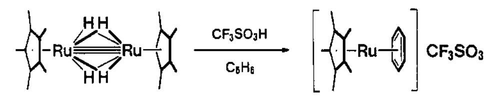
(1.954 (67) Å),[15] $Ru_2H(\mu\text{-}H)_3N_2(PPh_3)_4$ (1.89 Å),[16] and $[ReH_2(PEt_2Ph)]_2(\mu\text{-}H)_4$ (1.878 (7) Å).[5] The H–H distances, 0.99 (7) Å for H(1)–H(2) and 0.84 (8) Å for H(3)–H(4), are comparable to those of η^2-H_2 ligands,[17,18] but X-ray crystallography is not a good way to tell the H–H distances because the electron density maxima of the two-electron–three center (2e–3c) MHM bonds will be much closer than the nuclei themselves. We therefore conclude that 2 is not a η^2-H_2 complex but a σ-bonded metal hydride complex on the basis of the value of J_{HD} and the T_1 data.

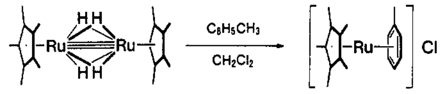
Transition-metal polyhydride complexes are known to have the potential for creating coordinative unsaturation by eliminating molecular hydrogen. While complex 2 is hardly decomposed upon irradiation of UV light, 2 evolves H_2 to generate the coordinatively unsaturated species by the addition of acid.

Treatment of 2 with 1.1 equiv of CF_3SO_3H in benzene quantitatively afforded the cationic 18-electron complex $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_6)](CF_3SO_3)$ (3) via the addition of benzene to the intermediary "$(\eta^5\text{-}C_5Me_5)Ru$" (eq 2).[19]

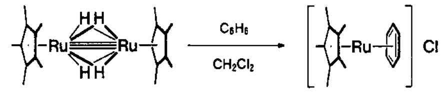


2 3 (2)

Cationic arene–ruthenium complexes 4 and 5 were also obtained in 99 and 91% yields, respectively, by reacting 2 with arenes in a halogenated solvent such as CH_2Cl_2 or $CHCl_3$ (eq 3 and 4).[20]



2 4 (3)



2 5 (4)

Acknowledgment. We thank the Instrument Center, Institute for Molecular Science, for the use of X-ray diffractmeter (Rigaku AFC-5). We are grateful to Drs. T. Inabe and T. Mori at Institute for Molecular Science for aid of X-ray structural analysis. Financial support for this work was generously provided in part by grants from the Kawakami Memorial Foundation and the Ministry of Education, Science and Culture of the Japanese Government (No. 62215009).

Supplementary Material Available: Tables of crystal data, bond distances and angles, positional parameters and isotropic temperature factors, and anisotropic temperature factors for 2 and field-desorption mass spectra and mass spectral data for $C_{20}H_{34}R_2$ (13 pages); a listing of structure factor amplitudes for 2 (6 pages). Ordering information is given on any current masthead page.

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[19] 3: IR (KBr) 3072, 2981, 2909, 1258, 1170, 1041, 645, 581, 528 cm^{-1}; ^1H NMR (CD_3COCD_3) δ 5.97 (s, 6 H, C_6H_6), 2.04 (s, 15 H); ^{13}C NMR (CD_3COCD_3) δ 96.5 (C_5Me_5), 87.0 (C_6H_6), 9.7 (C_5Me_5). Anal. Calcd for $C_{17}H_{21}O_3F_3SRu$: C, 44.06; H, 4.57. Found: C, 43.96; H, 4.65.

[20] 4: IR (KBr) 2987, 2941, 2899, 1616, 1473, 1451, 1385, 1129, 1072, 1033, 980, 860, 775 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.95–5.80 (m, 3 H, aromatic), 5.33–5.32 (m, 2 H, aromatic), 2.23 (s, 3 H), 2.00 (s, 15 H); ^{13}C NMR (CD_2Cl_2) δ 100.6 (s), 96.6 (s, C_5Me_5), 88.8 (d, J = 171.7 Hz), 88.1 (d, J = 151.9 Hz), 87.4 (d, J = 176.0 Hz), 19.0 (q, J = 129.2 Hz), 11.1 (q, J = 128.6 Hz). Anal. Calcd for $C_{17}H_{23}ClRu$: C, 56.11; H, 6.37; Cl, 9.74. Found: C, 55.85; H, 6.41; Cl, 9.53. 5: IR (KBr) 3053, 3026, 2960, 2906, 1483, 1445, 1399, 396 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93 (s, 6 H, C_6H_6), 2.03 (s, 15 H); ^{13}C NMR ($CDCl_3$) δ 98.1 (s, C_5Me_5), 88.5 (d, J = 176.4 Hz), 10.8 (q, J = 128.0 Hz). Anal. Calcd for $C_{16}H_{21}ClRu$: C, 54.93; H, 6.05; Cl, 10.13. Found: C, 54.59; H, 6.29; Cl, 10.92.

Silaaziridines from the Reaction of Isonitriles with Stable Silenes

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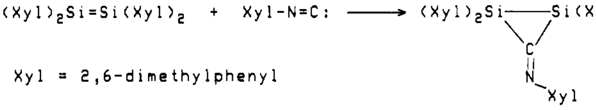
Summary: Stable silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ react with isonitriles $R'N{=}C$: to yield unstable silacyclopropanimines which rapidly rearrange below room temperature to form the isomeric silaaziridines, as shown by the crystal structure of one of the compounds (R = Ad, R′ = *t*-Bu). These are the first reported examples of three-membered rings containing both silicon and nitrogen.

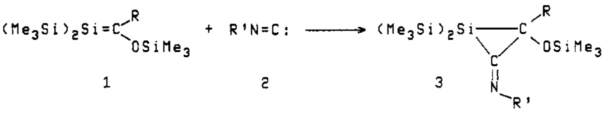
Silenes have been shown to undergo a variety of cycloaddition reactions,[1] including reactions with alkenes,[2,3] dienes,[2,3] aldehydes and ketones,[4,5] silylenes,[6] and imines[5] and diazenes.[5,7] We now report the cycloaddition reaction of stable silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (**1**) with isonitriles $R'N{=}C$: (**2**).

The reaction of an isonitrile with a disilene has recently been reported to yield a disilacyclopropanimine (eq 1), as



(1)

shown by the crystal structure of the product.[8,9] By analogy it might be expected that an isonitrile, 2, would react with a silene 1 to yield the related silacyclopropanimine 3 (eq 2), but this was not the structure of the compounds isolated at room temperature.



1 2 3 (2)

When members of our family of silenes 1 having R = *t*-Bu or Ad (1-adamantyl) were generated (by photolysis of the related acylsilane $(Me_3Si)_3SiCOR$ in C_6D_6 using 360-nm radiation at 10 °C) in the presence of an equivalent

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† On leave from the Department of Chemistry, Kyunggi University, Suwon, South Korea.

[1] For recent reviews on the chemistry of silenes see: Baines, K. M.; Brook, A. G. *Adv. Organomet. Chem.* 1986, *26*, 1. Michl, J.; Raabe, G. *Chem. Rev.* 1985, *85*, 419.

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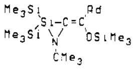
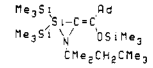
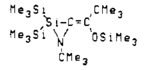
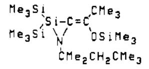
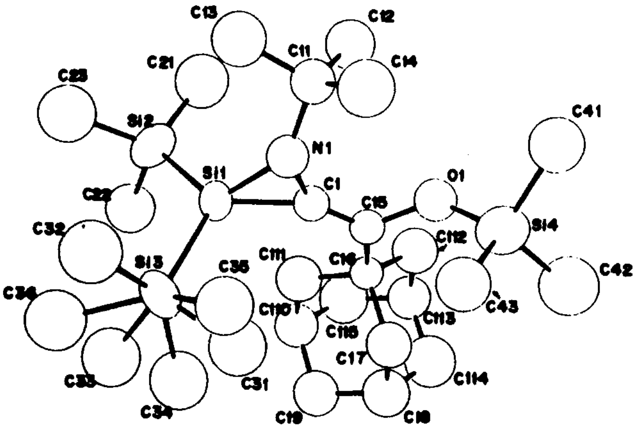
Table I. NMR Data (δ) for Silaaziridines (in C_6D_6)

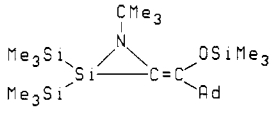
	 **4a**	 **4b**	 **4c**	 **4d**
^{1}H				
Me_3Si	0.26	0.25	0.26	0.21
Me_3SiO	0.44	0.44	0.41	0.40
Me_nCN	1.34	1.42	1.33	1.39
other Ad	1.6–2.1	1.7–2.1		
$Me_3CC{=}$			1.34	1.30
Me_3CC		1.08		1.05
CH_2		1.18		1.11
^{13}C				
Me_3Si	−0.66	−0.30	−0.67	−0.32
Me_3SiO	2.93	3.11	2.75	2.91
ring C	114.51	114.72	114.37	114.50
ring C=*C*	133.36	133.30	132.51	132.35
$\mathit{Me}_n\mathrm{CN}$	31.98	31.06	32.00	31.07
$\mathrm{Me}_n\mathit{C}\mathrm{N}$	52.45	56.19	52.52	56.22
other Ad CH	29.53	29.55		
Ad CH_2	37.59	37.58		
	43.17	43.22		
Ad quat	38.96	39.07		
$\mathit{Me}_3\mathrm{C}$		32.07		32.04
$\mathrm{Me}_3\mathit{C}$		31.76		31.75
CH_2		57.24		57.26
^{29}Si				
Me_3Si	−16.34[a]	−15.98	−16.21	−16.11
Me_3SiO	11.20	11.02	11.49	10.92
ring Si	−89.55	−89.87	−89.03	−89.47

[a] Additional data: Me_3Si, ^{1}J(Si–C) = 45.8 Hz; Me_3SiO, ^{1}J(Si–C) = 59.8 Hz; ring Si, ^{1}J(Si–C) = 38.7 Hz; ring Si, ^{1}J(Si–Si) = 73.2 Hz.

of isonitriles 2 having R′ = *t*-Bu or $CMe_2CH_2CMe_3$ (isooctyl), clean reactions occurred to give only one product in each case. Identical products were formed when the preformed silene was treated with the isonitrile in the dark. All four compounds had remarkably similar ^{1}H, ^{13}C, and ^{29}Si NMR spectral data as shown in Table I. An important feature of these spectra was that each compound had only one $\mathrm{Me_3}\mathit{Si}$-Si NMR signal, where two magnetically nonequivalent Me_3Si groups would be expected for the silacyclopropanimine 3, as has been observed by us for several related cyclic systems.[2,4,6] Hence it was clear that the products of these reactions were *not* silacyclopropanimines.

One of the compounds (R = Ad, R′ = *t*-Bu) could be sublimed at 70 °C (0.1 mm) to give yellow crystals. An X-ray structure, although hampered by crystal decomposition, clearly demonstrated that the compound was the silaaziridine 4a having an exocyclic double bond[10] (Figure 1). In light of the similarity of the NMR spectra of all the compounds 4a–d it is clear that all must have the





4a

Ad = adamantyl = $C_{10}H_{15}$

Figure 1. ORTEP view of the silaaziridine **4a** showing the crystallographic numbering scheme and the disorder of the $Me_3Si(3)$ group. Selected bond lengths (Å) and bond angles (deg): Si1–Si2 = 2.328 (7), Si1–Si3 = 2.353 (6), Si1–C1 = 1.830 (15), Si1–N1 = 1.764 (13), C1–N1 = 1.417 (17), C1–C15 = 1.313 (19), N1–C11 = 1.484 (19), C15–C16 = 1.484 (18), C15–O1 = 1.428 (15), Si4–O1 = 1.644 (11); Si2–Si1–C1 = 118.4 (5), Si2–Si1–N1 = 121.7 (5), Si3–Si1–C1 = 117.2 (5), Si3–Si1–N1 = 112.4 (5), Si1–C1–C15 = 152.4 (13), N1–C1–C15 = 143.2 (14), Si1–N1–C11 = 142.1 (11), C1–N1–C11 = 133.4 (13), C15–O1–Si4 = 131.1 (9), C1–C15–O1 = 119.5 (13), C1–C15–C16 = 126.3 (14), O1–C15–C16 = 114.0 (12).

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[10] Properties of 4a: highly reactive yellow solid, mp 74 °C; IR (neat) 1630 (weak, C=C) cm^{-1}. Anal. MS Calcd for $C_{25}H_{51}NOSi_4$: 493.3048. Found: 493.3073. Crystals of 4a with rounded irregular shapes were cut to size and rapidly transferred to Lindemann capillaries in a glovebag under dry argon. Crystal data: monoclinic, space group *C*2/*c*, *a* = 19.220 (6) Å, *b* = 17.325 (7) Å, *c* = 19.904 (6) Å, *β* = 103.04 (2)°, *U* = 6457 $Å^3$, D_{calcd} = 1.02 g cm^{-3} for *Z* = 8, *μ*(Mo K$\bar{\alpha}$) = 1.6 cm^{-1}, *T* = 298 K. Unit cell dimensions based on 25 reflections (6.8 < *θ* < 12.8°) centered on an Enraf-Nonius CAD4 diffractometer by the use of Mo K$\bar{\alpha}$ radiation (graphite monochromator) and a crystal of dimensions 0.23 × 0.24 × 0.32 mm. Intensity data collection (ω–2θ scans over (0.80 + 0.35 tan θ)°, maximum scan time 48 s] gave 5562 data in the octants $h,k,\pm l$ [shell with 42 < 2θ < 50° incomplete due to extensive loss of scattering experienced by crystal (48%)]. Lorentz, polarization, and crystal decay corrections (based on the intensities of three standards measured at regular intervals) applied to all data collected. Structure solution by standard methods; only H atoms in Ad group included in calculated positions; 2:1 disorder observed for the Me groups of $Si(3)Me_3$. Full-matrix least-squares refinement minimizing $\sum w\Delta F^2$ has converged (maximum Δ/σ = 0.31) to *R* = 0.109 (*wR* = 0.118) for 1438 reflections with $F > 6\sigma(F)$ {Si atoms anisotropic; 159 variables; $w = [\sigma^2(F) + 0.00441F^2]^{-1}$ and maximum $\Delta\rho$ = 0.63 e $Å^{-3}$}. Scattering factors stored in programs were from ref 11. Programs: Enraf-Nonius SDP package on PDP 11/23 and SHELX on Gould 9705 computers.[12]

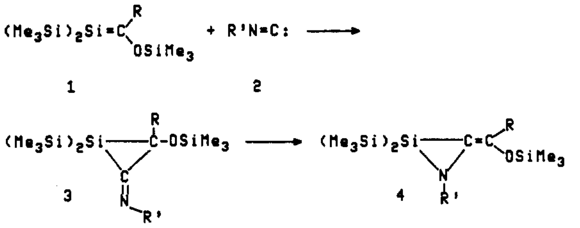
silaaziridine structure. These compounds are the first reported three-membered rings containing a silicon, carbon, and nitrogen atoms.

In the silaaziridine ring the endocyclic ring angles at Si, C, and N are 46.4 (5)°, 64.3 (8)°, and 69.3 (8)°, respectively. The angle at Si is intermediate between the values of 50.4° reported for a crowded oxasilacyclopropane[13] and the C–Si–C ring angle of 43.5 (1)° for 1,1-dimesityl-2-phenyl-3-(trimethylsilyl)-1-silacyclopropene.[14] In the latter compound the Si–C distances are 1.800 (2) and 1.839 (2) Å to the phenyl- and Me$_3$Si-substituted C atoms, respectively, compared with values of 1.830 (15) Å in **4a** and 1.849 Å in the above oxasilacyclopropane. Similarly in two other silacyclopropane structures[15,16] the Si–C distances and C–Si–C ring angles are 1.865 (5), 1.878 (6) Å, and 52.1 (2)° and 1.825 (3), 1.827 (3) Å, and 49.2 (1)°, indicating that when allowance is made for the small angles at Si, the resulting bent bonds would be quite long and weak.[17] Similarly, the observed Si–N ring distance in **4a** of length 1.764 (13) Å is already much longer than a standard single bond length (1.72 Å) for four-coordinate Si.[18] Consistent with the long Si–C and Si–N bonds, the C1–N1 bond length [1.417 (17) Å] is slightly shorter than the sum of the covalent radii for C(sp^2) and N of 1.44 Å. In comparison, the N–C(sp^2) and N–C(sp^3) ring distances in 1,1′-carbonylbis(aziridine) at −105 °C are 1.389 (1), 1.460 (2), and 1.485 (2) Å; the C–N–C angle is 61.2 (1)°.[19] The bond angle sums at C1 and N1 indicate that the former is planar while the latter is pyramidal with the N atom lying 0.31 Å above the Si1–C1–C11 plane (see Figure 1).

Compensation for the small Si ring angle is reflected in the large exocyclic Si2–Si1–Si3 bond angle [119.9 (3)°] and in the Si1–Si2 and Si1–Si3 bond lengths which are both shorter than values observed in a disilaoxetane [Si–Si$_{\text{ring}}$ = 2.409 (2) Å][20] and in a siloxetane with Me$_3$Si substituents [2.378 (5) and 2.394 (5) Å; Si–Si–Si = 106.8 (2)°].[4] Also, the Si–Si–C bond angles in **4a** are often <109.5°, indicating that these groups are not as sterically crowded as similar groups in other disilacyclobutanes and mono- and disilaoxetanes. Likewise the observed C–O–Si angle [131.1 (9)°] is comparable to that observed in a stable trimethylsiloxy-substituted silene (134.0°).[21] Finally, a least-squares mean plane through the atoms Si1, N1, C1, C15, C16, and O1 indicates that the double bond is planar to within 0.033 (14) Å; the angle between the planes Si2Si1Si3 and Si1C1N1 is 95.4°.

Relevant to the observed NMR data is the fact that the ring-nitrogen atom is pyramidal (see above). Hence the two Me$_3$Si groups in **4a** should be nonequivalent unless the ring nitrogen inverts at a speed comparable to the NMR time scale. Nitrogen in three-membered rings is frequently stereochemically stable with an appreciable inversion barrier,[22] but it is known that groups which can delocalize the electron density on nitrogen (e.g. C=C in **4a**) greatly reduce the inversion barrier.[23] In addition, the observed facile inversion of the nitrogen atom at room temperature should be assisted by its electronic interaction with the adjacent ring-silicon atom (some silylamines have been found to be near planar[24]).

The most reasonable explanation for the formation of the silaaziridines **4** involves the thermal isomerization of an initially formed silacyclopropanimine **3** (eq 3). This process would be the nitrogen analogue of the well-studied thermal 1,3-silyl migration of β-keto silanes leading to siloxyalkenes:[25] some β-keto silanes have been observed to rearrange under relatively mild conditions. Strong support for this proposal was obtained when the reaction between **1** (R = Ad) and **2** (R′ = *t*-Bu) was carried out at −70 °C where a different very unstable product was formed whose ^{1}H and ^{13}C NMR spectra were consistent with that of silacyclopropanimine **3a**.[26] When the reaction mixture was warmed to room temperature, the initially formed product rapidly disappeared, giving rise to the silaaziridine **4a**.



(3)

Currently we are attempting the isolation and better characterization of the silacyclopropanimine precursors, and we are also using other silenes or isonitriles which contain aryl groups, where preliminary observations have shown other modes of reaction are occurring.[27] In addition we are examining the hydrolysis reactions of these very air- and moisture-sensitive compounds, which are simultaneously enamines and silyl enol ethers.

Acknowledgment. We are indebted to the Natural Science and Engineering Research Council of Canada for support of this research and to Dr. Robin Walsh for stimulating discussions.

Supplementary Material Available: Tables of positional parameters and isotropic and anisotropic temperature factors and bond distances and angles for silaaziridine **4a** (4 pages); a listing of structure factors for **4a** (4 pages). Ordering information is given on any current masthead page.

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(17) A correction factor, θ, of ca. 20–25° to either side of the N–Si–C bond angle would give Si–C distances for the "bent" bonds of ca. 1.95–2.02 Å (= 1.830/cos θ).

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(26) NMR spectral properties at −60 °C in toluene-d_8 of intermediate ascribed the silacyclopropanimine structure **3a**: ^{1}H δ 0.35, 0.40 (9 H, s, Me$_3$Si), 0.46 (9 H, s, Me$_3$SiO), 0.81 (9 H, s, Me$_3$C), 1.62–2.08 (15 H, br m, Ad); ^{13}C δ 1.55, 1.72 (Me$_3$Si), 3.80 (Me$_3$SiO), 27.81 (*Me*$_3$C), 29.20 (CH Ad), 36.24, 39.86 (CH$_2$ Ad), 42.13 (C quat Ad), 51.21 (Me$_3$*C*), 178.99 (ring *C*-OSi), 246.33 (N=*C* ring). ^{29}Si NMR spectrum not obtainable because of instability of **3a** and slow relaxation rate of the Si nucleus at −60 °C.

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