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Introduction

Although the reactions of silvlenes (silicon divalent compounds)^{1,2} with carbon-oxygen double-bond compounds have been extensively studied up to date,³ less attention has been paid to the reactions of the silvlenes with related carbon-nitrogen double bond compounds, imines. In 1993, Weidenbruch and Piel reported the reaction of photochemically generated dimesitylsilylene with N-aryl-1-(2-pyridyl)methanimines (aryl = mesityl, 2,6-diisopropylphenyl) giving a mixture of 1 and 2 (Chart 1).⁴ Belzner et al. found that the reactions of a transient silylene, bis[2-(dimethylaminomethyl)phenyl]silylene, with N-phenylbenzophenimine and N-(2,6-dimethylphenyl)fluorenimine gave the corresponding silaazacycles 3 and 4, respectively.⁵ These 1:1 adducts 1-4 are usually considered to be produced via the initial formation of the corresponding silaylides 5 followed by the cyclization to the corresponding silaaziridines 6,^{4,5} although neither 5 nor 6 has been detected

Diverse reactivity of an isolable dialkylsilylene toward imines†

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The reactions of isolable dialkylsilylene **10** with various aldimines proceed smoothly at low temperatures to give diverse products depending on the substituents on the imine. The reactions of 10 with 4-XC₆H₄CH=NPh [X = H (11a), MeO (11b), and Cl (11c)] give the corresponding silaaziridines 12a-12c in high yields, which are thermally very stable and remain intact in the air and moisture for a long time. In contrast, the reactions of **10** with $4-F_3CC_6H_4CH=NPh$ (**11d**) and $3,5-(F_3C)_2C_6H_3CH=NPh$ (**11e**) having strong electron-withdrawing aryl substituents on imine carbon are accompanied by 1,2-trimethylsilyl migration rather unexpectedly to give silaazetidines 13d-13e incorporated into a bicyclo[3.2.0]heptane ring. The reaction of **10** with *N*-benzylbenzaldimine **11f** affords the corresponding (dibenzylamino)silane 14f in a moderate yield. Molecular structures of 12a-12c, 13d-13e and 14f were determined by X-ray crystallography. All these reactions are proposed to occur via the initial formation of the corresponding imine silaylides, while the subsequent reactions leading to the final products are controlled by the electronic structure of the ylide depending on the substituents. N-Phenylbenzophenimine **11g** does not react with 10.



during these reactions. Similar 1:1 adducts were obtained by Gehrhus et al. using the reaction of an isolable cyclic diaminosilylene with imines.⁶ Recently, Nevárez and Woerpel have reported that di-tert-butylsilylene generated from the corresponding silacyclopropane in the presence of AgOTf as a catalyst reacts with various ald- and ketimines affording the corresponding silaaziridines in high yields.⁷ However, only a limited number of these silaaziridines were isolated as pure liquid or powder; most of them were characterized by solution NMR spectroscopic studies or as their methanolysis products. Very recently, Roesky et al. have reported that a base-stabilized silvlene reacts with PhCH=NPh to afford the corresponding silaaziridine whose structure was determined by X-ray crystallography.8

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[†]Electronic supplementary information (ESI) available: X-ray analysis of 12c' and 14f, crystal and refinement data for 12a-12c, 13d, 13e, and 14f. NMR spectra of new compounds and the mechanism for the formation of 14f. CCDC 875388. 875347-875350, 875352. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32126b



As the first silaaziridine whose structure was determined by X-ray crystallography, silaaziridine 7 was synthesized by Brook *et al. via* a different route using the reaction of a stable silene **8** with *tert*-butylisocyanide (eqn (1)).⁹



The above reports have prompted us to investigate the reactions of imines with isolable dialkylsilylene 10^{10} (Scheme 1), which has been revealed to show remarkable reactivity towards numerous organic and organometallic substrates including ketones and alkenes.¹¹ While the reactions of **10** with *N*-phenylbenzaldimines having electron-donating (4-MeO) or less electron-withdrawing substituents (4-H, 4-Cl) on the imine C-phenyl ring afforded the corresponding silaaziridines 12 in high yields, rather unexpectedly, the reactions of 10 with those having strong electron-withdrawing substituents [4-CF₃, 3,5- $(CF_3)_2$ gave silaazetidines 13 exclusively (Scheme 1). The molecular structures of these silaaziridines and silaazetidines were determined by X-ray crystallography. The origin of the striking diversity of the reactions is discussed. The results of the reactions of 10 with N-benzylbenzaldimine and N-phenylbenzophenoimine are also reported.

Results and discussion

Reactions of 10 with ArCH=NPh (Ar = C_6H_5 , 4-MeOC₆H₄, and 4-ClC₆H₄)

The reactions of silylene **10** with *N*-phenylbenzaldimines **11a-11c** having less electron-withdrawing substitutents at -30 °C in hexane afforded the corresponding silaaziridines **12a-12c**, respectively, as single products in high yields (eqn (2)). Pure aziridines **12a-12c** were obtained in more than 80% yield as colorless solids using flash chromatography or GPC. In contrast to air- and moisture-sensitive nature of silaaziridines synthesized by Woerpel *et al.*^{7,12} and Brook *et al.*,⁹ **12a-12c** remain intact more than one year at rt in the air. They are thermally stable with high melting points and no decomposition was observed when a toluene solution of **12a** was refluxed for 8 h. Unusually high thermal and chemical stability of **12a-12c** suggests effective steric protection of the three-membered ring by bulky substituents on the silylene moiety.

$$10 + X - CH=NPh + hexane, -30 \circ C + Me_3Si + SiMe_3 + N_{,Ph} + Me_3Si + SiMe_3 + N_{,Ph} + Me_3Si + SiMe_3 + N_{,Ph} + Me_3Si + SiMe_3 + Me_3Si + Me_3Si + SiMe_3 + Me_3Si + SiMe_3 + Me_3Si + SiMe_3 + Me_3Si + Me_3Si$$

Silaaziridines **12a–12c** were characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopic studies in CDCl₃. Typically, in the ¹H NMR spectrum of **12a**, a characteristic singlet signal due to the benzylic proton appears at 3.71 ppm. Four resonances at 0.36, 0.32, 0.00 and –0.18 ppm correspond to protons of four different SiMe₃ groups, indicating that the environments of the four SiMe₃ groups are different from each other. In the ²⁹Si NMR spectrum of **12a**, five resonances assignable to four different SiMe₃ and ring silicon nuclei are found at 3.9, 3.7, 3.5, 3.0, and –24.3 ppm. Similar spectral features are observed for **12b** and **12c**. High-field shifted ²⁹Si signals at around –25 ppm are characteristic for the silaaziridine ring; ring ²⁹Si resonances for Woerpel's aziridines **6** (R = ^{*t*}Bu, R¹, R² = Ph, Alkyl, H, R³ = Ph, Bn) are reported to appear at around –45 ppm.⁷

As shown in Fig. 1–3, silaaziridine structures of **12a–12c** were confirmed by the single-crystal X-ray diffraction study.¹³ Ring structures of **12a–12c** are similar to each other but slightly different from that of a base-stabilized silaaziridine reported by Roesky *et al.*⁸ The Si–C and Si–N bond lengths of their silaaziridine are 0.012 Å shorter and 0.02 Å longer than those of **12a**, probably due to the pentacoordinate nature of the silicon atom of the former silaaziridine, while the difference in the C–Si–N bond angle is less than 1° between these compounds. Comparison of the molecular structures between



Fig. 1 ORTEP drawing of **12a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): N1–C1 = 1.488(3), N1–Si1 = 1.7113(17), C1–Si1 = 1.872(2), N1–C5 = 1.398(3), C1–C2 = 1.489(3), C3–Si1 = 1.885(2), C4–Si1 = 1.879(2); C1–N1–Si1 = 71.24(10), N1–Si1–C1 = 48.80(8), N1–C1–Si1 = 59.95(10), C3–Si1–C4 = 101.53(9). Dihedral angles between two planes (°): 14.42 for C1–Si1–N1/*N*-aryl planes, 79.98 for C1–Si1–N1/C4–Si1–C3 planes, 82.74 for C-aryl/*N*-phenyl planes.



Fig. 2 ORTEP drawing of **12b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1–N1 = 1.7134(18), Si1–C1 = 1.872(2), C1–N1 = 1.482(3), C1–C2 = 1.489(3), C5–N1 = 1.386(3), Si1–C3 = 1.878(2), Si1–C4 = 1.896(2); N1–Si1–C1 = 48.59(9), C1–N1–Si1 = 71.30(11), N1–C1–Si1 = 60.11(10), C3–Si1–C4 = 101.25(9). Dihedral angles between two planes (°): 15.11 for C1–Si1–N1/*N*-aryl planes, 80.68 for C1–Si1–N1/C4–Si1–C3 planes, and 81.94 for C-aryl/*N*-phenyl planes.



Fig. 3 ORTEP drawing of **12c**. One of the two crystallographically independent molecules is shown. Another molecular structure of **12c** (**12c**') is shown in the ESI.† Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1–N1 = 1.705(2), Si1–C1 = 1.878(3), C1–N1 = 1.489(3), C1–C2 = 1.483(4), C5–N1 = 1.395(3), Si1–C3 = 1.887(3), Si1–C4 = 1.874(3); N1–Si1–C1 = 48.80(11), C1–N1–Si1 = 71.66(14), N1–C1–Si1 = 59.54(12), C4–Si1–C3 = 101.92(12). Dihedral angles between two planes (°): 16.35 for C1–Si1–N1/*N*-aryl planes, 80.94 for C1–Si1–N1/C4–Si1–C3 planes, and 81.51 for C-aryl/*N*-phenyl planes.

12a and Brook's aziridine 7⁹ would also be interesting because the latter has an exocyclic methylene. The ring Si–C and C–N bond lengths of **12a** are slightly longer than those of 7 [1.830 (15) and 1.417(17) Å, respectively], while the ring Si–N bond length of **12a** is shorter than that of 7 [1.764(13) Å]. The N–Si– C and C–N–Si bond angles of **12a** are larger than those of 7 [46.4(5)° and 69.3(8)°], while the Si–C–N angle of **12a** is smaller than that of 7 [64.3(8)°]. The differences in bond lengths and angles between **12a** and 7 would be ascribed to the difference in the hybridization of the ring carbons; shorter bond lengths and wider bond angles are required around the unsaturated carbon, because it is intrinsically sp² hybridized.

Reactions of 10 with ArCH=NPh (Ar = $4 \cdot F_3 CC_6 H_4$ and $3, 5 \cdot (F_3 C)_2 C_6 H_3$)

When an imine with a strong electron-withdrawing substituent on the *C*-phenyl ring is used for the reaction of silylene **10**, an unexpected bicyclic compound with a silaazetidine ring was obtained exclusively, instead of the corresponding silaaziridine. Thus, the reactions of **10** with *N*-phenylbenzaldimines having trifluoromethyl substituents **11d** and **11e** gave **13d** and **13e** in 82 and 78% yields, respectively (eqn (3)).



The structures of silaazetidines **13d** and **13e** were confirmed by NMR spectroscopic studies and finally by X-ray crystallography. In their ¹H NMR spectra, the benzylic proton signal appeared as a singlet at 5.39 and 5.42 ppm for **13d** and **13e**, respectively; no signals due to the expected aziridine type compounds were detected. As expected from the unsymmetrical structures of **13d** and **13e**, five ²⁹Si resonances were observed at 41.2, 3.5, 2.9, -0.4, and -18.8 ppm for **13d** and 42.0, 3.5, 3.02, -0.3, and -18.6 ppm for **13e**. The lowest and highest field ²⁹Si signals that appeared at around 40 and -19 ppm are assigned as the bridgehead silicon and the Me₃Si silicon bonded to the silicon, respectively.

Molecular structures of **13d** and **13e** determined by X-ray crystallography are shown in Fig. 4 and 5, respectively, confirming their azasilabicyclo[3.2.0]heptane structure.¹³ The relative stereochemistry around the silaazetidine ring of **13d** and **13e** was determined as shown in eqn (3) by the X-ray structural analysis. The four membered ring of **13d** and **13e** is not planar but slightly folded with the C2–Si1–C1–N1 dihedral angle of 6.23 and 9.10°, respectively. The Si–C bridge bond length in **13d** and **13e** is a little longer than those of reported silaazetidines,¹⁴ while other bond lengths in the ring are not much different from each other.

Reactions of 10 with *N*-benzylbenzaldimine and *N*-phenylbenzophenimine

During the reaction of **10** with *N*-benzylbenzaldimine **11f** under similar conditions to eqn (2) and (3) was obtained a different type of product **14f** in a moderate yield of 37% (eqn (4)). The structure of **14f** was confirmed by NMR spectroscopic studies and X-ray crystallography (ESI[†]).¹³



Fig. 4 ORTEP drawing of **13d**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1–N1 = 1.7689(16), Si1–C2 = 1.937(2), C1–C2 = 1.595(3), C1–N1 = 1.478(2), Si1–Si2 = 2.3920(8), Si1–C4 = 1.895(2); N1–Si1–C2 = 78.44(8), C1–C2–Si1 = 85.82(11), N1–C1–C2 = 99.55(14), C1–N1–Si1 = 95.85(11), C4–Si1–C2 = 99.38(9), C3–C2–Si1 = 101.23(13). Dihedral angles between two planes (°): 78.31 for C-aryl/*N*-phenyl planes, 6.23 for C1–Si1–N1/C1–Si1–C2 planes, and 6.21 for C2–N1–Si1/C2–N1–C1.



The reaction of an imine with silylene **10** is sensitive to the bulkiness of the substituents on the imine. In contrast to the reaction of **10** with benzophenone giving 1:1 adduct 15,³² no reaction occurred between benzophenimine **11g** and **10** even at rt (eqn (5)).

No Reaction
$$4$$
 Ph₂C=NPh (11g)
hexane, rt 10 Ph₂C=O
 C_6D_6 Me_3Si SiMe₃ (5)
15

Reaction mechanisms

As proposed in the previous reports,^{4,5} the reactions of a silylene with an imine will proceed *via* the initial formation of the corresponding imine silaylide 5 (Chart 1) followed by cyclization or isomerization giving the corresponding 1:1 adducts. This mechanism is applied to the reactions of **10** with *N*-phenyl benzaldimines **11a**, **11b**, and **11c**, which bear hydrogen-, an electron-donating methoxy-, and a weakly electronwithdrawing chloro-substituent at the 4-position of the *C*-phenyl group, respectively (eqn (6)). Intermediary imine silaylides may have two major resonance forms **A** and **B**, whose relative importance depends on the electronic nature of the imine, by analogy with carbonyl silaylides formed by the addition of silylenes to carbonyl compounds.^{3z} Form **B** is less important for imines **11a–11c** with less electron-withdrawing



Fig. 5 ORTEP drawing of **13e**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1–N1 = 1.771(2), Si1–C2 = 1.921(3), C1–C2 = 1.585(4), C1–N1 = 1.462(3), Si1–Si2 = 2.3778(13), Si1–C4 = 1.886(3); N1–Si1–C2 = 78.38(11), C1–C2–Si1 = 85.69(17), N1–C1–C2 = 100.0(2), C1–N1–Si1 = 95.20(16), C4–Si1–C2 = 99.99(13), C3–C2–Si1 = 101.00(19). Dihedral angles between two planes (°): 76.13 for C2–N1–C1.

substituents, and hence, the 4π -electrocyclic reactions giving the corresponding silaaziridines **12a–12c** would occur preferentially.

$$10 + 11a-c \longrightarrow \begin{bmatrix} Ph & Ph \\ R_2Si \land N & Ar \\ H & H \\ A & B \\ imine silaylide \end{bmatrix} \xrightarrow{eyclization} 12a-c \\ Me_3Si & SiMe_3 \\ R_2Si = Si \\ Me_3Si & SiMe_3 \end{bmatrix}$$

The reactions of silvlene 10 with benzaldimines 11d and 11e having strong electron-withdrawing substituents are unusually accompanied by 1,2-trimethylsilyl migration of the silylene moiety. The mechanism of the reactions is not fully understood at present but a plausible mechanism is proposed as follows: although the 1,2-silyl migration of 10 is a wellknown process at higher temperatures than 0 °C in solution, it does not occur appreciably at low temperatures such as -30 °C.^{10,15} However, an imine silaylide formed between 10 and imine 11d or 11e may have preferred resonance form 16B, in which silylene silicon and imine carbon are positively and negatively charged, respectively. Thus, the 1,2-silyl migration from carbon to the neighboring cationic silicon center in the ylide 16B is facilitated to afford 1,4-zwitterionic intermediate 17. Intramolecular cyclization of 17 may give the corresponding silaazetidine 13d or 13e (path a). As another route to the silaazetidines from 17, we may anticipate the elimination of imine **11d** (or **11e**) giving silaethene **18** and the imine (path b) followed by the [2 + 2] cycloaddition between them. To differentiate between paths a and b, the reaction of imine 11d with silaethene 18¹⁵ that was synthesized by thermal isomerization



of silylene **10** was investigated. Silaazetidine **13d** was never detected after the reaction at -30 °C for 6 h, though at reflux, the reaction actually gave **13d**; cycloadduct **13d** was identified by ²⁹Si NMR spectroscopy and ¹H NMR spectroscopy after purification. Path b should be eliminated by the above experiments (Scheme 2).

Compound **14f** is not a simple 1:1 adduct between **10** and **11f** and for the formation are required two additional hydrogen atoms. The mechanism remains open but a plausible mechanism is proposed in MSI.

Experimental section

All synthetic experiments were performed under argon or nitrogen in a standard vacuum system unless otherwise noted. ¹H (400 MHz), ¹³C (100 MHz), ²⁹Si (80 MHz), and ¹⁹F NMR (376 MHz) spectra were recorded with TMS as an internal standard on a BRUKER AV-400 MH_z instrument. MS were measured with a Trance 2000 DSQ mass spectrometer. Highresolution MS were measured on a Thermo Scientific LTQ Orbitrap XL spectrometer. Melting points are uncorrected. Silylene **10**¹⁰ and imines **11a–11f**¹⁶ were prepared according to the literature procedures. Silylene **10** and other air-sensitive materials were handled in a MBraun glovebox. All products were purified by flash chromatography or GPC (LC-9101, Japan Analytical Industry Co. Ltd).

General procedure for the reactions of 10 with 11

An excess amount of imine **11** (0.3 mmol) was added to a solution of silylene **10** (75 mg, 0.2 mmol) in hexane at -30 °C. The reaction mixture was allowed to stir for 20 min at -30 °C. Then the solvent was removed under vacuum. The product was isolated as a pure substance from the resulting residue by flash chromatography or GPC (toluene).

12a: white solid (95 mg, 86%); mp 151–153 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.22–7.14 (m, 6H), 7.08–7.06 (m, 1H), 6.80–6.75 (m, 3H), 3.71 (s, 1H), 2.18–2.11 (m, 2H), 2.08–1.95 (m, 2H), 0.36 (s, 9H), 0.32 (s, 9H), 0.00 (s, 9H), -0.18 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 146.5, 142.2, 128.5, 128.2, 125.1,

124.6, 118.34, 118.29, 43.5, 32.2, 30.6, 8.2, 5.2, 4.0, 2.8, 2.4, 2.2. ²⁹Si NMR (80 MHz, CDCl₃) δ 3.9, 3.7, 3.5, 3.0, -24.3; MS (70 eV, EI) *m*/*z* (%) 553 (M⁺, 100), 538 (M⁺ - 15, 45), 476 (55), 299 (64); HRMS *m*/*z* calcd for C₂₉H₅₁NSi₅: 553.2868. Found: 553.2886.

12b: white solid (94 mg, 81%); mp 193–195 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.17–7.10 (m, 4H), 6.79–6.75 (m, 5H), 3.75 (s, 3H), 3.65 (s, 1H), 2.16–2.12 (m, 2H), 2.06–1.97 (m, 2H), 0.35 (s, 9H), 0.30 (s, 9H), -0.02 (s, 9H), -0.16 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 157.1, 146.6, 134.1, 128.5, 126.0, 118.3, 118.2, 113.8, 55.3, 42.8, 32.2, 30.6, 8.1, 5.1, 4.0, 2.8, 2.4, 2.1; ²⁹Si NMR (80 MHz, CDCl₃) δ 3.9, 3.7, 3.4, 2.9, -24.5; MS (ESI): *m/z* 606 (M + Na)⁺; HRMS *m/z* calcd for C₃₀H₅₃NOSi₅: 583.2974. Found: 583.3055.

12c: white solid (102 mg, 87%); mp 200–202 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.25–7.23 (m, 6H), 6.84–6.81 (m, 3H), 3.72 (s, 1H), 2.24–2.17 (m, 2H), 2.14–2.01 (m, 2H), 0.41 (s, 9H), 0.36 (s, 9H), 0.04 (s, 9H), -0.10 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 146.1, 141.0, 130.0, 128.6, 128.4, 126.5, 118.8, 118.3, 43.1, 32.2, 30.6, 8.3, 5.3, 4.1, 3.0, 2.5, 2.2; ²⁹Si NMR (80 MHz, CDCl₃) δ 4.0, 3.7, 3.5, 3.1, –23.7; ESI-HRMS [M + H]⁺ calcd for C₂₉H₅₁ClNSi₅: 588.2556. Found: 588.2567.

13d: white solid (102 mg, 82%). mp 247–249 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.31 (d, *J* = 7.2 Hz, 2H), 5.39 (s, 1H), 2.06–2.04 (m, 2H), 1.65–1.54 (m, 1H), 1.48–1.40 (m, 1H), 0.28 (s, 9H), 0.25 (s, 9H), 0.24 (s, 9H), 0. 12 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 147.6, 144.2, 128.5, 128.4, 127.6, 124.7, 124.3, 117.3, 115.0, 67.2, 32.5, 32.1, 29.7, 19.8, 3.6, 3.0, 2.0, 1.6; ¹⁹F NMR (376 MHz, CDCl₃) δ –62.2; ²⁹Si NMR (80 MHz, CDCl₃) δ 41.2, 3.5, 2.9, –0.4, –18.8; MS (70 eV, EI) *m*/*z* (%) 621 (M⁺, 100), 548 (78), 456(45), 372(43); HRMS *m*/*z* calcd for C₃₀H₅₀NF₃Si₅: 621.2742. Found: 621.2762.

13e: white solid (107 mg, 78%). mp 168–170 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.71 (s, 3H), 7.09 (t, J = 7.4 Hz, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.31 (d, J = 7.4 Hz, 2H), 5.41 (s, 1H), 2.11–2.07 (m, 1H), 1.97–1.89 (m, 1H), 1.56–1.44 (m, 2H), 0.30 (s, 9H), 0.27 (s, 9H), 0.26 (s, 9H), 0.14 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 147.1, 143.1, 131.0, 128.7, 127.6, 123.5, 120.4, 117.7, 114.8, 66.7, 32.5, 31.9, 29.8, 19.6, 3.6, 2.8, 2.0, 1.5; ¹⁹F NMR (376 MHz, CDCl₃) δ –62.6; ²⁹Si NMR (80 MHz, CDCl₃) δ 42.0, 3.5, 3.0, –0.3, –18.6; HRMS [M + H]⁺ calcd for C₃₁H₅₀F₆NSi₅: 690.2694. Found: 690.2702.

14f: white solid (43 mg, 37%). mp 121–123 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.21–7.19 (m, 6H), 7.10–7.08 (m, 4H), 5.54 (s, 1H), 4.04 (s, 4H), 2.12–2.05 (m, 2H), 2.02–1.95 (m, 2H), 0.25 (s, 18H), 0.20 (s, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 138.7, 129.0, 127.8, 126.6, 52.2, 32.4, 8.2, 4.0, 2.3; ²⁹Si NMR (80 MHz, CDCl₃) δ 15.5, 5.0, 1.7; MS (ESI): m/z 568 (M – H)⁺. HRMS [M – H]⁺ calcd for C₃₀H₅₄NSi₅: 568.3097. Found: 568.3075.

Reaction of silaethene 18 with imine 11d

A solution of silylene **10** (150 mg, 0.4 mmol) in hexane (8 mL) was heated at 60 °C for 24 h in the dark. Hexane was evaporated and the residue was determined as silaethene $18^{10,15}$ by

²⁹Si NMR: ²⁹Si NMR (80 MHz, C_6D_6) δ 137.0, 1.4, -9.4, -16.2. Compound **18** was used directly without further purification.

A solution of **18** (45 mg) obtained as above in hexane (3 mL) was added to imine **11d** (75 mg, 0.3 mmol) at -30 °C. After stirring the hexane solution at -30 °C for 6 h, the reaction mixture was exposed to air. No silaazetidine was detected by TLC.

After refluxing a mixture of **18** (45 mg) and **11d** (75 mg, 0.3 mmol) in hexane for 6 h, hexane was evaporated completely and the residue was purified by flash chromatography to afford silaazetidine **13d** as a major product. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.31 (d, *J* = 7.2 Hz, 2H), 5.39 (s, 1H), 2.06–2.04 (m, 2H), 1.65–1.55 (m, 1H), 1.48–1.40 (m, 1H), 0.29 (s, 9H), 0.25 (s, 9H), 0.24 (s, 9H), 0. 12 (s, 9H); ²⁹Si NMR (80 MHz, CDCl₃) δ 40.9, 3.5, 2.9, –0.6, –19.0.

Crystal structure determination

Single crystals of **12a–12c**, **13d**, **13e**, and **14f** suitable for X-ray analysis were obtained by the recrystallization from CHCl₃. The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELX-2000.¹⁷ All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Diamond.

The single crystal of compound 12c showed two crystallographically independent molecules in an asymmetric unit. In molecules 12a and 13d–e, one Me₃Si group in 12a, one CF₃ group in 13d, and two CF₃ groups in 13e are disordered over two sites, respectively. Crystal and refinement data for 12a– 12c, 13d, 13e and 14 are described in the ESI. CCDC Nos. 875350 (12a), 875349 (12b), 875388 (12c), 875347 (13d), 875352 (13e), and 875348 (14f) contain the supplementary crystallographic data for this paper.

Conclusions

In summary, isolable dialkylsilylene **10** reacts with various aldimines smoothly at low temperatures to give diverse products depending on the substituents on an imine. The reactions of **10** with *N*-phenyl benzaldimines **11a–11c** having electron-donating and less electron-withdrawing substituents on the *C*-phenyl ring give the corresponding silaziridines **12a–12c** in high yields, which are thermally very stable and remain intact in the air and moisture for a long time. Their structures were determined by X-ray crystallography. When *N*-phenyl benzaldimines with strongly electron-withdrawing substituents **11d** and **11e** are used as imines under similar conditions, rather unexpectedly, the reactions are accompanied by 1,2-trimethylsilyl migration to give silaazetidines **13d** and **13e** exclusively. The reaction of **10** with *N*-benzyl benzaldimine **11f** gives

the corresponding (dibenzylamino)silane **14f** in a moderate yield. All these reactions are proposed to occur *via* the initial formation of the corresponding imine silaylides, while the subsequent reactions leading to the final products are controlled by the electronic structure of the ylide depending on the substituents. Ketimine **11g** does not react with **10**.

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