

Anthryl-Substituted 3-Silylene-2-silaaziridine Obtained by Isomerization of Disilacyclopropanimine: An Exocyclic Silene Showing a Distinct Intramolecular Charge Transfer Transition

Takeaki Iwamoto,^{*,†} Nobuyoshi Ohnishi,[†] Naohiko Akasaka,[†] Koichi Ohno,^{†,‡} and Shintaro Ishida[†]

[†]Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

[‡]Institute for Quantum Chemical Exploration (IQCE), LOOP-X, 3-9-15 Kaigan, Minato-ku, Tokyo 108-0022, Japan

Supporting Information

ABSTRACT: An anthryl-substituted exocyclic silene, 3-silylene-2-silaaziridine, was synthesized by isomerization of the corresponding disilacyclopropanimine. The UV–vis spectrum of the silene shows a distinct intramolecular charge transfer (ICT) transition from the π orbital of the Si=C double bond to the π^* orbital of the anthryl moiety. The relatively high-lying π (Si=C) orbital of the 3-silylene-2-silaaziridine moiety and the low-lying π^* orbital of the anthryl group would be responsible for the distinct ICT band.

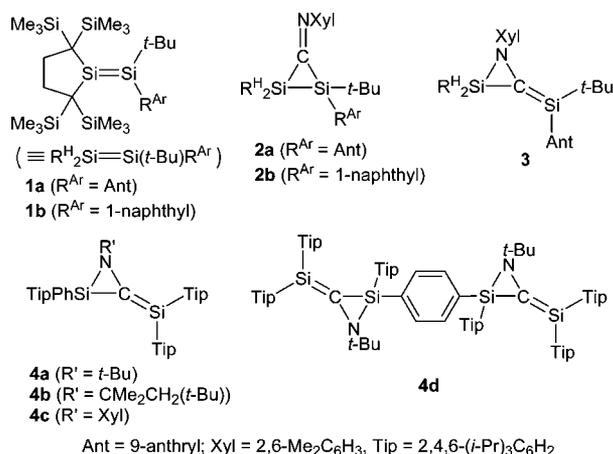
Stable silenes ($R_2Si=CR_2$) and disilenes ($R_2Si=SiR_2$) with electronic communication between the silicon π -electron (π Si) systems and other electron systems such as carbon π -electron (π C) and transition-metal d-electron systems have received considerable attention as novel functional compounds in recent years.¹ Although stable silenes and disilenes with conjugative π Si– π C interactions have been reported, π Si systems showing intramolecular charge transfer (ICT) interactions are still quite rare. We recently synthesized stable trialkyldisilenes with a polycyclic aromatic substituent, $R^H_2Si=Si(t-Bu)R^{Ar}$ (**1**) [$R^H_2 = 1,1,4,4$ -tetrakis(trimethylsilyl)butane-1,4-diyl, R^{Ar} = an aromatic substituent] (Chart 1), and we found that disilene **1a** ($R^{Ar} = 9$ -anthryl) shows a distinct ICT transition band due to charge transfer from the π Si donor (Si=Si) to the π C acceptor

(anthryl), the first example of an ICT absorption band observed for π Si systems.² Here we report that disilacyclopropanimine **2a**, which was obtained from disilene **1a** using xylyl isocyanide (XylNC, Xyl = 2,6-Me₂C₆H₃), isomerizes to give an exocyclic silene, 3-silylene-2-silaaziridine **3**, that shows an ICT transition where the silene moiety serves as the electron donor and the anthryl moiety as the electron acceptor, representing the first example of a silene ICT absorption band. Very recently, Scheschkewitz and co-workers reported reversible reactions of the tetraaryldisilenes Tip₂Si=SiTipPh and 1,4-(Tip₂Si=SiTip)₂C₆H₄ [Tip = 2,4,6-(*i*-Pr)₃C₆H₂] with isocyanides to give 3-silylene-2-silaaziridines **4a–d** and proposed that the reactions proceed via formation of the corresponding disilacyclopropanimines and subsequent isomerization.³ In our study, isomerization of disilacyclopropanimine to 3-silylene-2-silaaziridine was clearly observed.

The reaction of disilene **1a** with XylNC gave a [2 + 1] adduct, disilacyclopropanimine **2a**, in 58% yield, similar to reactions reported for other disilenes.^{4–6} In a similar manner, disilene **1b** ($R^{Ar} = 1$ -naphthyl) reacted with XylNC to afford naphthyl derivative **2b** in 76% yield. The structures of **2a** and **2b** were determined by NMR spectroscopy, mass spectrometry (MS), and X-ray diffraction (XRD) [see the Supporting Information (SI)]. Although **2a** is isolable at room temperature, it undergoes thermal isomerization via 1,3-migration of the SiR^H₂ unit, which is trans to the xylyl group (vide infra), from Si to N to give 3-silylene-2-silaaziridine **3** quantitatively in 16 days at room temperature (or in 3 h at 60 °C) in benzene-*d*₆.^{7,8} Recrystallization from hexane gave pure **3** as air-sensitive, blue-purple crystals in 39% yield. The structure of **3** was determined by NMR, MS, and XRD analysis (vide infra). In contrast to **2a**, **2b** is stable at room temperature.

The molecular structures of **2a** and **3** determined by XRD are shown in Figure 1 (for **2b**, see Figure S17 in the SI). Both **2** and **3** contain two crystallographically independent molecules with similar structural characteristics in the asymmetric unit. The xylyl groups on the N atom of **2a** are trans to the silacyclopentane (R^H_2Si) moiety in the solid state to avoid severe steric congestion between the xylyl and R^H_2Si moieties (Figure 1a). The endocyclic Si–Si distances in **2a** [2.359(1) Å av] are longer than those in **2b** [2.347(1) Å av] and West's pentaxylyldisilacyclopropanimine [2.328(3) Å],⁴ suggesting more severe steric

Chart 1



Received: April 23, 2013

Published: July 8, 2013

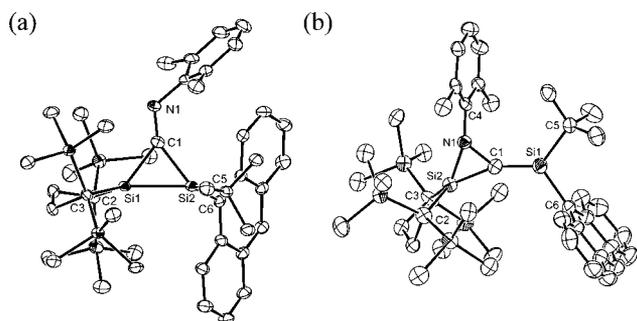
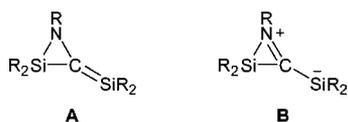


Figure 1. ORTEP drawings of (a) **2a** and (b) **3**. Thermal ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity. For **2a** and **3**, one of the two crystallographically independent molecules with similar structural characteristics in the asymmetric unit is shown.

congestion between the R^H_2Si and $Si(t-Bu)(9\text{-anthryl})$ moieties in **2a**.

A noticeable structural feature of **3** is the flat geometry around the $Si=C$ double bond (Figure 1b). The $Si=C$ distance in **3** [1.730(5) Å] is close to that in **4a** [1.735(2) Å],³ longer than that in Wiberg's silene $Me_2Si=C(SiMe_3)\{SiMe(t-Bu)_2\}$ having C groups at the unsaturated Si atom and Si groups at the unsaturated C atom [1.702(5) Å],⁹ and shorter than those in neutral Brook-type silenes with a π -donor substituent at the tricoordinate C atom [$R_2Si=CR(OR')$, 1.76–1.78 Å].¹⁰ The geometry around the tricoordinate Si in **3** is very flat, with the sum of the bond angles ($\sum Si$) being 358.7(2)° versus 355.85(18)° in **4a**.³ The average C1–N1 distance of 1.447(6) Å in the three-membered ring of **3** is much longer than those of the $C=N$ double bonds in **2** [1.283(4) Å] and close to those of typical C–N single-bonds (1.47–1.50 Å). These structural features of **3** can be rationalized by the major contribution of neutral resonance structure **A** rather than the zwitterionic structure **B** that places negative charge on the silene Si atom (Chart 2).^{11,12} Another important structural feature of **3** is that

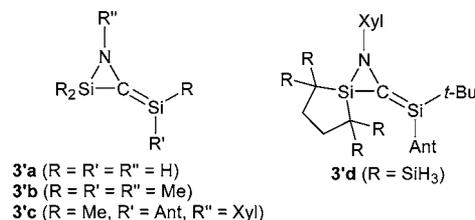
Chart 2. Canonical Structures of 3-Silylene-2-silaaziridines



the silene π and anthryl π moieties are almost perpendicular to each other [dihedral angle (θ) = 81.7°],¹³ which is probably due to severe steric hindrance between the $SiMe_3$ groups on the R^H_2Si moiety and the anthryl group and suggests that there are no remarkable conjugative interactions between the two π systems.

The B3LYP/6-311G(d)-optimized structures of model 3-silylene-2-silaaziridines **3'a–c** (Chart 3) showed significant contribution of resonance structure **B**, which is inconsistent with the X-ray structure of **3** (Table 1). The parent compound **3'a** shows relatively long $Si=C$ (1.785 Å) and short C–N (1.370 Å) distances and considerably pyramidalized tricoordinate Si atoms ($\sum Si = 327.9^\circ$). These structural characteristics are consistent with the results of the previous theoretical study of silenes having π -donor substituents at the tricoordinate C atom.¹² The permethylated derivative **3'b** and methyl/anthryl/ N -xylyl derivative **3'c** have relatively shorter $Si=C$ and longer C–N bonds than in **3'a** but still have a pyramidalized

Chart 3



tricoordinate Si atom. However, the structure of **3'd**, in which only the $SiMe_3$ groups of **3** are replaced by SiH_3 groups, reproduced well the geometry around the $Si=C$ bond of **3** as determined by XRD ($d_{Si=C} = 1.740$ Å, $d_{C-N} = 1.440$ Å, $\sum Si = 357.1^\circ$, $\theta = 83.6^\circ$). Severe steric repulsion between the silyl groups on the silacyclopentane, anthryl, xylyl, and $t-Bu$ groups would destabilize the pyramidalized geometry around the tricoordinate Si, resulting in the more planar geometry around the $Si=C$ bond in **3**.¹⁴

The ^{29}Si resonance for the tricoordinate Si nucleus (δ_{Si}) of **3** appeared at +36.7 ppm, which is downfield-shifted compared with those of **4a** (−4.40 ppm), **4b** (−4.58 ppm), and **4c** (+2.48 ppm),³ while the ^{13}C resonance for the unsaturated C nucleus (δ_C) appeared at +141.4 ppm, which is close to those of **4a–c** (ca. 144 ppm).³ The δ_{Si} and δ_C values are in good accord with those of **3'd** calculated at the GIAO/B3LYP/6-311+G(2df,p) level ($\delta_{Si} = +49.0$ ppm, $\delta_C = +146.9$ ppm) rather than those of **3'c** having a nonplanar structure ($\delta_{Si} = +7.6$ ppm, $\delta_C = +165.7$ ppm), suggesting that the structure of **3** in solution is planar, similar to that observed in the solid state. Accordingly, two singlet signals due to $SiMe_3$ protons on the R^H_2Si ring were observed in the 1H NMR spectrum. The $^1J_{Si-C}$ coupling constant of the $Si=C$ double bond (98 Hz) is larger than for typical silenes (76–92 Hz),^{1c} which can be rationalized by the higher s character of the C orbitals in the exocyclic Si–C bond of the three-membered ring.

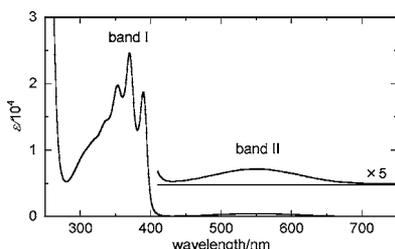
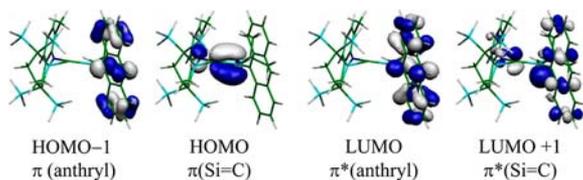
Although silenes usually show absorption bands below 400 nm,^{1f} silene **3** in hexane exhibited an intense structured band at 300–400 nm (band I) and a weak and distinct absorption band at 550 nm (band II) (Figure 2). Band I is assignable to the 1L_a band of the anthryl moiety overlapped with the band due to the $Si=C$ moiety because the reported 1L_a band maximum of 9-(trimethylsilyl)anthracene is 387.5 nm¹⁵ and the $\pi \rightarrow \pi^*$ transitions of **4a** and **4b** appear at 397 and 400 nm,³ respectively. It should be noted that band II observed at 550 nm in hexane was red-shifted in polar and poorly coordinating solvents [556 nm in fluorobenzene, 560 nm in CH_2Cl_2 , and 561 nm in o -dichlorobenzene (o DCB)] and blue-shifted in polar coordinating solvents [547 nm in tetrahydrofuran (THF) and 549 nm in 1,3-dimethylimidazolidin-2-one (DMI)].¹⁶ Although the mechanism of the solvatochromism has not been determined, the red shift suggests the ICT nature of band II and the blue shift may be due to significant stabilization of the ground state by coordination of the solvent to the Si atom of the $Si=C$ bond as observed for other silenes.¹

Further calculations on model compound **3'd** disclosed the nature of bands I and II. The frontier Kohn–Sham (KS) orbitals of **3'd** are the $\pi(Si=C)$ orbital (interacting with the N lone-pair orbital), the $\pi^*(Si=C)$ orbital, and the $\pi^{(*)}$ (anthryl) orbitals (Figure 3). The experimental spectrum of **3** was qualitatively reproduced by the absorption maxima and oscillator strengths of **3'd** calculated at the TD-B3LYP/6-311+G(d,p) level (see the SI). By comparison of the experimental and theoretical

Table 1. Selected Metric Parameters of **3** and **3'a–d**

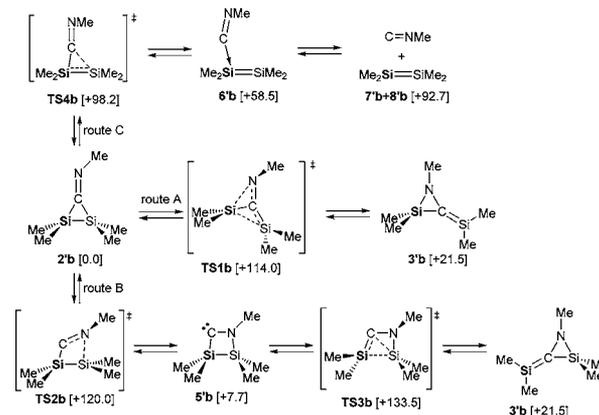
compd	distances (Å)		angles (deg)		chemical shifts (ppm) ^a	
	Si=C	C–N	$\sum\text{Si}^b$	θ^c	δ_{Si}	δ_{C}
3	1.730(s) ^d	1.447(6)	358.7(2)	81.7	+36.7	+141.4
3'a ^e	1.785	1.370	327.9	–	–58.7 ^f	+196.0 ^f
3'b ^e	1.762	1.397	344.4	–	+29.8 ^f	+171.7 ^f
3'c ^e	1.753	1.405	346.5	87.6	+7.6 ^f	+165.7 ^f
3'd ^e	1.740	1.440	357.1	83.6	+49.0 ^f	+146.9 ^f

^aChemical shifts for the Si=C moiety. ^bSum of the bond angles around the tricoordinate Si. ^cDihedral angle between the Si=C and anthryl moieties. ^daveraged. ^eOptimized at the B3LYP/6-311G(d) level. ^fCalculated at the GIAO/B3LYP/6-311+G(2df,p) level.

Figure 2. UV-vis spectrum of **3** in hexane at 298 K.Figure 3. Frontier KS orbitals of **3'd** calculated at the B3LYP/6-311G+(d,p)//B3LYP/6-311G(d) level.

absorption spectra, bands I and II are assigned as $\pi(\text{anthryl}) \rightarrow \pi^*(\text{anthryl})$ transition overlapped by a $\pi(\text{Si}=\text{C}) \rightarrow \pi^*(\text{Si}=\text{C})$ transition and a $\pi(\text{Si}=\text{C}) \rightarrow \pi^*(\text{anthryl})$ ICT transition, respectively, which is consistent with the red shift of band II in a more polar aromatic solvent. To the best of our knowledge, this is the first observation of a silene ICT transition. It is noteworthy that the ICT band of **3** at 550 nm is close to that of disilene **1** (526 nm) even though the π orbital level in silenes are usually predicted to be lower than those in disilenes [e.g., –8.41 for $\text{H}_2\text{C}=\text{SiH}_2$ and –7.64 eV for $\text{H}_2\text{Si}=\text{SiH}_2$ calculated at the MP2/6-31G(d)//B3LYP/6-31G(d) level].¹⁷ The interaction of the $\pi(\text{Si}=\text{C})$ orbital with the N lone-pair orbital in the 3-silylene-2-silaaziridine moiety, which was pointed out by Scheschkewitz and co-workers,³ would be responsible for the higher energy of the $\pi(\text{Si}=\text{C})$ orbital that results in the observation of the distinct ICT band of **3**.¹⁸

To gain further insight into the isomerization of disilacyclopropanimine to 3-silylene-2-silaaziridine, calculations on model reactions using permethylated disilacyclopropanimine **2'b** were carried out at the B3LYP/6-311G(d) level.¹⁹ Three reaction routes (A–C) from **2'b** were predicted (Scheme 1). Route A is a concerted 1,3-migration of the silyl group trans to the N-methyl group (shown in bold) from Si to N with inversion of configuration of the silyl group,²⁰ while route B is a stepwise migration of the silyl group cis to the N-methyl group via cyclic carbene intermediate **5'b**.²¹ Route C is a dissociation to give disilene **7'b** and isocyanide **8'b** via the weak disilene–isocyanide complex **6'b**. The activation barrier for route C (+98.2 kJ/mol) is lower than those for route A (+114.0 kJ/mol) and the second step of route B (125.8 kJ mol^{–1}), which is consistent with

Scheme 1. Reaction Routes from **2'b**^a

^aCalculated at the B3LYP/6-311G(d) level.¹⁹ Values in brackets are relative energies in kJ/mol.

observation of free disilene **1a** and XylNC during thermolysis of **2a** at 55 °C by monitoring ¹H NMR spectrum.⁸ Although the activation barrier for route A is slightly lower than that of route B, the observed geometries of **2a** and **3** can be explained by route A, suggesting that the isomerization of **2a** to **3** proceeds in a concerted fashion similar to route A.^{22,23} Although the model reaction to give **3'b** is predicted to be endothermic, the energy difference between **2'b** and **3'b** is very small (+21.5 kJ/mol). Destabilization due to the more severe steric repulsion between the bulky R₂Si and Si(*t*-Bu)(aryl) moieties in **2a** bearing a longer endocyclic Si–Si distance compared with **2b** would make the reaction exothermic, resulting in the observation of the isomerization.

In conclusion, 3-silylene-2-silaaziridine **3** was synthesized as a novel exocyclic silene having a polycyclic aromatic substituent via isomerization of disilacyclopropanimine **2**. Silene **3** shows a distinct ICT transition where the Si=C and anthryl moieties serve as the electron donor and acceptor, respectively. The $\pi(\text{Si}=\text{C})$ orbital, which has a relatively high energy due to interactions with the lone-pair orbital of the N atom in the 3-silylene-2-silaaziridine skeleton, and the low-lying $\pi^*(\text{anthryl})$ orbital would be responsible for the distinct ICT band of **3**.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and computational details and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

iwamoto@m.tohoku.ac.jp

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported in part by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (KAKENHI 21350007, 21655010, 23655021, 24655024, 25248010). We thank Dr. Satoshi Maeda (Hokkaido University) for helpful suggestions of theoretical study and also the reviewers for valuable comments.

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- (13) The dihedral angle θ is defined as the angle between the axes that bisect the C(sp²)–Si(sp²)–C(*t*-Bu) and C(sp²)–C(ippo)–C(sp²) angles as viewed along the Si(sp²)–C(ippo) bond axis.
- (14) The potential energy of pyramidalization at the tricoordinate Si atom in **3'b** is predicted to be very shallow at the B3LYP/6-311G(d) level. The permethylated 3-silylene-2-silaaziridine with a planar Si=C double bond [**3'b**(planar), two imaginary frequencies] is only 6.4 kJ/mol higher in energy than the fully optimized structure of **3'b** having a pyramidalized tricoordinate Si atom ($\sum \text{Si} = 344.2^\circ$).
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- (21) Isomerization of monosilacyclopropanimine to 3-methylene-2-silaaziridine (a monosila version of the isomerization of **2a** to **3**) has also been predicted to proceed in a stepwise mechanism via a 1-sila-2-azacyclobut-3-ylidene intermediate, similar to route B. See: Nguyen, M. T.; Vansweevel, H.; Neef, A. D.; Vanquickenborne, L. G. *J. Org. Chem.* **1994**, *59*, 8015.
- (22) Dissociation of disilacyclopropanimine into silylene (R₂Si) and silaketenimine (R₂Si=C=NR) followed by insertion of R₂Si into the C=N bond of the silaketenimine to give 3-silylene-2-silaaziridine may be ruled out because the formation of Me₂Si and Me₂Si=C=NMe from the corresponding disilacyclopropanimine was calculated to be highly endothermic [+190.0 kJ/mol at the B3LYP/6-311G(d) level].
- (23) The polycyclic aromatic substituents on the three-membered ring do not electronically affect the activation energy for concerted isomerization (route A). For details, see Figure S25.