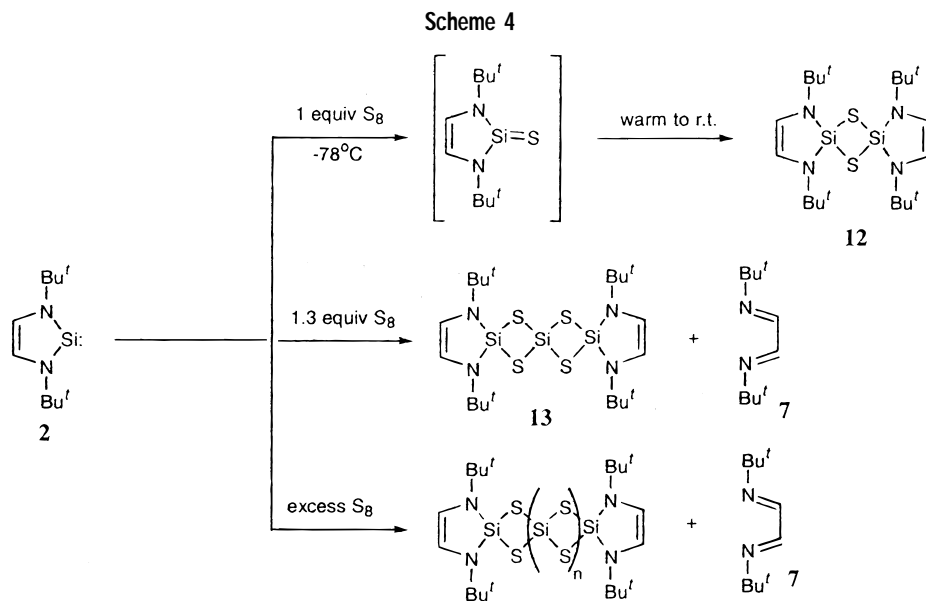


FIGURE 3. Schematic representations and vertical ionization energies of MOs of **2** and **11**.



stabilization of **2** compared to **3** is reasonably assigned to aromatic delocalization. The corresponding value for the isostructural carbenes is 29 kcal mol^{-1} , indicating that aromatic delocalization is significantly greater in **1** than in **2**.

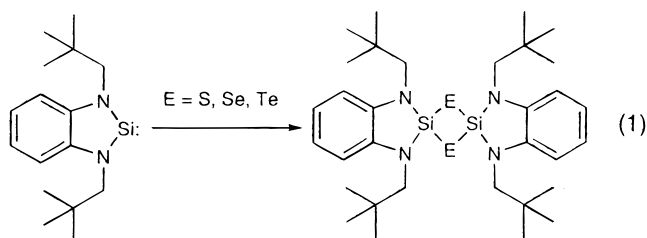
Another semiquantitative estimate of aromatic delocalization can be provided by nucleus-independent chemical shift (NICS) calculations.¹⁵ These were carried out for **2**, **3**, and **4a**, and for the known aromatic molecules benzene and thiophene, placing the ghost atom 2.0 \AA above the ring centroid to avoid anisotropic effects. These NICS calculations gave values of -5.3 ppm for benzene and -4.7 ppm for thiophene, reflecting the substantial ring currents in these molecules. For **2** and **4a**, the values were -2.7 ppm , consistent with a ring current about half as large as in benzene.

Thus, the consensus at present is that there is some aromatic delocalization in silylenes **2** and **4a**, albeit much less than in **1** and conventional aromatic compounds.

Chemical Reactions

I. With Main Group Elements. The stable silylene **4a** undergoes facile reactions with chalcogens to form the

corresponding spirocyclic dimers (eq 1).²²



Although silylene **2** shows results completely analogous with those obtained for selenium, its reaction with sulfur and oxygen is more complicated.²³ Reaction of **2** with exactly 1 equiv of elemental sulfur affords **12** (Scheme 4). Using variable-temperature $^{29}\text{SiNMR}$, a short-lived intermediate with a chemical shift of $+122.7 \text{ ppm}$ can be detected at $-78 \text{ }^\circ\text{C}$, most likely the silanethione. This intermediate can then dimerize to form the product, a mechanism which is also possible for the chalcogen reactions with **4a** mentioned earlier.

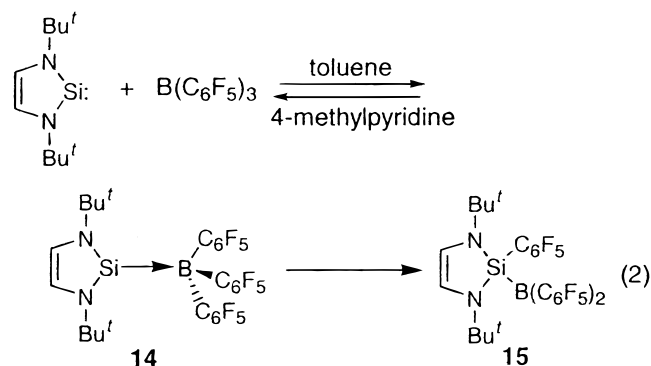
Interestingly, combining **2** with a slight excess of sulfur results in the further reaction of **12** to form **13**, with simultaneous release of dimine, **7**. With a large excesses of sulfur, a mixture of SiS_2 oligomeric products is formed.

This series of reactions reveals the high lability of the enediamine ligand on the silicon in **2** in comparison to the less labile ligand in **4a**.

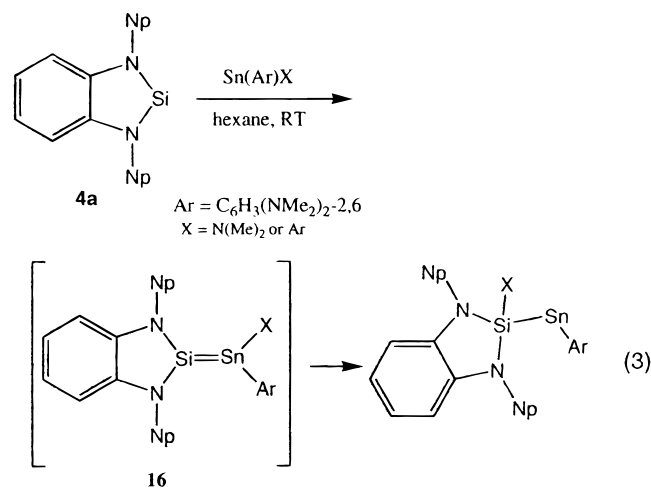
Silylene **2** reacts with oxygen in a similar fashion, though this reaction is too vigorous to allow the isolation of appreciable amounts of products other than SiO₂ and the liberated diimine, **7**.²³

When mixed with elemental white phosphorus in a solution of THF, **2** appeared not to react. However, this combination afforded a marked color change in the solution from the initial pale yellow to a deep orange-red color accompanied by the formation of a glassy, insoluble red substance. Apparently, the silylene simply catalyzed the conversion of white phosphorus to its more stable allotropic form, red phosphorus.²³

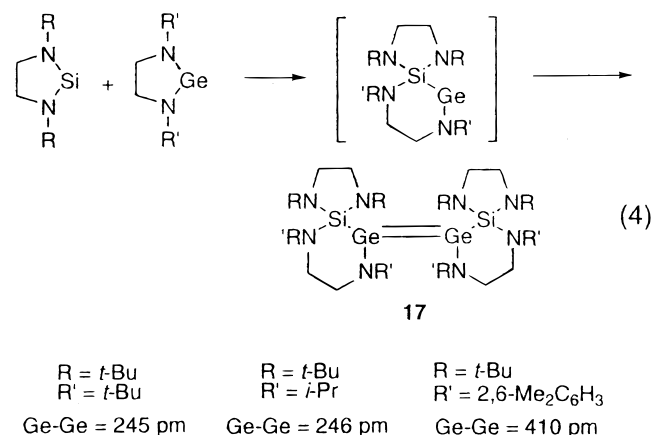
Silylene **2** undergoes a reversible reaction with tris(pentafluorophenyl)borane to form a Lewis acid–base adduct in a solution of toluene, **14**. Although this complex can be isolated and stored at room temperature, it slowly transforms into a silylborane, **15**, over a period of weeks (eq 2).²⁴



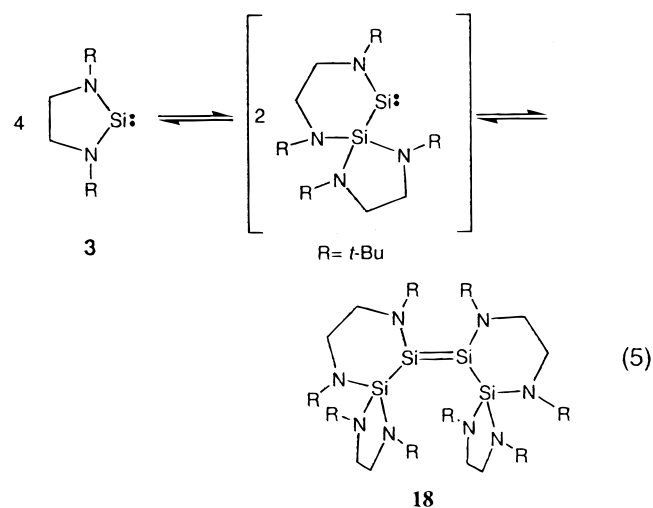
II. With Divalent Group 14 Compounds.²⁵ The reaction of silylene **4a** with a diarylstannylene (or an aminoaryl-stannylene) resulted in the isolation of novel silastanylenes (eq 3).²⁶ An intermediate compound containing a tin–silicon double bond, **16**, was proposed. **16** could rearrange to the more stable silylstannylenes by either an aryl or amino migration from tin to silicon.



The ability of silylene **3** to insert into M–N bonds²⁷ has been a crucial step in a series of remarkable reactions that have produced novel digermenes and disilenes with unusually long M–M bond lengths. The reaction of the silylene **3** with the analogous germylene leads not to the germsilene but to the formation of the novel digermene **17** (eq 4).²⁸ The silylene inserts into the Ge–N bond to generate an aminosilylgermylene which can then dimerize to a digermene. The length of the germanium–germanium bond changes with the N-substituent on the germylene.

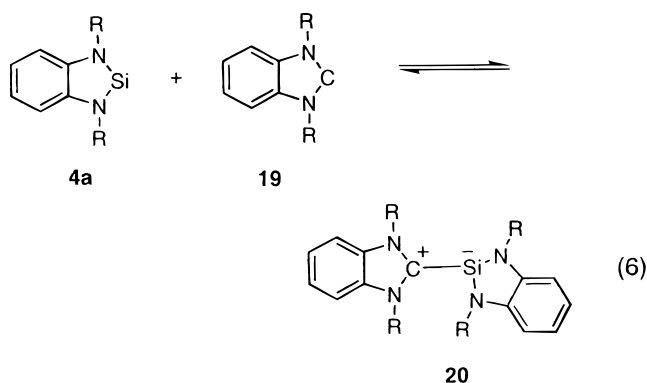


A similar reaction was found to occur with silylene **3** by itself in concentrated solution or in the solid state (eq 5).²⁹ Upon concentration of a solution of **3**, the silylene inserts into a Si–N bond to form an aminosilylsilylene which can now dimerize to generate a disilene, **18**. Again, the resulting disilene has an exceptionally long Si–Si bond length for a disilene. Surprisingly, the observed reaction is reversible—in solution **3** is almost exclusively present, while in the solid state the equilibrium favors **18**.



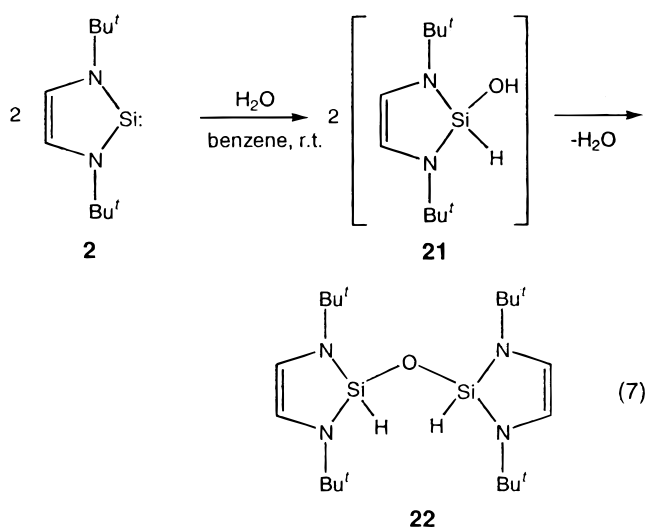
Lappert and co-workers were able to synthesize a carbene–silylene adduct by reacting **4a** with stable carbene **19** (eq 6).³⁰ The crystal structure of **20** showed a C–Si bond length of 216.2(5) pm, much longer than for a typical

silylene, and DFT calculations support the dipolar nature of the C–Si bond. Under the same conditions, **2** was found not to react with carbene **19**.



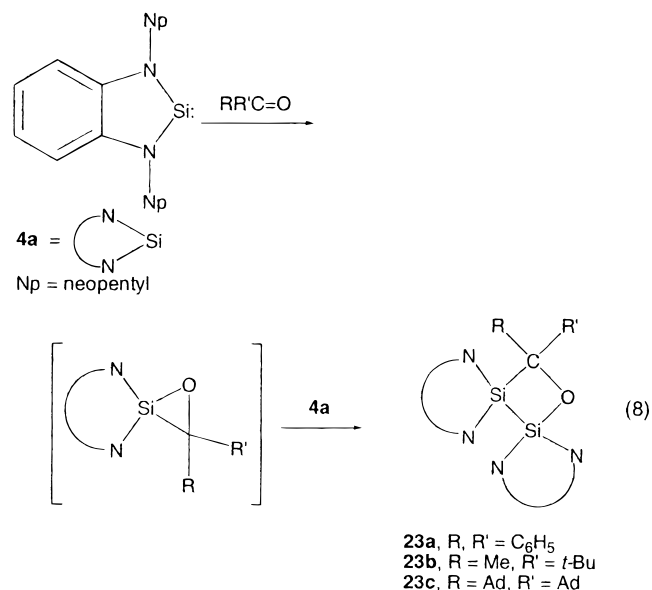
III. With Organic Substrates. Like transient silylenes, stable silylenes insert into the C–I bond of organic iodides. For example, **2**,²³ **3**,¹³ **4a**,⁹ and **6**¹¹ all react with iodomethane to afford the corresponding iodomethylsilane. Surprisingly, stable silylenes do not insert into all carbon–halogen bonds. As a case in point, silylene **2** shows no reaction with 1-chlorohexane, even at elevated temperatures, although it does react with carbon tetrachloride to afford a mixture of products.³¹

Stable silylenes all react with alcohols via an expected insertion into the O–H bond to afford the corresponding alkoxyhydrosilane.^{9,11,13,23} Similarly, silylene **2** inserts into the O–H bond of water to initially give silanol **21**, which eventually self-condenses to give the disiloxane, **22** (eq 7).²³ Silylene **3** undergoes an identical transformation.¹³



Reactions of stable silylenes with ketones and imine functionalities have thus far been explored primarily for silylene **4a**. Reaction of this silylene with ketones such as benzophenone, 3,3-dimethylbutan-2-one, and 2-adamantan-2-one afforded four-membered disilaoxetane compounds **23a**, **b**, and **c** in high yields (eq 8).³² The mechanism for this transformation most likely occurs via a [2 +

1] cycloaddition to form an ephemeral oxasilacyclopropane intermediate, a transformation common for transient silylenes, which further reacts with a second silylene to give the final product.³³

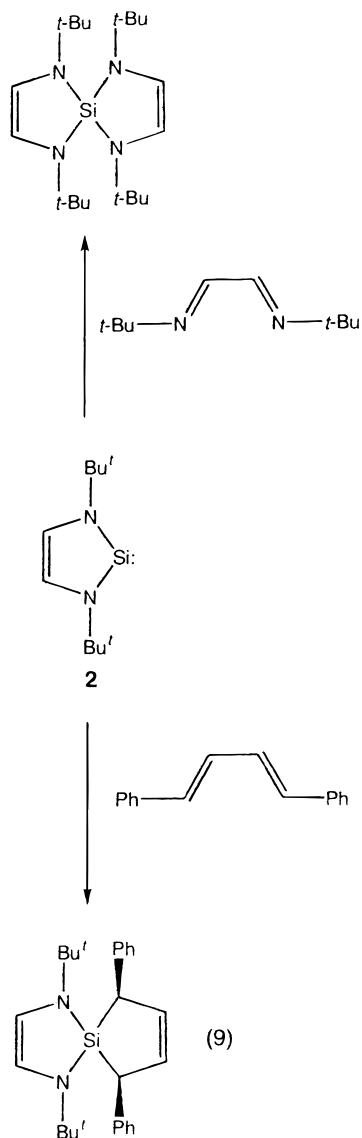


A departure from this trend occurs when the reaction conditions are altered; when a solution of **4a** is slowly added to the refluxing benzene solution, a different product is observed, resulting from an intramolecular rearrangement of the initially formed oxasilacyclopropane followed by a second silylene insertion. **4a** also reacts with imines to give 1:1 or 2:1 adducts, depending on the imine used and on the reaction conditions.³⁴

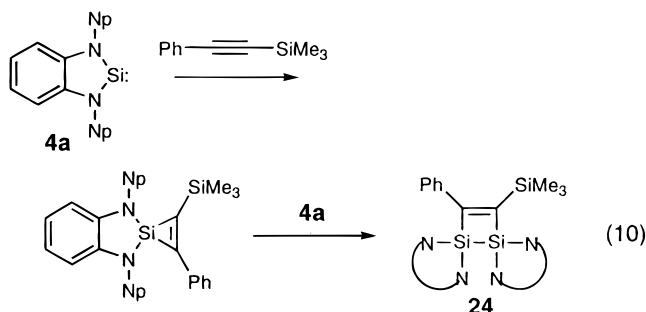
Not surprisingly, reactions of silylenes **2** and **4a** with heterodienes such as 1,4-diaza- or 1,4-dioxanes yielded the corresponding 1,4-diaza- or 1,4-dioxasilacyclopentenes (eq 9).

Similarly, the stable silylenes undergo [1 + 4] cycloadditions with dienes. For example, silylenes **3** and **6** react with 2,3-dimethylbutadiene to form the expected silacyclopentene product. Although silylene **2** undergoes a similar transformation with *trans,trans*-1,4-diphenylbutadiene to afford the corresponding spiro compound (eq 9), the reaction between **2** and 2,3-dimethyl-1,3-butadiene is more complicated, leading to a highly cross-linked butadiene polymer. The silylene is recovered unreacted. This transformation represents a marked difference in the reactivity of **2** and the saturated analogue, **3** as well as other stable silylenes. Preliminary results show that silylene **2** also polymerizes alkenes such as styrene, but does not react at all with isobutene. Further investigations of these polymerization reactions are underway.

Silylene **2** also differs from other stable silylenes in its reactivity with alkynes. Although silylene **2** does not react with alkynes such as bis(trimethylsilyl)acetylene or diphenylacetylene, **6** reacts with the latter to form the anticipated silacyclopentene.¹¹ Silylene **4a** reacts with phenyltrimethylsilylacetylene to form the disilacyclobutene, **24**, a reaction which likely proceeded through a

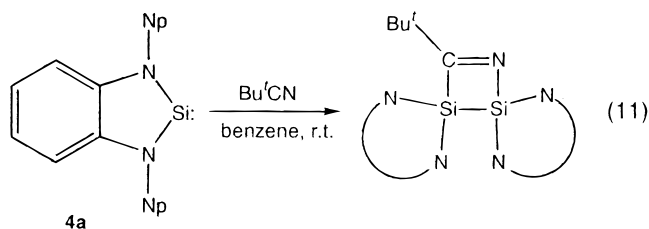


silacyclopentane intermediate followed by insertion of a second silylene (eq 10).³⁵

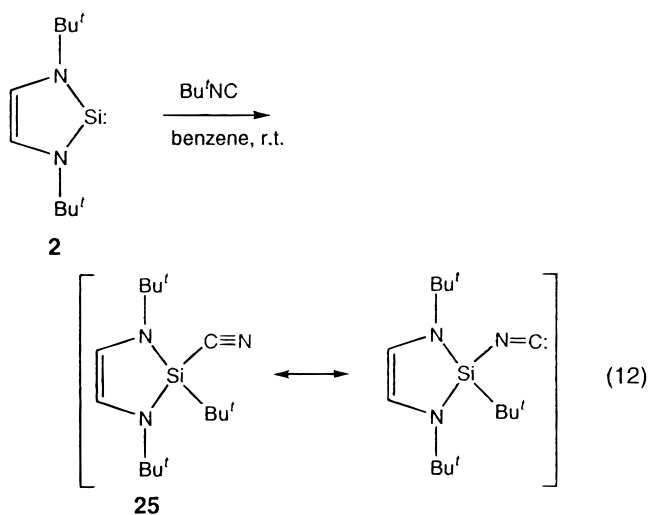


Further, the stable silylene **2** is unreactive toward even excess quantities of nitriles, even at elevated temperatures, though again this behavior is not general for all stable silylenes. For example, treatment of **4a** with *t*BuCN yields a disilaazetene product (eq 11), the formation of which is thought to proceed via a mechanism similar to that discussed for the reaction of **4a** with acetylene (i.e., via a three-membered ring intermediate that under-

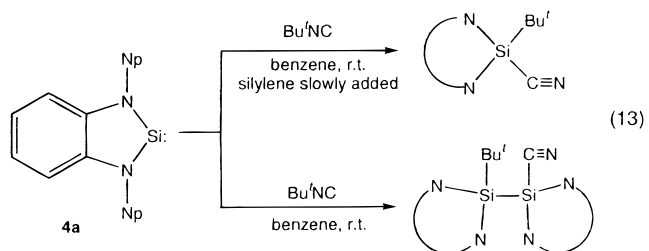
goes an additional insertion of another silylene molecule).³⁵



A more general transformation of the stable silylenes appears to be their reaction with the more reactive isonitrile functional groups. Silylene **2** reacts with isonitriles to afford the corresponding silanitride, **25** (eq 12).³¹ According to IR studies, the silanitride (2182 cm⁻¹) is in equilibrium with small amounts of the silaisonitrile (2075 cm⁻¹), a discovery consistent with previous findings for silanitrides.³⁶ This interconversion is fast on the NMR time scale.

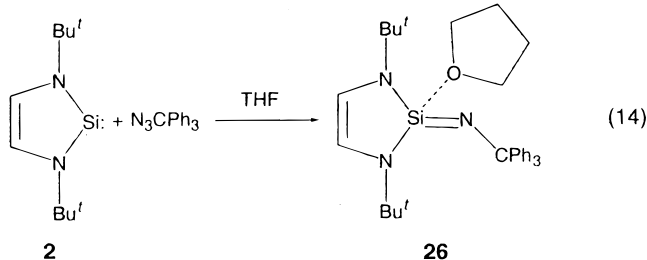


Silylene **4a** also reacts with Bu'⁺NC to give the corresponding silanitride as the major product.³⁵ However, this reaction afforded two different products, depending on the reaction conditions (eq 13). The mechanism could proceed either by initial silylene insertion into the C–N single bond, followed by isomerization to the more thermodynamically stable silanitride, or via rearrangement of a silaketene intermediate.³⁷

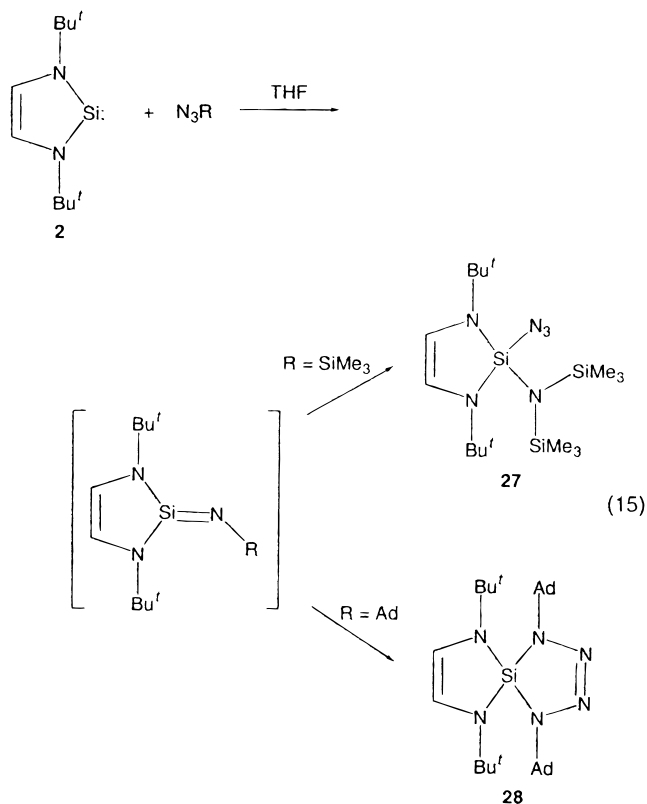


Stable silylenes react readily with substituted azides to give varying products. Reaction of **2** with the very hindered azide Ph₃CN₃ resulted in the clean formation of silaketimine, **26**, stabilized by a THF molecule coordinated

to the silicon (eq 14).³⁸ This reaction provides a novel route to doubly bonded Si compounds.

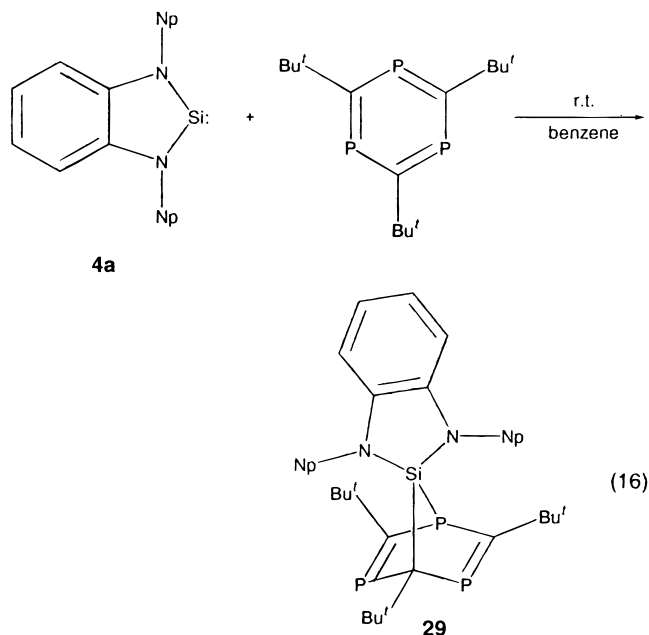


However, reactions of **2** and **4a** with less hindered azides are more complex. Combining **2** with trimethylsilyl azide affords the isolated azidosilane product, **27**,³⁸ and with 1-adamantyl azide, the silatriazoline, **28**.⁸ Silylene **4a** undergoes an analogous transformation.³⁵ These products may all have resulted from the initial formation of a silanimine followed by further insertion or cycloaddition reactions (eq 15).

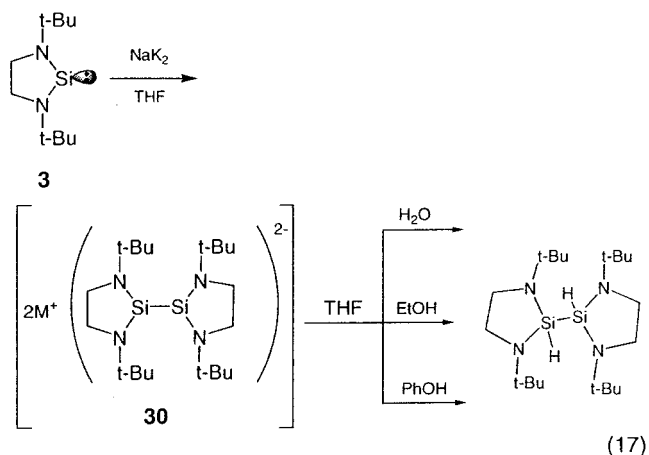


An interesting reaction takes place between **4a** and the even more recently synthesized 1,3,5-triphospha-benzene (eq 16).³⁹ This combination affords the orange compound, **29**, a [1 + 4] cycloaddition product. No further reaction of **4a** with **29** took place, and the reaction did not appear to be reversible.

IV. With Metals. A. Alkali Metals. Silylene **3** reacts with alkali metals to generate a silyl anion, as evidenced by the isolation and characterization of trapping products (eq 17).¹³ The reaction of **3** with sodium potassium alloy leads to the formation of a dimer dianion **30**, which can be



trapped by electrophiles in high yield. Reduction of silylene **2** leads to decomposition.



B. Transition Metals. The synthesis and structure of Ni(**2**)₂(CO)₂,⁴⁰ published in 1994, were remarkable in that unlike previously synthesized metal coordinated-transient silylene complexes,⁴¹ Ni(**2**)₂(CO)₂ was a metal complex of a stable silylene, and introduced the concept that stable silylenes might resemble phosphines as transition metal ligands. Since then, many more metal complexes of stable silylenes have been synthesized, and the incorporation of stable silylenes as ligands for transition metals is becoming an active area of research. Raman, IR, and NMR studies on these complexes indicate that the stable silylenes, like phosphines, are excellent σ -donors and exhibit only very weak π -back-bonding ability.

Cr, Mo, W. Reaction of the group 6 transition metal hexacarbonyls with silylenes **2** and **3** under photolytic conditions generates metal silylene complexes of the generic formula M(CO)_x(silylene)_{6-x} (eq 18).³¹ The silylene ligands are rather bulky and tend to occupy the least sterically crowded spot. For octahedral complexes, *trans*-disubstitution is the only geometry observed so far (e.g.,

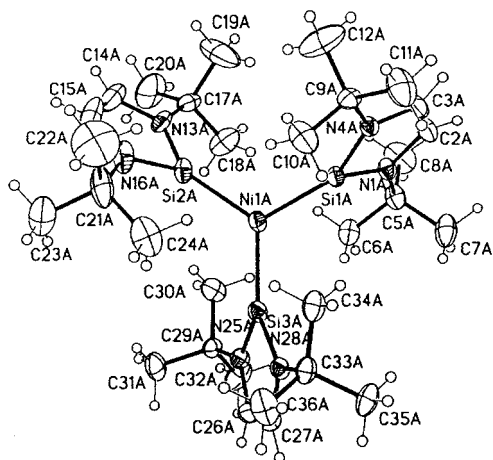
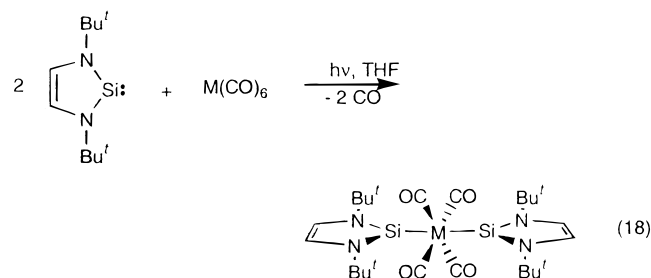


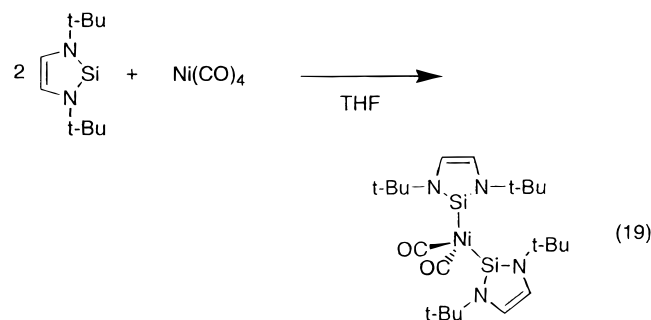
FIGURE 4. Crystal structure of Ni(2)₃.

Cr(2)₂(CO)₄, Mo(2)₂(CO)₄, W(2)₂(CO)₄, and W(3)₂(CO)₄, although there is evidence of monosubstitution as a minor product. *Cis*-substituted octahedral complexes are not observed, presumably due to steric constraints.



A trigonal molybdenum–silylene complex, Cp₂Mo(2), has also been synthesized by reacting Mo(Cp)₂(PEt₃) with 2.⁴²

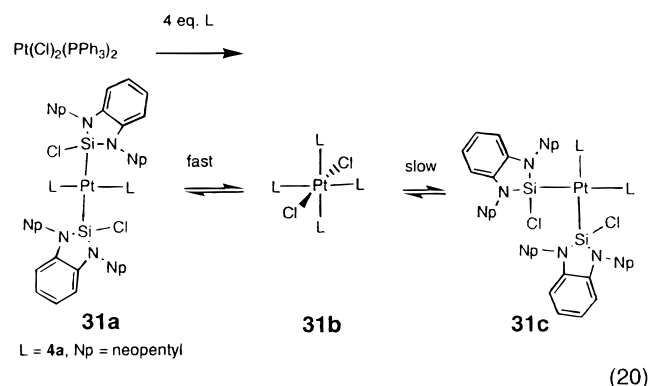
Ni, Pd, Pt. Ni(2)₂(CO)₂ was generated by mixing Ni(CO)₄ with unsaturated silylene (eq 19).⁴⁰ No evidence for the formation of mono-, tri-, or tetrasubstituted products was observed.



A series of complexes with nickel demonstrates the significance of the N-substituent in geometry determination. Direct reaction of 4a with Ni(COD)₂ resulted in formation of the tetrahedrally substituted complex Ni(4a)₄.⁴³ By comparison, direct reaction of excess silylenes 2 and 3 with Ni(COD)₂ resulted in formation of trigonal planar Ni(2)₃ and Ni(3)₃, respectively.⁴⁴ The crystal structure of the Ni(2)₃ compound is shown in Figure 4. The difference in geometry is explained by the higher steric

requirement of silylenes 2 and 3 resulting from the *tert*-butyl group on the nitrogens compared to the less sterically demanding neopentyl groups on 4a.

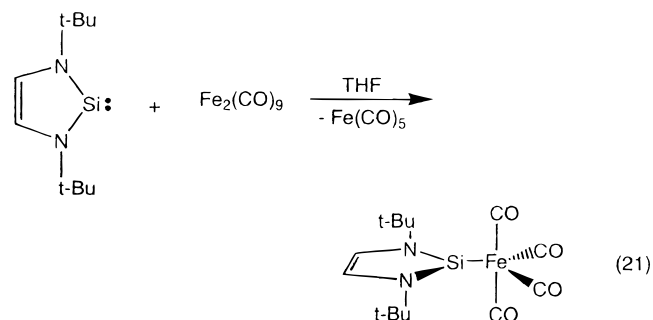
The reaction of stable silylenes with metal halides can lead to various products. In some cases the silylene can act as a reducing agent, as shown in the reaction of 4a with NiCl₂(PPh₃)₂, which led to the isolation of Ni(PPh₃)-(4a)₃ and Ni(4a)₄. In other cases the silylene inserts into the M–X bond, as demonstrated by the reaction of 4a with PtCl₂(PPh₃)₂ to form 31a. The product of this reaction was shown to be in equilibrium with other isomers, 31b and 31c (eq 20).⁴³



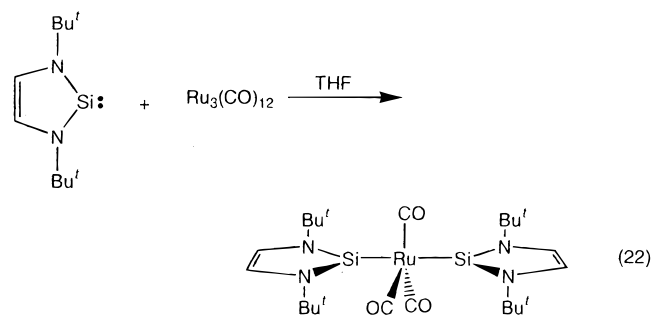
L = 4a, Np = neopentyl

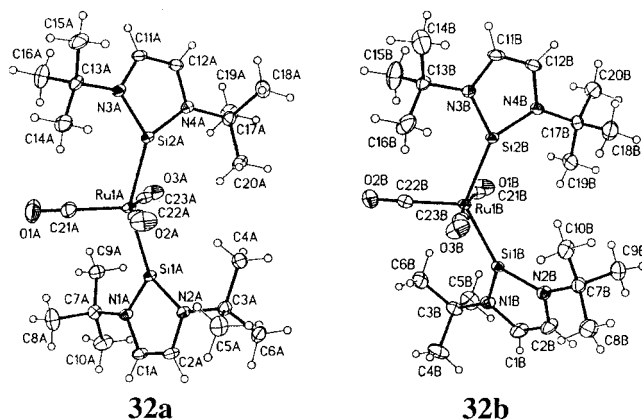
(20)

Fe, Ru. Mixed carbonyl–silylene metal complexes of the group 8 metals have been synthesized by reacting reactive metal carbonyl precursors with silylene 2. Diiron nonacarbonyl reacts at room temperature with 2 to generate the monosubstituted complex in high yield (eq 21). A crystal structure of this compound determined that the silylene was in an equatorial position.⁸



Reaction of Ru₃(CO)₁₂ with silylene 2 (eq 22) generated the pentacoordinate complex, 32, with the formula Ru(2)₂(CO)₃.⁴⁵ The crystal structure shows two different



FIGURE 5. Crystal structures of **32a,b**.**Table 3. M–Si Bond Lengths and ²⁹Si NMR Values for Reported Metal Silylene Complexes**

compound	ref	²⁹ Si (ppm)	average M–Si bond length (pm)
Ni(CO) ₂ (2) ₂	40	97.5	221.2
Ni(2) ₃	43	110.6	215.1
Ni(3) ₃	43	144.6	215.8
Ni(4a) ₄	42	145.9	na ^a
Ni(PPh ₃)(4a) ₃	42	136.2	216.5
31a	42	142.5	226.6
31b	42	146.9	na ^a
31c	42	143.0, 146.5	na ^a
Cr(2) ₂ (CO) ₄	44	136.9	232.9
Cr(3) ₂ (CO) ₄	44	170.3	232.6
Mo(2) ₂ (CO) ₄	44	119.3	247.1
Mo(3) ₂ (CO) ₄	44		248.0
Mo(Cp) ₂ (2)	41	139.3	241.3
W(2) ₂ (CO) ₄	44	97.8	247.1
W(3) ₂ (CO) ₄	44	137.1	
Fe(2) ₂ (CO) ₄	8, 43	111.6	219.6
Ru(2) ₂ (CO) ₃	43	110.2	233.0

^a Not applicable.

molecules in the asymmetric unit—one approximating a square pyramid (**32a**) and another (**32b**) approximating a trigonal bipyramid—in which the silylenes occupy equatorial positions. Figure 5 shows the crystal structures of **32a,b**. NMR experiments indicate only one signal for the silylenes, suggesting that in solution the two structures interconvert rapidly and that the distortion is due to packing forces in the crystal structure. In contrast to iron, the additional space resulting from the longer Ru–Si bond length apparently allows the Ru center to accommodate more than just one silylene. Table 3 shows the M–Si bond lengths and ²⁹Si NMR values for the reported silylene complexes.

Status and Future Prospects

Now, 7 years after the first synthesis of **2**, structures have been determined for **2**, **3**, and **4a**, and fairly extensive spectroscopic and theoretical studies of these compounds have been carried out. Consequently, the unusual chemical bonding in these molecules is now moderately well understood. And although doubtless new and unexpected reactions remain to be discovered, the chemistry of these stable silylenes is known at least in general outline.

What further advances can be expected in this field? The number of stable silylenes is still very small, and it

seems possible that many other such molecules will be made. The use of silylenes as Lewis bases toward metals is still at an early stage of development, and much more is likely to be done in this subfield. Moreover, the discovery that metal complexes of stable carbenes⁷ are powerful catalysts for several organic reactions invites the study of catalytic properties of silylene–metal complexes. Such compounds may also be studied as precursors to silicon–metal alloys, by chemical vapor deposition.

Except for the marginally stable **6**, the isolable silylenes are all stabilized by π -bonding from N to Si. Stabilization by nitrogen may also be effective for elements outside group 14. Already, interesting communications have appeared describing isostructural rings containing gallium,⁴⁶ phosphorus, and arsenic.⁴⁷ Finally, π -bonding stabilization might be provided by other atoms, O, S, or P, alone or in combination with nitrogen. Attempts to synthesize such silylenes seem very likely.

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References

- (1) For a review on silylenes, see: Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappaport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, 1998; Vol. 2, Part 3, pp 2463–2567.
- (2) See, for example: Drahnak, T. J.; Michl, J.; West, R. Dimethylsilylene, (CH₃)₂Si. *J. Am. Chem. Soc.* **1979**, *101*, 5427–5428.
- (3) Arduengo, A. J., III; Harlow, R. L.; Kline, M. J. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
- (4) A few divalent, but not dicoordinate, silicon compounds were, however, known. See: Jutzi, P.; Kanne, D.; Krüger, C. Decamethylsilylocene—Synthesis and Structure. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164–165. Karsch, H. M.; Keller, U.; Gamper, S.; Müller, G. Si[(Me₂P)₂C(SiMe₃)]₂, a Stable σ -Bonded Compound Containing Divalent Silicon. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 295–296.
- (5) For a review, see: Lappert, M. F. Recent Chemistry of Bivalent Compounds of Germanium, Tin and Lead. *Main Group Metal Chem.* **1994**, *17*, 183–207.
- (6) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Haaland, A.; Belyakov, H.; Verne, P.; Wagner, M.; Metzler, N. Synthesis and Structure of a Stable Silylene. *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692.
- (7) Herrmann, W. A.; Köcher, C. N-Heterocyclic Carbenes. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162–2187.
- (8) West, R.; Denk, M. Stable Silylenes: Synthesis, Structure, Reactions. *Pure Appl. Chem.* **1996**, *68*, 785–788.
- (9) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. Synthesis, Structure and Reactions of New Stable Silylenes. *J. Chem. Soc., Chem. Commun.* **1995**, 1931–1932.
- (10) Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpoti, T.; Nyulaszi, L.; Veszpremi, T. Unsymmetrical Carbene Homologs: Isolable Pyrido[b]-1,3,2λ²-diazasilole, -germole and -stannole and Quantum Chemical Comparison with Unstable Pyrido[c] Isomers. *Chem. Eur. J.* **1998**, *4*, 541–545.
- (11) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. The First Isolable Dialkylsilylene. *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723.
- (12) The known stable carbenes are all singlet-state species, but many unstable carbenes are known with unpaired electrons, and hence in a triplet ground state. For reasons which are quite complicated, all silylenes, stable and unstable, have singlet ground states with an electron pair in an s-like, in-plane orbital. See: Apeloig, Y.; Pauncz, R.; Karni, M.; Chapman, D.; Steiner, W.; West, R. Abstracts of Papers, 31st Organosilicon Symposium, New Orleans LA, 1998; p A-10, and manuscript in preparation.
- (13) Haaf, M.; Schmedake, T. A.; Paradise, B. J.; West, R. Synthesis and Reactivity of the Stable Silylene *N,N'*-Di-*tert*-butyl-1,3-diaza-2-sila-2-ylidene. *Can. J. Chem.*, in press.

- (14) Hargittai, I.; Schultz, G.; Tremmel, J.; Kagramanov, N. D.; Maltsev, A. K.; Nefedov, O. M. Molecular Structure of Silicon Dichloride and Silicon Dibromide from Electron Diffraction Combined with Mass Spectrometry. *J. Am. Chem. Soc.* **1983**, *105*, 2895–2896.
- (15) West, R.; Buffy, J. J.; Haaf, M.; Mueller, T.; Gehrhuss, B.; Lappert, M. F.; Apeloig, Y. Chemical Shift Tensors and NICS Calculations for Stable Silylenes. *J. Am. Chem. Soc.* **1998**, *120*, 1639–1640.
- (16) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. Electronic Structure of a Stable Silylene—Photoelectron-spectra and Theoretical Calculations of Si(NRCHCHNR) Si(NRCH₂CH₂NR) and SiH₂(NRCHCHNR). *J. Chem. Soc., Dalton Trans.* **1994**, 2405–2410.
- (17) Blakeman, P.; Gehrhuss, B.; Green, J. C.; Heinicke, J.; Lappert, M. F.; Kindermann, M.; Veszpremi, T. Electronic Structure of Stable Benzodiazasilylenes: Photoelectron Spectra and Quantum-chemical Investigations. *J. Chem. Soc., Dalton Trans.* **1996**, 1475–1480.
- (18) Arduengo, A. J. III.; Bock, H.; Chen, H.; Denk, M.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. Photoelectron Spectroscopy of a Carbene/Silylene/Germylene Series. *J. Am. Chem. Soc.* **1994**, *116*, 6641–6649.
- (19) Lehmann, J. F.; Urquhart, S. G.; Ennis, L. E.; Hitchcock, A. P.; Hatano, K.; Gupta, S.; Denk, M. K. Core Excitation Spectroscopy of Stable Cyclic Diaminocarbenes, -silylenes and -germylenes. *Organometallics* **1999**, 1862–1872.
- (20) Leites, L. A.; Bukalov, S. S.; Denk, M.; West, R.; Haaf, M. Raman Evidence of Aromaticity in the Thermally Stable Silylene (tBuNCH=CHtBu)Si. *J. Mol. Struct.*, in press.
- (21) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwartz, H. On the Question of Stability, Conjugation and “Aromaticity” in Imidazol-2-ylidenes and Their Silicon Analogs. *J. Am. Chem. Soc.* **1996**, *118*, 2023–2038.
- (22) Gehrhuss, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. Synthesis, structures and oxidative addition reactions of new thermally stable silylenes; crystal structures of [Si{(N(CH₂tBu)₂C₆H₄-1,2)}₂] and [Si{(N(CH₂tBu)₂C₆H₄-1,2)}₂(E)] (E = Se or Te). *J. Organomet. Chem.* **1996**, *521*, 211–220.
- (23) Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. Synthesis and Reactivity of a Stable Silylene. *J. Am. Chem. Soc.* **1998**, *120*, 12714–12719.
- (24) Metzler, N.; Denk, M. Synthesis of a silylene–borane adduct and its slow conversion to a silylborane. *Chem. Commun.* **1996**, 2657–2658.
- (25) Denk, M.; Hatano, K.; Lough, A. J. Reaction of a Stable Silylene with Divalent Group 14 Compounds. *Eur. J. Inorg. Chem.* **1998**, 1067–1070.
- (26) Drost, C.; Gehrhuss, B.; Hitchcock, P. B.; Lappert, M. F. Synthesis and characterization of the first stable, heteroleptic silylstanlylenes. *Chem. Commun.* **1997**, 1845–1846.
- (27) Gehrhuss, B.; Hitchcock, P. B.; Lappert, M. F. New Reactions of a Silylene: Insertion into M–N Bonds of M[N(SiMe₃)₂]₂ (M = Ge, Sn, or Pb). *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2514–2518.
- (28) Schäfer, A.; Saak, W.; Weidenbruch, M.; Marsmann, H.; Henkel, G. Reactions of a Silylene with a Germylene and a Stannylene: Formation of a Digermene with an Unusual Arrangement of the Substituents and of a Stannane. *Chem. Ber./Recl.* **1997**, *130*, 1733–1737.
- (29) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. Reversible Transformation between a Diaminosilylene and a Novel Disilene. *J. Am. Chem. Soc.* **1999**, *121*, 9479–9480.
- (30) Boesveld, W. M.; Gehrhuss, B.; Hitchcock, P. B.; Lappert, M. F.; Schleyer, P. R. A crystalline carbene-silylene adduct 1,2-C₆H₄-[N(R)]₂-Si[N(R)]₂C₆H₄-1,2 (R = CH₂tBu[†]); synthesis, structure and bonding in model compounds. *Chem. Commun.* **2000**, 755–756.
- (31) Haaf, M.; Schmedake, T. A.; West, R., unpublished work.
- (32) Gehrhuss, B.; Hitchcock, P. B.; Lappert, M. F. The Thermally Stable Silylene Si[{N(CH₂tBu)[†]]₂C₆H₄-1,2]: Reactivity toward CO Double Bonds. *Organometallics* **1997**, *16*, 4861–4864.
- (33) Gehrhuss, B.; Lappert, M. F. Novel Ring Systems by Reaction of a Stable Bis(amino)silylene with Multiply Bonded Compounds. *Phosphorus, Sulfur, Silicon* **1997**, *125*, 537–540.
- (34) Gehrhuss, B.; Hitchcock, P. B.; Lappert, M. F. The Thermally Stable Silylene Si[{N(CH₂tBu)[†]]₂C₆H₄-1,2]: Reactivity toward CN Double Bonds. *Organometallics* **1998**, *17*, 1378–1382.
- (35) Gehrhuss, B.; Lappert, M. F. Reactions of the stable bis(amino)silylene Si[{N(CH₂tBu)[†]]₂C₆H₄-1,2] with multiply bonded compounds. *Polyhedron* **1998**, *17*, 999–1000.
- (36) Bither, T. A.; Knoth, W. H.; Lindsey, R. V., Jr.; Sharkey, W. H. Trialkyl- and Triaryl(iso)cyanosilanes. *J. Am. Chem. Soc.* **1958**, *80*, 4151–4153.
- (37) Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Saak, W. A Cyclo-dimeric Silaketenimine. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 90–93.
- (38) Denk, M.; Hayashi, R.; West, R. Reaction of a Stable Silylene with Covalent Azides: An New Synthesis for Silaimines. *J. Am. Chem. Soc.* **1994**, *116*, 10813–10814.
- (39) Clendinning, S. B.; Gehrhuss, B.; Hitchcock, P. B.; Nixon, J. F. [1+4]-cycloaddition of a stable silylene to 2,4,6-tri-tert-butyl-1,3,5-triphosphabenzene. *Chem. Commun.* **1999**, *24*, 2451–2452.
- (40) Denk, M.; Hayashi, R.; West, R. Silylene Complexes from a Stable Silylene and Metal Carbonyls: Synthesis and Structure of [Ni{(Bu[†]-NCH=CH-NBu[†])Si}₂(CO)₂], a Donor-free Bis-silylene Complex. *J. Chem. Soc., Chem. Commun.* **1994**, 33–34.
- (41) For related studies involving metal-coordinated silylene complexes derived from transient silylenes, see: (a) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. Base-Free Silylene Complexes [(η⁵-C₅Me₅)(PMe₃)₂Ru=Si(SR)₂]BPh₄ (R = Et, *p*-MeC₆H₄). *J. Am. Chem. Soc.* **1990**, *112*, 7801–7802. (b) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. Synthesis and Structure of a Transition Metal-Substituted Silylene Complex, (CO)₄OsSi(STol-*p*)[Ru(η⁵-C₅Me₅)(PMe₃)₂]. *J. Am. Chem. Soc.* **1993**, *115*, 358–360. (c) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L.; Arnold, F. P. A Fischer-Type Silylene Complex of Platinum: [*trans*-(C₃P)₂(H)Pt=Si(SEt)₂]BPh₄. *J. Am. Chem. Soc.* **1993**, *115*, 7884–7885. (d) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. Base-Free Silylene Complexes Without π-Donor Stabilization. Molecular Structure of [Cp^{*}(PMe₃)₂Ru=SiMe₂][B(C₆F₅)₄]. *J. Am. Chem. Soc.* **1993**, *115*, 7884–7885.
- (42) Petri, S. H.; Eikenberg, D.; Neumann, B.; Stammner, H.; Jutzli, P. Reaction of Molybdenocene and Tungstenocene Derivatives with the Divalent Silicon Species SiN[†]BuCHCHN[†]Bu and (C₅Me₅)₂Si. *Organometallics* **1999**, *18*, 2615–2618.
- (43) Gehrhuss, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. Silylenenickel(0) or Silyl(silylene)platinum(II) Complexes by Reaction of Si[(NCH₂tBu)[†]]₂C₆H₄-1,2] with [NiCl₂(PPh₃)₂], [Ni(cod)₂], or [PtCl₂(PPh₃)₂]. *Organometallics* **1998**, *17*, 5599–5601.
- (44) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Powell, D. R.; West, R. *Organometallics*, in press.
- (45) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Powell, D. R.; West, R., submitted for publication.
- (46) Schmidt, E. S.; Jockisch, A.; Schmidbauer, H. A Carbene Analogue with Low-Valent Gallium as a Heteroatom in a *quasi*-Aromatic Imidazolate Anion. *J. Am. Chem. Soc.* **1999**, *121*, 9758–9759.
- (47) Carmalt, C. J.; Lomeli, V.; McBurnett, B. G.; Cowley, A. H. Cyclic phosphonium and arsenium cations with 6 pi electrons and related systems. *Chem. Commun.* **1997**, 2095–2096.

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