Extremely Regioselective Intramolecular Silylformylation of Bis(silylamino)alkynes

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Intramolecular silylformylation of *ω*-bis(dimethylsilylamino)-*i*-alkynes is investigated. This process affords *exo*-(1-formylalkenylidene)azasilacycloalkane as the initial product, which is converted to the more stable *exo*-(1-hydroxymethylalkenylidene)azasilacycloalkane through $NaBH_4$ reduction in methanol in high overall yield. Both *exo*-alkenylidene azasilacycloalkanes are literature unknown compounds and would be versatile polyfunctionalized intermediates in organic syntheses. It should be noted that only the *exo*-$SiMe_2H$ group is removed in this reduction, and the resulting cyclic silylamine is stable against methanolysis and hydrolysis, which is unexpected and unprecedented. The observed stability of the Si−N bond in the cyclic silylamine is found to be ascribed to the existence of the *exo*-alkylene group at the C-5 position. Thus, the hydrogenation of this double bond leads to a facile Si−N bond cleavage by methanol. In a similar manner, the reactions of 1-bis(dimethylsilyl)amino-2-(1-hexynyl)-cycloalkane, followed by $NaBH_4$ reduction, give the corresponding *exo*-(1-formylalkyl-1-ene)-azasilabicyclo[*x*.3.0]alkanes in high yields. When the diphenylsilyl group is employed in place of the dimethylsilyl group, the reaction gives the corresponding intramolecular silylformylation product in good yield. The *exo*-HPh_2Si−N bond of this product is found to be stable for the reduction with $NaBH_4$, giving the corresponding allylic alcohol.

The intermolecular silylformylation of alkynes[1−3] and aldehydes[4] catalyzed by Rh and Rh−Co complexes, which gives the corresponding *β*-formylvinylsilanes in high yields, has been studied extensively in recent years. Silylcarbocyclizations (SiCaCs) of alkenynes,[5] diynes,[6] and alkynals[7] have also been investigated. In the silylformylation of 1-alkynes, the reaction gives 1-silyl-2-formyl-1-alkenes with complete regioselectivity.[1−3] This extremely high regioselectivity is very useful, but it will be even more attractive if the corresponding 3-silylalk-2-en-1-als become accessible. The reactions of simple internal alkynes, however, are virtually nonselective and provide a mixture of regioisomers. Some selectivity could be obtained by introducing bulky groups on one side of the triple bond, but this method is still unreliable.[2]

To solve this problem, we successfully developed the intramolecular version of the silylformylation reaction of 1-alkynes and internal alkynes by introducing a dimethylsiloxy, i.e., HMe_2SiO, moiety as the directing group.[8] The intramolecular silylformylation of *ω*-(dimethylsiloxy)-*i*-alkynes (**1**) catalyzed by Rh and Rh−Co complexes proceeds with complete regioselectivity, giving 3-*exo*-(formylmethylene)oxasilacycloalkanes (**2**) with or without an alkyl substituent at the *exo*-methylene carbon. On the other hand, the standard intermolecular silylformylation of an *ω*-(*tert*-butyldimethylsiloxy)-1-alkyne (**3**) yields the corresponding *ω*-(*tert*-butyldimethylsiloxy)-2-formyl-1-silylalkene (**4**) (eq 2).

A similar reversal of selectivity was achieved by introducing a $HSiR_2$ moeity to the alkyl terminal carbon of alkynes.[9] Recently, intramolecular silylformylation of *ω*-hydrosiloxyalkenes was also realized using Rh(acac)-$(CO)_2$ as catalyst under very high pressure of CO (1000 psi).[10]

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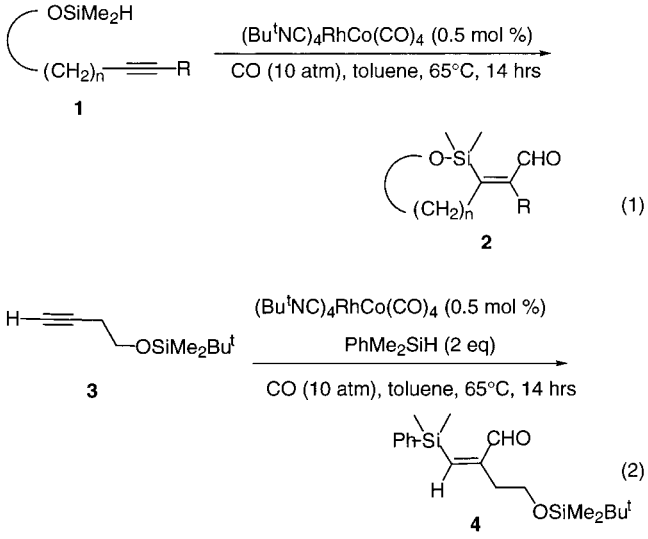
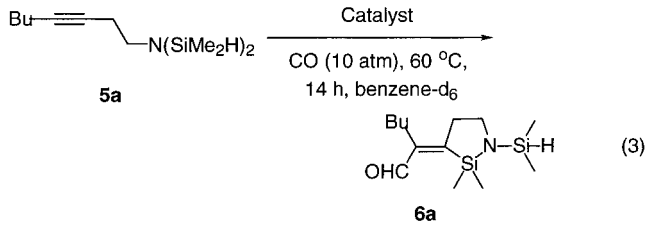


In this study, we investigated the application of the intramolecular silylformylation to *ω*-bis(dimethylsilylamino)-*i*-alkynes (**5**), because this process should provide a novel and efficient route to aminoformylvinylsilanes, which would be versatile polyfunctionalized intermediates in organic syntheses. Also, the reaction should yield literature unknown *exo*-alkenylazasilacycloalkanes as the initial products. *ω*-Bis(dimethylsilylamino)-*i*-alkynes were prepared through iterative reaction of 1-amino-*i*-alkynes with n-BuLi followed by silylation with chlorodimethylsilane adapting Tamao's procedure for bis(dimethylsilylamino)alkenes.[11]

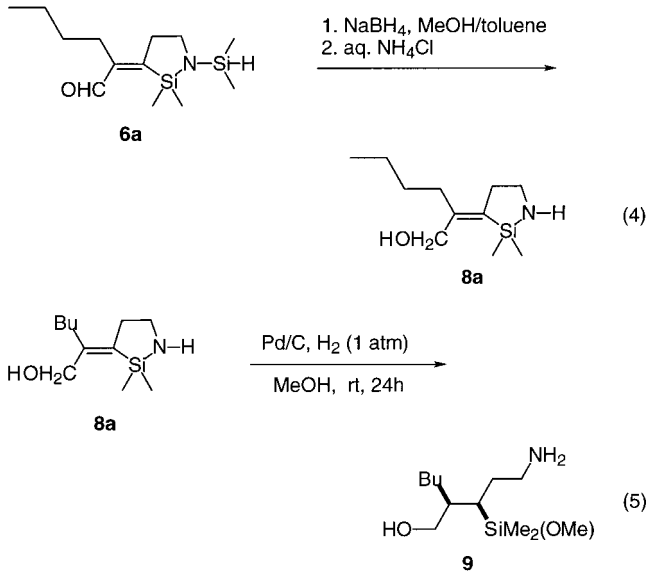
The reaction of 1-bis(dimethylsilylamino)-3-octyne (**5a**) was carried out in the presence of (^{t}BuNC)$_4$RhCo(CO)$_4$,[12] Rh$_2$Co$_2$(CO)$_{12}$,[13] or Rh(acac)(CO)$_2$ (0.5 mol %) in toluene at 60 °C for 14 h to give 2-silyl-5-*exo*-(1-formylpentyl-1-ene)-2-aza-1-silacyclopentane (**6a**) as the single product in high yield (eq 3). However, azasilacy-



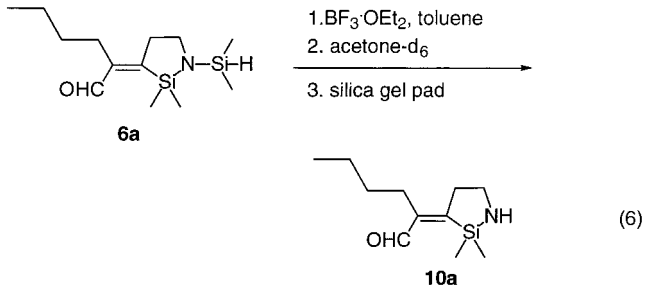
Catalyst: (^{t}BuNC)$_4$RhCo(CO)$_4$, Rh$_2$Co$_2$(CO)$_{12}$, Rh(acac)(CO)$_2$

clopentane **6a** was very unstable in benzene-d_6 solution (0.2−1.0 M) and almost immediately converted to the corresponding trioxane **7a**, i.e., the aldehyde trimer that was a sticky gel. Attempts to isolate trioxane **7a** proved futile. However, the intramolecular silylformylation reaction of **5a** in a dilute solution (0.05 M) of benzene-d_6 enabled us to acquire spectroscopic proof for the structure of **6a**. In fact, **6a** was stable in a 0.05 M solution of benzene-d_6 at least for several hours. Removal of the solvent in vacuo led to the formation of **7a** as a single stereoisomer (Scheme 1).

To obtain a stable derivative of **6a**, the reaction mixture in 0.05 M toluene was added to a suspension of NaBH$_4$ in methanol at 0 °C and reacted for 10 min, which yielded the corresponding alcohol **8a** (eq 4). It should be noted that only the *exo*-SiMe$_2$H group was removed in this reduction, and the resulting cyclic silylamine **8a** is stable against methanolysis and hydrolysis and thus is easily purified by chromatography on silica gel, which is totally unexpected. To the best of our knowledge, the observed stability of the Si−N bond in **8a** is unprecedented; that is, usually, the removal of the first silyl group of a disilylamine results in the concomitant facile cleavage of the second Si−N bond. It appears that the existence of the *exo*-alkylene group at C-5 is responsible for this unexpected stability of the Si−N bond. To confirm this hypothesis, **8a** was subjected to hydrogenation on Pd/C in dry methanol at ambient temperature and pressure of hydrogen (eq 5). As expected, upon hydrogenation of the double bond, the methanolysis of the Si−N bond took place immediately to open the ring, yielding amino alcohol **9**.



The reaction of **6a** with BF$_3$·Et$_2$O followed by removal of the solvents, addition of acetone-d_6, and filtration through a silica gel pad gave 5-*exo*-(1-formylpentyl-1-ene)-2-aza-1-silacyclopentane **10a**. It should be noted that this operation removed the *exo*-dimethylsilyl group on the nitrogen selectively, and **10a** is not prone to trimerization.



Since this protocol leading to **8a** worked very well for the reaction of **6a**, we employed it for all other reactions as well (see Table 1). Thus, the reactions of 1-bis(dimethylamino)-4-alkynes, **5b** and **5c**, at 60 °C and 50

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Scheme 1

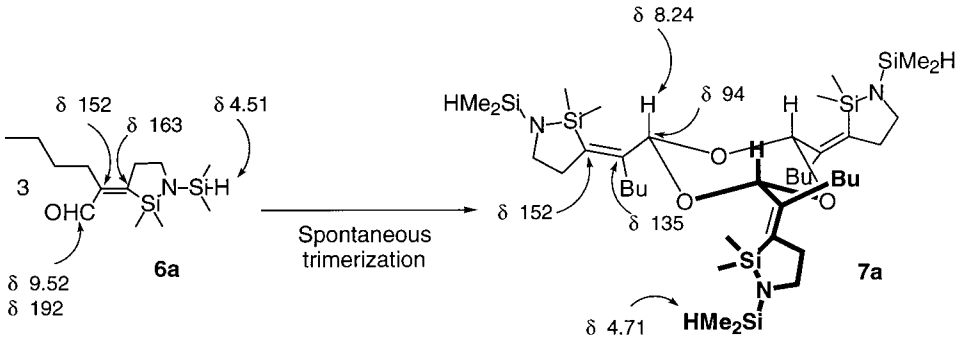
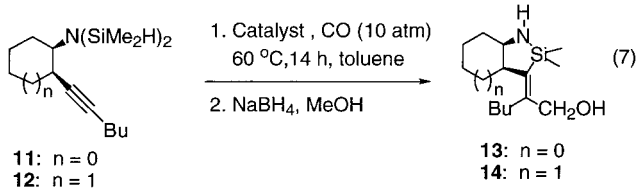


Table 1. Intramolecular Silylformylation of Bis(silyl)aminoalkynes

Entry	Substrate	Catalyst	Product	Yield (%)[a]
1	Bu, $(Me_2Si)_2N$ **5a**	$Rh(acac)(CO)_2$	Bu, HOH_2C, Si–N–H **8a**	52
2		$(^tBuNC)_4RhCo(CO)_4$		80
3		$Rh_2Co_2(CO)_{12}$		75
4	Ph, $(HMe_2Si)_2N$ **5b**	$Rh(acac)(CO)_2$	Ph, HOH_2C, Si–NH **8b**	71
5		$(^tBuNC)_4RhCo(CO)_4$		87
6	Bu, $(HMe_2Si)_2N$ **5c**	$Rh(acac)(CO)_2$	Bu, HOH_2C, Si–NH **8c**	90
7	$N(SiMe_2H)_2$, Bu **11**	$Rh(acac)(CO)_2$	H, N, Si, Bu, CH_2OH **13**	84
8	$N(SiMe_2H)_2$, Bu **12**	$Rh(acac)(CO)_2$	H, N, Si, Bu, CH_2OH **14**	61
9		$(^tBuNC)_4RhCo(CO)_4$		78

[a] Isolated yield for two steps.

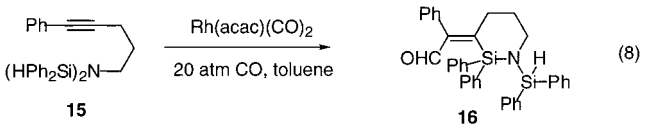
atm of CO for 14 h, immediately followed by $NaBH_4$ reduction gave 6-*exo*-(1-hydroxylmethylalkyl-1-ene)-2-aza-1-silacyclopentanes **8b** and **8c**, respectively, in high yield. In a similar manner, the reactions of 1-bis-(dimethylsilyl)amino-2-(1-hexynyl)cyclohexane (**11**) and 1-bis(dimethylsilyl)amino-2-(1-hexynyl)cyclopentane (**12**) at 60 °C and 10 atm of CO for 14 h, followed by $NaBH_4$ reduction, gave the corresponding *exo*-(1-formylalkyl-1-ene)azasilabicyclo[*x*.3.0]alkanes, **13** ($x = 4$) and **14** ($x = 3$), in high yields (eq 7).



(7)

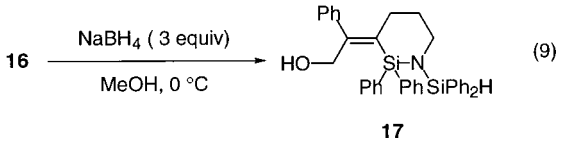
Catalyst: $(^tBuNC)_4RhCo(CO)_4$, $Rh(acac)(CO)_2$

When a diphenylsilyl group was employed in place of the dimethylsilyl group, the reaction gave the corresponding intramolecular silylformylation product in good yield. Thus, the reaction of 1-bis(diphenylsilyl)-amino-5-phenyl-4-pentyne (**15**) catalyzed by $Rh(acac)(CO)_2$ at 60 °C and 20 atm of CO for 14 h gave 1,1-diphenyl-2-silyl-6-(1-formyl-1-benzylidene)azasilacyclohexane (**16**) in 63% yield. In contrast to **6a**, **16** does not easily trimerize and is stable for chromatographic purification on silica gel (eq 8).



(8)

When **16** was treated with $NaBH_4$ in methanol, the corresponding alcohol **17** was obtained, in which the *exo*-diphenylsilyl group was kept intact (eq 9). This makes a sharp contrast with the case of **6a** bearing a dimethylsilyl group, which gave the reduction product **8a** losing the *exo*-dimethylsilyl group under the same reaction conditions (eq 4).



(9)

Further studies on the applications of this unique process are actively underway in these laboratories.

Experimental Section

General Methods and Materials. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-250 or Gemini 2300 using $CDCl_3$ or C_6D_6 as the internal standard. The IR spectra were measured with a Perkin-Elmer 1600 FT-IR spectrophotometer with a Hewlett-Packard 7470A plotter using samples as neat oils or as KBr disks. High-resolution mass spectra were obtained at the Mass Spectrometry Facility, University of California at Riverside. Analytical gas chromatography was performed with a Hewlett-Packard 5890 Series II gas chromatograph equipped with FID detectors using a 30 m DB-17 or a 15 m DB-1 capillary column (J&W Scientific). Elemental analyses were performed at the M-H-W Laboratories, Phoenix, AZ. All solvents were reagent grade and distilled before used. Rhodium complex, $Rh(acac)(CO)_2$, was obtained from the Mitsubishi Kasei Corporation and used as received. Rhodium−cobalt mixed metal complexes, $Rh_2Co_2(CO)_{12}$[12,13] and $Rh(CNBu^t)Co(CO)_4$,[12] were prepared by literature methods. Silica gel used for chromatography, MN−Kieselgel 60, was purchased from Brinkman Instruments Inc.

General Procedure for the Preparation of 1-Bis-(dimethylsilylamino)-*i*-alkynes (5, 11, and 12) via Disilylation of *ω*-Aminoalkynes. All aminoalkynes were disilylated following the literature procedure.[11] Preparation of 1-bis(dimethylsilyl)amino-3-octyne (**5a**) is described as an

example: A solution of 1-amino-3-octyne (1.00 g, 8.0 mmol) in THF (32 mL) under nitrogen was cooled to −78 °C. To this solution was added, dropwise via syringe, n-BuLi in hexanes (3.6 mL, 2.43 M, 8.8 mmol). The solution was stirred for 30 min and then slowly warmed to −40 °C and stirred further at this temperature for 0.5 h. The solution was cooled to −78 °C, and $ClSiMe_2H$ (0.83 g, 8.8 mmol) was added. The solution was warmed to −40 °C and stirred at this temperature for 1 h. The solution was cooled to −78 °C, and n-BuLi (4.0 mL, 2.43 M, 9.6 mmol) was added. The solution was warmed to −40 °C and stirred further for 1 h. The solution was cooled to −78 °C, and $ClSiMe_2H$ (0.90 g, 9.6 mmol) was added. The reaction mixture was stirred overnight while slowly warming to room temperature. Hexanes (50 mL) were added to the reaction mixture to precipitate resulting LiCl. The precipitate was filtered off and the filtrate concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation to give **5a** (1.42 g, 5.92 mmol, 74% yield) as a yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.17 (d, J = 3.2 Hz, 12 H), 0.90 (t, J = 7.0 Hz, 3 H), 1.38−1.49 (m, 4 H), 2.11−2.24 (m, 4H), 2.93−2.99 (m, 2 H), 4.43 (septet, J = 3.2 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ −0.54, 13.60, 18.44, 21.95, 23.87, 31.12, 45.82, 77.91, 81.08; IR (neat) 2958, 2862 cm^{-1}.

1-Bis(dimethylsilyl)amino-5-phenyl-4-pentyne (5b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.036 (d, J = 3.3 Hz, 12 H), 1.56 (m, 2 H), 2.22 (t, J = 6.9 Hz, 2 H), 2.82 (t, J = 6.9 Hz, 2 H), 4.29−4.32 (m, 2 H), 7.08−7.17 (m, 3 H), 7.22−7.26 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ − 0.49, 16.92, 32.77, 45.12, 89.782, 99.98, 127.53, 128.20, 129.03, 131.49.

1-Bis(dimethylsilyl)amino-4-nonyne (5c): H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 12 H), 0.90 (t, J = 7.1 Hz, 3 H), 1.22−1.71 (m, 6 H), 2.00−2.11 (m, 4 H), 2.82 (t, J = 7.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -95, 15.12, 20.54, 25.31, 29.21, 30.13, 32.65, 42.52, 80.32, 82.66.

***cis*-2-(1-Hexynyl)-1-bis(dimethylsilyl)aminocyclohexane (11):** ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.31 (d, J = 2.8 Hz, 12 H), 1.03 (t, J = 7.0 Hz, 3 H), 1.33−1.93 (m, 12 H), 2.26−2.35 (m, 2 H), 2.74−2.90 (m, 2 H), 4.80 (septet, J = 2.8 Hz), 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 0.54, 13.62, 18.44, 21.53, 21.96, 24.47, 30.30, 31.35, 32.08, 36.6, 51.59, 79.90, 83.91.

***cis*-2-(1-Hexynyl)-1-bis(dimethylsilyl)aminocyclopentane (12):** ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.92 (t, J = 7.0 Hz, 3 H), 0.18 (d, J = 3.1 Hz, 6 H), 0.19 (d, J = 3.1 Hz, 6 H), 1.31−1.52 (m, 5 H), 1.68−1.95 (m, 5 H), 2.17−2.21 (m, 2 H), 2.64−2.79 (m, 1 H), 3.31−3.47 (m, 1 H), 4.55 (septet, J = 3.1 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 0.53, 13.62, 18.49, 21.96, 22.02, 30.86, 31.30, 32.51, 33.24, 38.01, 545.26, 80.19, 83.62.

General Procedure for the Silylformylation of 1-Bis(dimethylsilylamino)-*i*-alkynes (5, 11, and 12). A 25 mL round-bottomed flask containing a catalyst (2.5×10^{-3} mmol) in toluene (5.0 mL) and a stirring bar was placed under CO atmosphere. A solution of 1-bis(dimethylsilylamino)-*i*-alkyne (**5**, **11**, or **12**) (0.50 mmol) in 10.0 mL of toluene was added to the reaction flask, which was then placed in a 300 mL stainless steel autoclave. Carbon monoxide was introduced to substitute the remaining air. After the CO pressure was adjusted to 10 atm (or 50 atm) at room temperature, the autoclave was immersed into an oil bath and allowed to stir magnetically at 60 °C for 14 h. Carbon monoxide was carefully released, and the reaction mixture was immediately poured into a solution of $NaBH_4$ (10 equiv) in methanol at 0 °C and stirred for 10 min. The reaction was then quenched with a saturated solution of NH_4Cl and immediately extracted with ether (3 × 10 mL). The ether extracts were combined, dried over K_2CO_3, and concentrated on a rotary evaporator to yield the corresponding alcohol.

For the characterization of 1,1-dimethyl-2-dimethylsilyl-5-*exo*-(*Z*-1-formyl-1-pentylidene)-2-aza-1-silacyclopentane (**6a**), the ^{1}H and ^{13}C NMR analyses of the reaction mixture were performed immediately after the reaction. After the measurements, the solvent was removed from the reaction mixture in vacuo for 2 h. The residue was dissolved in benzene-d_6 and subjected to ^{1}H and ^{13}C NMR analyses of the resulting aldehyde trimer **7a**.

1,1-Dimethyl-2-dimethylsilyl-5-*exo*-(*Z*-1-formylpentyl-1-ene)-2-aza-1-silacyclopentane (6a): ^{1}H NMR (250 MHz, benzene-d_6) δ 0.25 (s, 6 H), 0.28 (d, J = 2.8 Hz, 6 H), 0.93 (t, J = 7.1 Hz, 3 H), 1.35−1.55 (m, 4 H), 2.66 (t, J = 7.6 Hz, 2 H), 3.01 (t, J = 7.6 Hz, 2 H), 3.27 (m, 2 H), 4.66−4.62 (m, 1 H), 9.52 (s, 1 H); ^{13}C NMR (62.9 MHz, benzene-d_6) δ 0.72, 3.18, 14.07, 23.11, 30.72, 31.94, 44.53, 61.09, 151.56, 162.70, 192.21.

2,4,6-Tris[(1,1-dimethyl-2-dimethylsilyl-2-aza-1-silacyclopentyl-5-ene)pentyl-1-enyl]-1,3,5-trioxane (7a): ^{1}H NMR (250 MHz, benzene-d_6) δ 0.17 (s, 6 H), 0.28 (d, J = 2.8 Hz, 6 H), 0.89 (m, 3 H), 1.35 (m, 4 H), 2.49−2.61 (m, 4 H), 3.42 (m, 2 H), 4.70 (sept, J = 2.8 Hz 1 H), 8.24 (s, 1 H); ^{13}C NMR (62.9 MHz, benzene-d_6) δ 0.78, 3.15, 14.11, 23.18, 30.76, 32.01, 44.54, 61.09, 94.02, 135.31, 152.05.

1,1-Dimethyl-5-*exo*-(*Z*-1-hydroxymethylpentyl-1-ene)-2-aza-1-silacyclopentane (8a): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.24 (s, 6 H), 0.88 (t, J = 6.8 Hz, 3 H), 1.31 (m, 4 H), 2.16 (t, J = 7.2 Hz, 2 H), 2.62−2.68 (m, 2 H), 2.89−2.95 (m, 2H), 4.48 (s, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 0.88, 13.95, 22.75, 26.04, 27.47, 30.66, 40.00, 74.11, 127.09, 157.36; MS (EI) *m*/*z* 213 (M^+), 198 ($M^+ - CH_3$), 184 ($M^+ - CH_2CH_3$).

1,1-Dimethyl-6-*exo*-(*Z*-1-hydroxymethylbenzylidene)-2-aza-1-silacyclohexane (8b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 6 H), 1.66 (m, 2 H), 2.63 (m, 2 H), 3.02 (m, 2 H), 7.11−7.30 (m, 5 H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 0.55, 17.16, 32.63, 45.01, 64.32, 127.53, 129. 53, 128.20, 129.03, 131.49, 166.43; IR (neat) 3321 cm^{-1} (O−H), 1654 cm^{-1} (C═C); MS (EI) *m*/*z* 247 (M^+), 232 ($M^+ - CH_3$).

1,1-Dimethyl-6-*exo*-(*Z*-1-hydroxymethylpentyl-1-ene)-2-aza-1-silacyclohexane (8c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.53 (s, 6 H), 0.89 (t, J = 7.1 Hz, 3 H), 1.23−1.69 (m, 6 H), 2.05−2.12 (m, 4 H), 2.85−2.92 (m, 2 H), 4.31 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.76, 15.16, 20.42, 25.32, 29.31, 30.22, 32.77, 41.25, 66.23, 133.93, 156.62; MS (EI) *m*/*z* 227 (M^+), 212 ($M^+ - CH_3$).

***cis*-8,8-Dimethyl-7-*exo*-(*Z*-1-hydroxymethylpentyl-1-ene)-9-aza-8-silabicyclo[4.3.0]nonane (13):** ^{1}H NMR (250 MHz, benzene-d_6) δ 0.15 (d, J = 2.9 Hz, 6 H), 0.22 (s, 3 H), 0.34 (s, 3 H), 0.88 (*t*, J = 7.2, 3 H), 1.09−1.57 (m, 12 H), 2.56−2.67 (m, 1 H), 3.24−3.26 (m, 1 H), 4.62−4.66 (m, 1 H), 9.71 (s, 1 H); ^{13}C NMR (62.9 Mz, benzene-d_6) δ 0.27, 2.363, 3.21, 14.15, 19.58, 23.33, 25.80, 27.40, 30.06, 32.29, 47.06, 55.64, 147.00, 171.42, 192.50; MS (EI) *m*/*z* 267 (M^+), 252 ($M^+ - CH_3$).

***cis*-3,3-Dimethyl-4-*exo*-(*Z*-1-hydroxymethylpentyl-1-ene)-2-aza-3-silabicyclo[3.3.0]octane (14):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04, (s, 6 H), 0.85 (t, J = 7.2 Hz, 3 H), 1.17−1.39 (m, 4 H), 1.41−1.98 (m, 6 H), 2.09 (t, J = 7.2 Hz, 2 H), 2.63−2.72 (m, 1 H), 3.11−3.14 (m, 1 H), 4.35 (s, 2 H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 0.75, 13.77, 21.65, 22.83, 28.87, 30.07, 30.62, 34.70, 44.66, 55.02, 72.14, 133.00, 154.56; HRMS (CI) calcd for $C_{14}H_{28}NOSi$ (MH^+) 282.2253, found 282.1706 (Δ = +1.2 ppm).

Reaction of 6a with Boron Trifluoride Etherate. To the reaction mixture containing **6a** in toluene (15 mL) obtained as mentioned above was added dropwise $BF_3{\cdot}Et_2O$ (0.31 mL, 2.5 mmol) at room temperature with stirring. Purple-brown precipitate formed immediately. The solvents were removed under vacuum, and acetone-d_6 was added. Then, all precipitate was dissolved to become a light brown solution. The solution was passed through a silica gel pad and the filtrate transferred to an NMR tube for measurements. The NMR spectrum clearly showed the clean formation of desilylated aldehyde **10a**.

1,1-Dimethyl-5-*exo*-(*Z*-1-formylpentyl-1-ene)-2-aza-1-silacyclopentane (10a): ^{1}H NMR (250 MHz, acetone-d_6) δ 0.14 (s, 3 H), 0.17 (s, 3 H), 0.81 (t, J = 7.0 Hz, 3 H), 1.17−1.41 (m, 4 H), 2.50−2.56 (m, 2 H), 2.82−2.89 (m, 2 H), 3.73 (t, J = 8.4 Hz, 2 H), 9.39 (s, 1 H); ^{13}C NMR (62.9 MHz, acetone-d_6) 0.63, 14.41, 23.29, 30.17, 31.44, 45.31, 52.97, 149.32, 157.03, 190.44;

HRMS (CI) calcd for $C_{11}H_{22}NOSi$ (MH^+) 212.3895, found 212.3884 (Δ = +5.17 ppm).

Hydrogenation of 8a. To a suspension of 5% Pd/C (10.6 mg) in dry methanol (5 mL) under hydrogen atmosphere was a added a solution of **8a** (106 mg, 0.50 mmol) in dry methanol (5 mL) at room temperature with stirring. The mixture was stirred at room temperature for 24 h. TLC analysis of the reaction mixture showed the complete conversion of the starting **8a** and very clean formation of single product. Thus, the reaction mixture was passed through a Celite pad and washed with ethyl acetate. The filtrate was concentrated in vacuo to give **9** as a yellow oil.

2,3-*syn*-5-Amino-3-dimethoxydimethylsilyl-2-*n*-butylpentan-1-ol (9): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.01 (s, 6 H), 0.43 (m, 1 H), 0.81 (t, J = 7.8 Hz, 3 H), 1.21−1.79 (m, 8 H), 2.24−2.31 (m, 1 H), 3.15 (t, J = 7.2 Hz, 2 H), 3.48 (d, J = 6.9, 2 H), 3.54 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −1.80, 5.32, 18.61, 20.52, 23.22, 23. 97, 31.26, 33.30, 45.11, 63.91, 64.22; HRMS (CI) calcd for $C_{12}H_{30}NO_2Si$ (MH^+) 248.2045, found 248.2031 (Δ = 5.64 ppm).

Preparation of 1-Bis(diphenylsilyl)amino-5-phenyl-4-pentyne (15). Compound **15** was prepared following the same procedure as that for the synthesis of **5a** with the exception of the chlorosilane used; that is, $ClSiPh_2H$ was used for this reaction. ^{1}H NMR (300 MHz, $CDCl_3$): 1.59 (quintet, J = 8.10 Hz, 2H), 2.08 (t, J = 6.6 Hz, 2 H), 3.21 (t, J = 8.4 Hz, 2 H), 5.40 (s, 2 H), 7.140−7.678 (m, 25 H). ^{13}C NMR (75 MHz, $CDCl_3$): 16.9, 31.7, 45.9, 80.9, 89.3, 123.9, 127.5, 127.9, 128.00, 128.1, 129.9, 130.3, 130.5, 131.5, 134.4, 134.8, 135.5, 136.2.

Silylformylation of 15. The silylformylation of **15** was carried out following the same procedure as that for the silylformylation of 1-bis(dimethylsilamino)-*i*-alkynes **5** with the exception of CO pressure; that is, 50 atm was employed. After releasing carbon monoxide, the reaction mixture was concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (4;1) as the eluant to yield **16** as a yellow oil (63%).

2,2-Diphenyl-2-diphenylsilyl-6-exo-(1-formyl-1-benzylidene)-2-aza-1-silacyclohexane (16): ^{1}H NMR (250 MHz, $CDCl_3$) 1.751−1.831 (m, 2 H), 2.696 (t, J = 5.9 Hz, 2 H), 3.293 (t, J = 5.5 Hz, 2 H), 4.925 (s, 1 H), 7.124−7.691 (m, 25 H), 9.781 (s, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 28.71, 35.22, 45.53, 127.61, 127.82, 128.22, 129.32, 129.75, 130.19, 134.10, 134.29, 135.16, 135.34, 135.62, 151.15, 162.68, 192.37; HRMS (CI) calcd for $C_{36}H_{34}NOSi_2$ (MH^+) 552.8494, found 552.8481 (Δ = −2.45 ppm).

$NaBH_4$-Reduction of 16. A solution of **16** (41 mg, 0.076 mmol) in methanol (5 mL) was added to a solution of $NaBH_4$ (9 mg, 0.23 mmol) in methanol (10 mL) at 0 °C, and the mixture was stirred for 10 min. TLC analysis of the reaction mixture indicated a complete conversion of the starting material **16** and very clean formation of single product. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (20 mL) and extracted with ether (2 × 20 mL). The ether extracts were combined and dried over Na_2SO_4, and the solvent was removed under reduced pressure to give **17** as a yellow oil (18 mg, 0.032 mmol, 43% yield).

2,2-Diphenyl-2-diphenylsilyl-6-*exo*-(2-hydroxyl-1-phenylethylidene)-2-aza-1-silacyclohexane (17): ^{1}H NMR (250 MHz, $CDCl_3$) 1.721−1.816 (m, 2 H), 2.471 (t, J = 5.9 Hz, 2 H), 3.149 (t, J = 5.5 Hz, 2 H), 3. 537 (s, 2 H), 5.111 (s, 1 H), 7.045−7.531 (m, 25 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 28.83, 35.32, 45.86, 63.81, 127.34, 127.71, 127.99, 130.88, 131.21, 132.45, 134.66, 134.90, 135.34, 135.88, 136.08, 147.32, 159.33; HRMS (CI) calcd for $C_{36}H_{36}NOSi_2$ (MH^+) 554.2335, found 554.2351 (Δ = −2.88 ppm).

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