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SILYLFORMYLATION CATALYZED BY Rh AND Rh-Co MIXED METAL COMPLEXES AND ITS APPLICATION TO THE SYNTHESIS OF PYRROLIZIDINE ALKALOIDS

IWAO OJIMA*, ROBERT J. DONOVAN, MASAKATSU EGUCHI, WILLIAM R. SHAY, PATRIZIA INGALLINA,[1] ANNA KORDA,[2] and QINGPING ZENG

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400, U. S. A.

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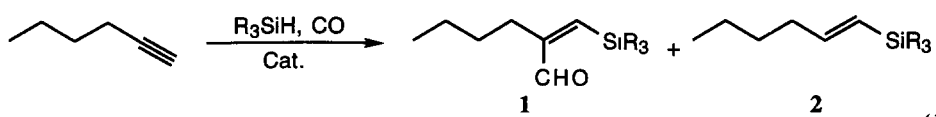
Summary: Reactions of hydrosilanes with 1-hexyne catalyzed by $Co_2Rh_2(CO)_{12}$, $Rh_4(CO)_{12}$, $(^tBuNC)_4RhCo(CO)_4$, and Rh(acac)$(CO)_2$ at 25°C and atmospheric pressure to 10 atm of carbon monoxide give (*Z*)-1-silyl-2-formyl-1-hexenes (**1**), which are the products of "silylformylation", and/or (*E*)-1-silyl-1-hexenes (**2**). The ratio of silylformylation vs. hydrosilylation products depends on the electronic nature of hydrosilane used, e.g., $PhMe_2SiH$ gives **1** almost exclusively whereas $(MeO)_3SiH$ favors the formation of **2**. When trialkylsilanes such as Et_3SiH and $EtMe_2SiH$ are used, the reaction catalyzed by $Co_2Rh_2(CO)_{12}$ or $(^tBuNC)_4RhCo(CO)_4$ gives 2,5-bis(n-butyl)-3-silylcyclopent-2-en-1-one (**3**) as a major product, which is a unique silylcarbocyclization product. Mechanism of the formation of **3** is discussed on the basis of deuterium-labeling experiments. Chemoselective silylformylations of alkenynes, a dialkyne, and an alkynyl nitrile proceed in high yields in which alkene and nitrile functionalities are inert for the reaction. Silylformylation is successfully applied to the syntheses of pyrrolizidine alkaloids, (±)-isoretronecanol and (±)-trachelanthamidine, from 5-ethynyl-2-pyrrolidinone (**6**) in combination with amidocarbonylation.

We have been exploring new catalytic synthetic reactions promoted by Rh and Rh-Co carbonyl clusters and related complexes such as $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$ and $CoRh(CO)_7$, which include highly regioselective hydroformylations fluoro-olefins,[3] chelation-controlled amidocarbonylations,[4] hydrosilylations,[5] and silylcarbocyclizations (SiCAC).[6] We have also been investigating the reactions of $Co_2Rh_2(CO)_{12}$, and $CoRh(CO)_7$ with hydrosilanes in the presence and absence of carbon monoxide and/or substrates in order to determine the active sites of these Co-Rh mixed metal catalyst systems by identifying active catalyst species as well as intermediates for catalytic cycles. In the course of such a mechanistic study, we carried out the reaction of 1-hexyne with a hydrosilane catalyzed by $Co_2Rh_2(CO)_{12}$ at ambient temperature and pressure of carbon monoxide. Then, we discovered that the reaction gave (*Z*)-1-silyl-2-formyl-1-hexene (**1**) in addition to the usual hydrosilylation product.[7] This reaction yielding the compound **1** from an alkyne is a new type of silylcarbonylation, i.e., "silylformylation", that is different from the Murai's "silylcarbonylation" catalyzed by $Co_2(CO)_8$ giving silyl enol ethers of homologous aldehydes in which silicon moiety always attaches to oxygen, viz., any silicon migration to olefinic bond to form silicon-carbon bond is not observed at all.[8] While our study was in progress,[9] Matsuda et al. independently reported the discovery of "silylformylation" catalyzed specifically by $Rh_4(CO)_{12}$ using a variety of alkynes and dimethylphenylsilane as the specific hydrosilane at 100°C and 10 – 30 atm of carbon monoxide in the presence of triethylamine.[10] A preliminary study on the mechanism of silylformylation catalyzed by $Co_2Rh_2(CO)_{12}$ was reported from our laboratory, which unveiled the presence of

$(R_3Si)_2Rh(CO)_n$-$Co(CO)_4$ (n = 2 or 3) and RhCo(*n*-Bu-C≡C-H)$(CO)_5$ as key active catalyst species for the reaction and possible occurrence of unique *homogeneous bimetallic catalysis*.[7] We describe here our further study on the synthetic aspect of silylformylation of alkynes and its application to the synthesis of pyrrolizidine alkaloids.

RESULTS AND DISCUSSION

Reactions of 1-hexyne with a variety of hydrosilanes were carried out in toluene at 25°C and ambient pressure or 10 atm of carbon monoxide in the presence of $Co_2Rh_2(CO)_{12}$ (substrate/cat. = 1,000; 6.7 x 10^{-4} M) for 24 h to give (*Z*)-1-silyl-2-formyl-1-hexene (**1**) and/or (*E*)-1-silyl-1-hexene (**2**) (eq. 1); $Rh_4(CO)_{12}$ was also employed for comparison purposes. Results are summarized in Table 1. As Table 1 shows, the structure of hydrosilane exerts a marked influence on the selectivity of the reaction, i.e., silylformylation vs. hydrosilylation. Trimethoxysilane clearly favors hydrosilylation whereas dimethylphenylsilane gives silylformylation product selectively, and trialkylsilanes give ca. 40:60 mixture of the hydrosilylation and silylformylation products. At 25°C and ambient pressure of carbon monoxide, the reaction catalyzed by $Rh_4(CO)_{12}$ proceeds at a similar rate to that catalyzed by $Co_2Rh_2(CO)_{12}$ and the ratio of the hydrosilylation vs. silylformylation is similar. In both cases, considerable amounts of side product(s) are formed. At 25°C and 10 atm of carbon monoxide, however, $Co_2Rh_2(CO)_{12}$ acts as an excellent catalyst giving the silylformylation product (**1**) with 93-100% selectivity (Entries 2,4,6) except the case using $HSi(OMe)_3$ (Entry 8). Formation of side product(s) is also substantially decreased. Under the same conditions, the $Rh_4(CO)_{12}$-catalyzed reactions give a larger amount of side product(s) compared with the $Co_2Rh_2(CO)_{12}$-catalyzed ones, and $HSi(OMe)_3$ does not give any silylformylation product (**1**) (Entry 16). As $Co_2(CO)_8$ is found to be virtually inactive even under forced conditions, it is apparent that there is a synergistic effect in the Co-Rh mixed metal system. Catalyst concentration has a significant influence on the selectivity of the reaction: When lower catalyst concentration (2.6 x 10^{-4} M) with the same substrate/catalyst ratio (1,000) was employed, the reaction gives excellent results (Entries 1A and 2A). It is worth mentioning that all silylformylation products (**1**) have (*Z*)-1-silyl-2-formyl structure, i.e., the reaction is extremely regioselective as well as stereoselective. All hydrosilylation products (**2**) are (E)- isomers exclusively. This makes a sharp contrast to the rhodium complex - catalyzed hydrosilylation of 1-alkenes,[5a] which gives a mixture of (*Z*)-isomer (major), (*E*)- and α-isomers (minor).



1 **2** (1)

Cat = $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $(^tBuNC)_4RhCo(CO)_4$, $Rh(acac)(CO)_2$

R_3Si = (a) $PhMe_2Si$; (b) $EtMe_2Si$; (c) Et_3Si; (d) $(MeO)_3SiH$, (e) Ph_3SiH, (f) Ph_2MeSiH

Since dimethylphenylsilane gave the best product selectivity for silylformylation, other phenyl-containing hydrosilanes, triphenylsilane and diphenylmethylsilane, were also examined. Indeed, the reactions with these phenyl-containing hydrosilanes cleanly gave the corresponding silylformylation products, **1e** and **1f**, respectively

in virtually quantitative yields at 25°C and ambient pressure of carbon monoxide for 36 h (100% conversion) using $Co_2Rh_2(CO)_{12}$ as the catalyst (substrate/cat. = 1,000; 2.7 x 10^{-4} M): **1e** and **1f** were isolated in 97% and 98% yields, respectively, after passing the reaction mixture through a short silica gel column to remove the catalyst.

Table 1. Reactions of hydrosilanes with 1-hexyne catalyzed by $Co_2Rh_2(CO)_{12}$ and $Rh_4(CO)_{12}$ in the presence of carbon monoxide[a]

Entry	Catalyst	Hydrosilane	CO (atm)	Conversion (%)[c]	Yield (%)[d]	Product 1	Ratio[c] 2
1	$Co_2Rh_2(CO)_{12}$	$HSiMe_2Ph$	1	50	72	100	--
1A[b]			1	100	96	100	--
2			10	100	92	100	--
2A[b]			10	100	98	100	--
3		$HSiMe_2Et$	1	27	48	60	40
4			10	100	84	100	--
5		$HSiEt_3$	1	48	49	58	42
6			10	100	80	93	7
7		$HSi(OMe)_3$	1	100	86	20	80
8			10	100	95	38	62
9	$Rh_4(CO)_{12}$	$HSiMe_2Ph$	1	98	72	100	--
10			10	100	76	100	--
11		$HSiMe_2Et$	1	84	61	65	35
12			10	100	80	91	9
13		$HSiEt_3$	1	100	62	71	29
14			10	100	77	86	14
15		$HSi(OMe)_3$	1	100	76	--	100
16			10	100	80	--	100

[a]All reactions were run with 5.0 mmol of 1-hexyne, 5.5 mmol of a hydrosilane, and 5.0 x 10^{-3} mmol of a catalyst in toluene (7.5 mL) at 25°C for 24 h unless otherwise noted. Reactions under ambient pressure of carbon monoxide were carried out in a Schlenk flask; Reactions under 10 atm of carbon monoxide were carried out in a stainless steel autoclave using a Pyrex reaction vessel (50 mL). [b]Reactions were run with 4.0 mmol of 1-hexyne, 4.5 mmol of a hydrosilane, and 4.0 x 10^{-3} mmol of a catalyst in toluene (15 mL) at 25°C for 36 h. [c]Determined by GLC analyses. [d]Yield was determined by GLC analysis based on 1-hexyne consumed.

We looked further at the effect of catalyst structure on the selectivity of the reaction by using $(^tBuNC)_4RhCo(CO)_4$ and $Rh(acac)(CO)_2$ as catalysts besides $Co_2Rh_2(CO)_{12}$, $Rh_4(CO)_{12}$, and $RhCl(PPh_3)_3$ in the reactions of 1-hexyne with dimethylphenylsilane and diphenylmethylsilane. In order to make a fair comparison, the concentration of each catalyst was properly adjusted so that the rhodium metal concentration remained constant (5.3 x 10^{-4} M; substrate/Rh = 500) in each reaction. Results are shown in Table 2.

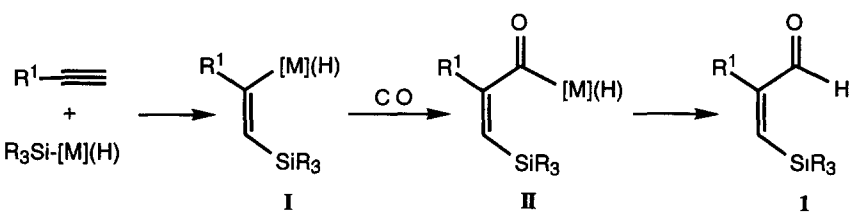
Table 2. Effect of catalyst structure on the selectivity of silylformylation[a]

Catalyst	$PhMe_2SiH$ Yield(%) of **1a**[b]	Ph_2MeSiH Yield(%) of **1f**[b,c]
$(^tBuNC)_4RhCo(CO)_4$	99	99.5
$Rh(acac)(CO)_2$	97	92
$Co_2Rh_2(CO)_{12}$	92.5	97
$Rh_4(CO)_{12}$	90	--
$RhCl(PPh_3)_3$	0	0
$Co_2(CO)_8$	0	--

[a]Reactions were run with 4.00 mmol of 1-hexyne and 4.00 mmol of $HSiMe_2Ph$ in the presence of 2.00 x 10^{-3} mmol of $Rh_4(CO)_{12}$, 4.00 x 10^{-3} mmol of $Co_2Rh_2(CO)_{12}$, 8.00 x 10^{-3} mmol of $(^tBuNC)_4RhCo(CO)_4$, 8.00 X 10^{-3} mmol, 8.00 x 10^{-3} mmol of $RhCl(PPh_3)_3$ and 8 x 10^{-3} mmol of $Co_2(CO)_8$, respectively, in 15 mL of toluene at 25°C. [b]All reactions were monitored by GLC analysis until 100% completion of the reaction was achieved. [c]Isolated yield.

As Table 2 shows, $(^tBuNC)_4RhCo(CO)_4$ turns out to be the best catalyst for silylformylation. This unique Rh-Co bimetallic complex can readily be prepared by reacting eight equivalents of *tert*-butylisocyanide with $Co_2Rh_2(CO)_{12}$ in high yield.[11] It is rather surprising that $Rh(acac)(CO)_2$ can catalyze the reaction very effectively. However, a preliminary study on the basis of FT-IR analyses strongly suggests that this monomeric rhodium catalyst precursor forms a dimer or a higher nuclearity complex upon reacting with alkynes.

Although the understanding of the detailed mechanism of silylformylation must await further investigation, it is clear at present that the reaction includes extremely regioselective insertion of 1-alkyne to the metal-Si bond to form a β-silylethenyl-metal complex (**I**), followed by carbon monoxide insertion giving a β-silylacryloyl-metal complex (**II**), and subsequent reductive elimination yields **1** (eq. 2).[7] It should be noted that the alkyne insertion takes place across the metal-Si bond exclusively and *not* across the metal-hydrogen bond

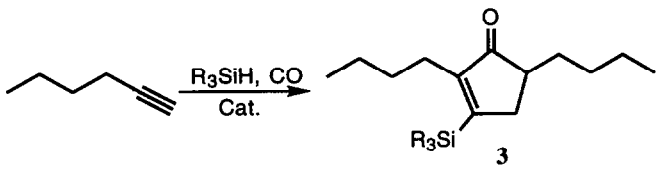


(2)

With regard to the side products formed in the reaction, we carried out a detailed investigation and found that 2,5-bis(*n*-butyl)-3-silylcyclopent-2-en-1-one (**3b** or **3c**) was the predominant side product in the reaction with dimethylethylsilane or triethylsilane, which is a novel carbocyclization product. It was also found that **3a** and the hydrosilylation products of **1a** were the side products in the reaction with dimethylphenylsilane.

The silylcarbocyclization product **3** becomes the major product of the reaction under certain conditions (eq. 3). For example, the reaction of 1-hexyne with triethylsilane catalyzed by $Co_2Rh_2(CO)_{12}$ (substrate/cat. = 1,000; 2.7 x 10^{-4} M) at 25°C and ambient pressure of carbon monoxide in toluene for 40 h gave **3c** in 49% selectivity together with **1c** (38%) and **2c** (13%) at 82% conversion; **3c** was obtained in 54% conversion yield when

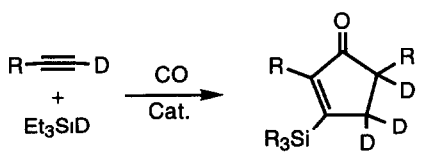
(^{t}BuNC)$_4$RhCo(CO)$_4$ was employed as the catalyst at 60°C. It appears that the silylcarbocyclization is favorable only with trialkylsilanes since the yield of **3a** using dimethylphenylsilane has never exceeded 5% and the formation of **3** has not been detected on using triphenylsilane and diphenylmethylsilane. The use of excess 1-hexyne increases the selectivity of **3** at low conversion, but unfortunately the reaction does not go to high conversion due to deactivation of the catalyst species by excess alkyne.



3 + **1** + **2** (3)

Cat. = $Rh_4(CO)_{12}$, (t-BuNC)$_4$RhCo(CO)$_4$, $Rh_2Co_2(CO)_{12}$
R_3Si = (a) $PhMe_2Si$, (b) $EtMe_2Si$, (c) Et_3Si.

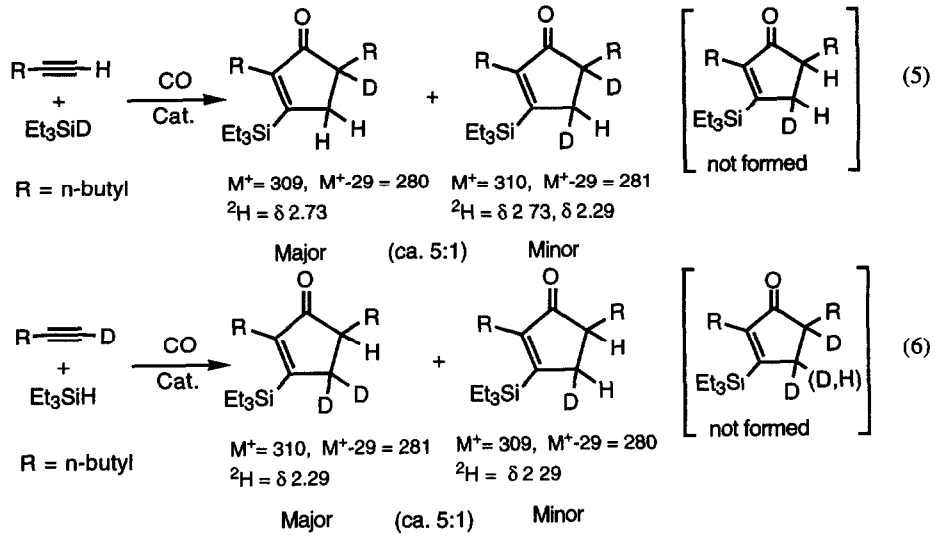
For the formation of **3**, it is apparent that two molecule of 1-hexyne, one molecule of carbon monoxide, and one molecule of a hydrosilane are incorporated. The left half of the molecule strongly suggests the intermediacy of β-silylacryloyl-metal species (**II**), which is then trapped by another molecule of 1-hexyne and carbocyclization takes place to give **3**. A very regioselective reduction of the non-silylated double bond should be involved after the carbocyclization since the final product is not a cyclopentadienone. A mechanism that can accommodate these points is proposed in Scheme 1. As Scheme 1 shows, the proposed mechanism includes a formal acetylenic hydrogen migration from one 1-hexyne to the other so that one of the methylene hydrogen at the C-4 of **3** should come from the first 1-hexyne that forms the β-silylacryloyl-metal species (**II**). This means that the methine hydrogen at the C-5 should come from a hydrosilane. Highly regioselective reduction of the intermediate **III** should take place at the sterically less congested site. There is a possibility of hydrogen exchange between the metal hydride of **III** and a hydrosilane. To elucidate the proposed mechanism, we carried out three deuterium-labeling experiments (eqs. 4-6) using 1-deuterio-1-hexyne (>98% purity) and/or deuteriotriethylsilane (95% purity), and analyzed by ^{2}H NMR and GC-MS. As the equations 4-6 illustrate, the results unambiguously support the proposed mechanism.



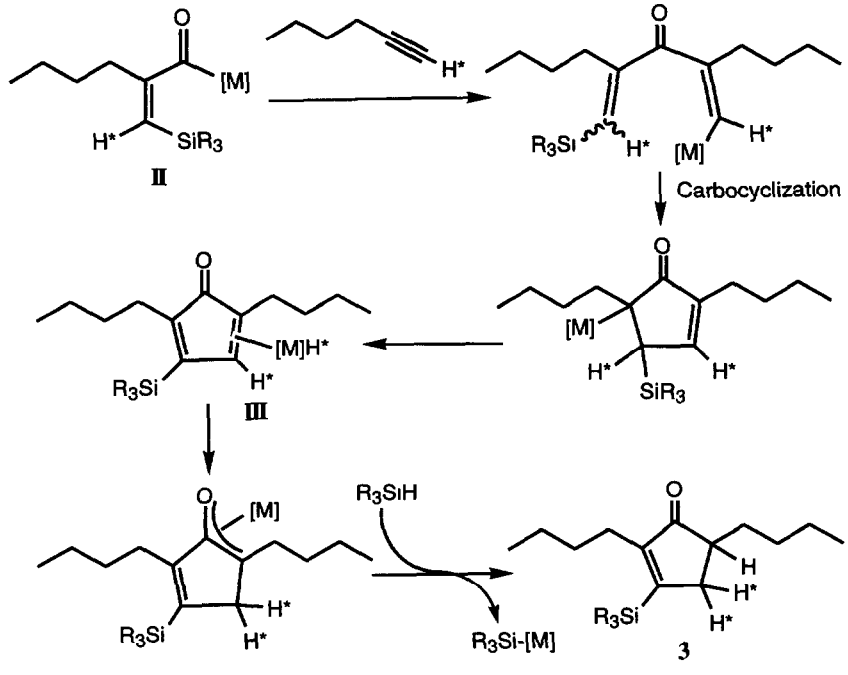
(4)

R = n-butyl

M^+ = 311, M^+-29 = 282
^{2}H = δ 2.73, δ 2.29

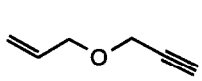
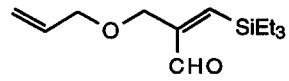
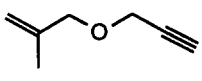
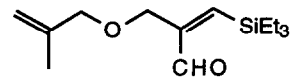
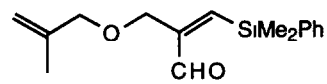
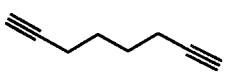
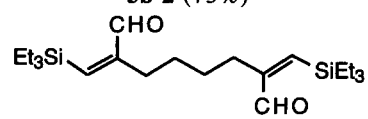
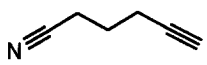
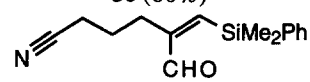

R—≡—H
+
Et3SiD
CO
Cat.
R = n-butyl
M+= 309, M+-29 = 280
2H = δ 2.73
Major
(ca. 5:1)
M+= 310, M+-29 = 281
2H = δ 2 73, δ 2.29
Minor
not formed
(5)
R—≡—D
+
Et3SiH
CO
Cat.
R = n-butyl
M+= 310, M+-29 = 281
2H = δ 2.29
Major
(ca. 5:1)
M+= 309, M+-29 = 280
2H = δ 2 29
Minor
not formed
(6)

Scheme 1


[M]
H*
SiR3
II
R3Si
H*
[M]
H*
Carbocyclization
[M]
H*
H*
SiR3
[M]H*
R3Si
H*
III
[M]
R3Si
H*
H*
R3SiH
R3Si-[M]
H
H*
R3Si
H*
3

Next, we applied silylformylation to alkenynes, a dialkyne, and an alkynyl nitrile at 25°C and 10 – 50 atm of carbon monoxide. The reactions gave the corresponding silylformylation products in excellent yields with excellent chemoselectivity, i.e., alkene and nitrile functionalities were inert for the reaction. Results are summarized in Table 2. It should be noted that a novel intramolecular silylcarbocyclization (SiCAC) reaction take place when the reaction of **4a** is carried out at 65°C and ambient pressure of carbon monoxide or under nitrogen.[6]

Table 3. Silylformylation of alkenyne, dialkyne, and alkynyl nitrile

Substrate	Hydrosilane	Conditions[a]	Product (Yield)[b]
 **4a**	Et_3SiH	$Rh_4(CO)_{12}$ (0.1 mol%) CO (50 atm) 25°C, 48 h	 **5a-1** (94%)[c]
 **4b**	Et_3SiH	$Rh(acac)(CO)_2$ (0.1 mol%) CO (10 atm) 70°C, 75 h	 **5b-1** (73%)
	$PhMe_2SiH$	$Rh(acac)(CO)_2$ (0.1 mol%) CO (20 atm) 70°C, 44 h	 **5b-2** (73%)
 **4c**	Et_3SiH	$Rh_4(CO)_{12}$ (0.1 mol%) CO (20 atm) 25°C, 48h	 **5c** (80%)
 **4d**	$PhMe_2SiH$	$Rh(acac)(CO)_2$ (0.2 mol%) CO (ambient press.) 25°C, 48 h	 **5d** (96%)

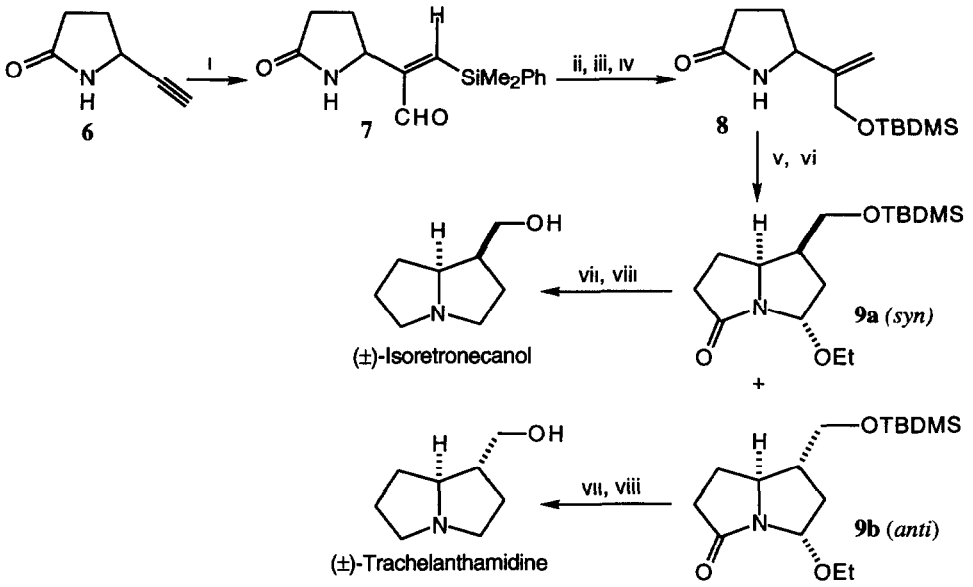
[a]All reactions were run with 4.0 mmol of substrate, and 4.0 mmol of hydrosilane in toluene. [b]Isolated yield unless otherwise noted. [c]GLC yield.

Finally, we applied silylformylation to the synthesis of precursors of pyrrolizidine alkaloids. Construction of the basic skeleton of pyrrolizidine alkaloids, aza[3.3.0]octane ring system, can be achieved by using rhodium–catalyzed amidocarbonylation.[4] This protocol was successfully incorporated into the synthesis of (±)-isoretronecanol and (±)-trachelanthamidine from 5-ethynyl-2-pyrrolidinone (**6**) via silylformylation followed by amidocarbonylation (Scheme 2).[12]

Silylformylation of 5-ethynyl-2-pyrrolidinone (**6**) was carried out with a catalytic amount of $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, or $Rh(acac)(CO)_2$ under 20 atm of carbon monoxide in toluene at ambient temperature to afford (*Z*)-5-[(2-dimethylphenylsilyl-1-formyl)ethenyl]pyrrolidinone (**7**) as the only product in 65-97% yield. Among the catalysts employed, $Rh(acac)(CO)_2$ gave the best yield (97%). The reduction of formyl group in **7** with sodium borohydride followed by desilylation with *p*-toluenesulfinic acid in wet acetonitrile[13] gave 5-(1-hydroxymethyl-ethenyl)-2-pyrrolidinone (**8**) in 75% yield. Then, the hydroxyl group of **8** was protected by *t*-

butyldimethylsilyl (TBDMS) group and subjected to the amidocarbonylation catalyzed by $HRh(CO)(PPh_3)_3$ The reaction gave a diastereomer mixture (*syn/anti* = 2) of the desired product **9** through an intramolecular amidocarbonylation in 72% yield. The diastereoisomers (*syn/anti*) of **9** were separated by preparative HPLC (silica gel, 3% 2-propanol in hexanes). Both diastereoisomers, **9a** and **9b**, were successfully converted to pyrrolizidine alkaloids, (±)-isoretronecanol (**10a**) and (±)-trachelanthamidine (**10b**), respectively, through removal of TBDMS group with tetrabutylammonium fluoride followed by $LiAlH_4$ reduction of the amidal and amido groups in good yields.

Scheme 2



i) $HSiMe_2Ph$, CO (300 psi), $Rh(acac)(CO)_2$ (0.8 mol%), toluene, 25°C, 24 h, 98%; ii) $NaBH_4$, $EtOH/H_2O$ (1:1), 0°C - 25°C, overnight, 100%; iii) TsH, MeCN (2% H_2O), reflux, 5h, 75%; iv) TBDMS-Cl, imidazole, DMF, 40°C, 3h, 98%; v) CO/H_2 (1/1, 1,600 psi), $HRh(CO)(PPh_3)_3$, $HC(OEt)_3$, 100°C, 24 h, 72% (syn/anti = 2/1); vi) SiO_2 column; vii) n-Bu_4NF, THF, 25°C,1 h, 96%; viii) $LiAlH_4$, THF, reflux, 6 h, 65-70%.

EXPERIMENTAL SECTION

General methods. ^1H NMR spectra were recorded on a General Electric QE-300, or a Bruker AC-250 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer with a Hewlett-Packard HP 7470A Plotter, using samples as neat liquid, nujol mulls or solution. Mass spectra (GC-MS) were obtained at 70 eV on a Hewlett-Packard HP 5980A

mass spectrometer equipped with a HP 5710A gas chromatograph and a HP 5933A data system or a Hewlett-Packard HP 5971A mass spectrometer with a HP 5890 gas chromatograph and a HP Vecta QS/20 workstation. High resolution mass spectra (HRMS) were measured with a Kratos MS-80RFA mass spectrometer with Chrompack Carlo Erba/Kratos gas chromatograph and DATA General Eclipse S/120 data station. Analytical gas chromatography (GLC) was performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with a HP 3396A integrator or a Perkin-Elmer 3920 gas chromatograph equipped with a Hewlett-Packard 3393A integrator, using columns packed with 3% OV-17 or 3% Dexsil-300. Column chromatography was performed on Silica gel 60 (230-400 mesh) purchased from Krackeler Scientific. HPLC separation was performed on a Waters 600E multisolvent delivery system equipped with a μ-Porasil column (19 mm x 15 cm). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Toluene, THF and ether were dried over and distilled from sodium/benzophenone ketal. The complexes, $HRh(CO)(PPh_3)_3$ and $Co_2(CO)_8$, were obtained from Strem Chemicals, Inc. and used as received. Catalyst complexes, $Rh_4(CO)_{12}$,[14] $Co_2Rh_2(CO)_{12}$,[15] and $(^tBuNC)_4RhCo(CO)_4$[11] were prepared according to the literature methods. All alkynes and hydrosilanes were purchased from Aldrich Chemical Co., Inc or Lancaster Chemicals, and distilled under nitrogen and stored over molecular sieves. Rhodium complexes, $RhCl(PPh_3)_3$ and $Rh(acac)(CO)_2$, were obtained from Aldrich Chemical Co., and Mitsubishi Kasei Corp., respectively, and used as received.

General procedure for silylformylation. *(A) Reaction under ambient pressure of carbon monoxide.* In a 50 mL Schlenk tube connected to an atmospheric pressure of carbon monoxide line, a catalyst (4.0×10^{-3} mmol) in 6 mL or 15 mL of toluene is placed, and 1-hexyne (4.0 mmol) and a hydrosilane (4.5 mmol) are added via syringe. The mixture is stirred at 25°C for 24 h. Then, the reaction mixture is submitted to GLC analysis. After the removal of the solvent, the reaction mixture is also analyzed by ^1H NMR. Silylformylation product (**1**), hydrosilylation product (**2**), and silylcarbocyclization product (**3**) are isolated by bulb-to-bulb distillation or column chromatography on silica gel using hexane-EtOAc as the eluant. *(B) Reaction under 10 atm of carbon monoxide.* A 50 mL Pyrex reaction vessel containing the catalyst, 1-hexyne and a hydrosilane [the same scale as described for (A)] is placed in a 300 mL stainless steel autoclave. The reaction is run at 25°C and 10 atm of carbon monoxide with stirring for 24 h. Carbon monoxide is released and the reaction mixture is submitted to GLC analysis. ^1H NMR analysis is also carried out after the removal of the solvent. Products, **1**, **2**, and **3** are isolated by bulb-to-bulb distillation or column chromatography on silica gel using hexane-EtOAc as the eluant.

(*Z*)-Dimethylphenylsilyl-2-formyl-1-hexene (1a): ^1H NMR ($CDCl_3$) δ 0.51 (s, 6H), 0.91 (t, J = 7.1 Hz, 3H); 1.26-1.45 (m, 4H), 2.30 (t, J = 7.2 Hz, 2H), 6.93 (s, 1H), 7.35-7 41/7.50-7.54 (m, 5H), 9.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -0.08, 13.91, 22.45, 30.53, 31.51, 128.16, 129.46, 133.51, 149.09, 157.16, 193.39. Anal. Calcd for $C_{15}H_{22}OSi$: H, 73.11; H, 9.00. Found: C, 72.93; H, 9.10.

(*Z*)-1-Dimethylethylsilyl-2-formyl-1-hexene (1b): ^1H NMR ($CDCl_3$) δ 0.22 (s, 6H), 0.68 (q, J = 7.9 Hz, 2H), 0.89 (t, J = 7.9Hz, 3H), 0.96 (t, J = 7.8 Hz, 3H), 1.26-1.43 (m, 4H), 2.27 (t, J = 7.4Hz, 2H), 6.79

(s, 1H), 9.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -1.16, 7.32, 8.91, 13.92, 22.40, 30.60, 31.46, 151.06, 156.77, 193.55. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.59; H, 11.18. Found: C, 66.52; H, 11.28.

(*Z*)-1-Triethylsilyl-2-formyl-1-hexene (1c): ^1H NMR ($CDCl_3$) δ 0.71 (q, 6H, J = 7.5 Hz), 0.87-1.02 (m, 12H), 1.26-1.42 (m, 4H), 2.30 (t, J = 7.2 Hz, 2H), 6.75 (s, 1H), 9.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 5.39, 7.41, 13.89, 22.37, 30.73, 31.56, 149.05, 157.72, 193.81. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.71; H, 11.45.

(*Z*)-1-Trimethoxysilyl-2-formyl-1-hexene (1d): ^1H NMR ($CDCl_3$) δ 0.91 (t, J =7.2 Hz, 3H), 1.25-1.50 (m, 4H), 2.29 (t, J = 7.0 Hz, 2H), 3.48 (s, 9H), 6.29 (s, 1H), 9.93 (s, 1H). Anal. Calcd for $C_{10}H_{20}O_4Si$: C, 51.69; H, 8.68. Found: C, 51.59; H, 8.86.

(*Z*)-1-Triphenylsilyl-2-formyl-1-hexene (1e): ^1H NMR ($CDCl_3$) δ 0.61 (t, J = 6.5 Hz, 3H), 1.45 (m, 2H), 1.55 (m, 2H), 2.47 (t, J = 7.15 Hz, 2H), 7.4 (s, 1H), 7.5-7.8 (m, 15H), 9.75 (s, 1H). GC-MS (m/e) (%) 370 (M^+, 15), 327 (15), 313 (70), 293 (100), 259 (20), 251 (75), 199 (60), 181 (60), 155 (13), 129 (25), 105 (50), 77 (12). Anal. Calcd for $C_{25}H_{26}OSi$: C, 81.03; H, 7.07. Found: C, 80.86; H, 7.25.

(*Z*)-1-Diphenylmethylsilyl-2-formyl-1-hexene (1f): ^1H NMR($CDCl_3$) δ 0.88 (bs, 6H), 1.02 (t, J = 7.2Hz, 3H), 1.45 (m, 2H), 1.57 (m, 2H), 2.48 (t, J = 7.5 Hz, 2H), 7.45 (m, 6H), 7.65 (m, 4H), 9.84 (s, 1H). ^{13}C δ -1.00, -1.05, 13.82, 22.38, 30.55, 31.61, 128.11, 129.61, 134.33, 135.97, 146.32, 158.17, 193.05. IR (neat) 1682 (νC=O), 1587 cm^{-1}. Anal. Calcd. for $C_{20}H_{24}OSi$: C, 77.87, H,7.84. Found: C, 77.90, H, 7.81.

2,5-Bis(n-butyl)-3-dimethylphenylsilylcyclopent-2-en-1-one (3a): ^1H NMR($CDCl_3$) δ 2.75 (dd, J = 6.75, 17.5Hz, 1H) . GC-MS (m/e) (%) 328 (M^+, 1), 313 (M^+-CH_3, 50), 272 (M^+-C_4H_9), 250 (25), 221 (20), 207 (28), 194 (40), 152 (100), 135 (30), 121 (10), 107 (10), 91 (10), 75 (12). HRMS (m/e) Calcd. for $C_{21}H_{32}OSi$ 328.224. Found: 328.2218.

2,5-Bis(n-butyl)-3-dimethylethylsilylcyclopent-2-en-1-one (3b): ^1H NMR ($CDCl_3$) δ 0.19 (s, 6H), 0.69 (q, J = 6.7 Hz, 2H), 0.89 (t, J = 7 4 Hz, 3H), 0.95 (t, J = 7.21 Hz, 3H), 1.29 (m, 5H), 1.40 (m, 2H), 1.55 (m, 2H), 1.78 (m, 1H), 2.22 (dd, J = 2.95 Hz, 18.9 Hz, 1H), 2.28 (m, 1H), 2.48 (t, J = 8.19 Hz, 2H), 2.74 (dd, J = 7.3, 18.9 Hz, 1H). Anal. Calcd for $C_{17}H_{32}OSi$: C, 72.79, H, 11.50. Found: C, 72.66, H, 11.26.

2,5-Bis(n-butyl)-3-triethylsilylcyclopent-2-en-1-one (3c): ^1H NMR ($CDCl_3$) δ 0.77 (m, 6H), 0.82-1.02 (m, 15H), 1.29 (m, 5H), 1.39 (m, 2H), 1.58 (m, 2H), 1.78 (m, 1H), 2.25 (dd, J = 2.9, 19.0 Hz, 1H), 2.29 (m, 1H), 2.48 (t, J = 7.5 Hz, 2H), 2.76 (dd, J = 7.5, 19.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 3.5, 7.5, 14.0, 22.7, 23.0, 29.6, 30.8, 31.43, 34.0, 39.6, 46.5, 136.2 (=C-Si), 189.2 (=C-CO), 216.4 (CO); FT-IR (neat) 1688 (νCO), 1584 (νC=C) cm^{-1}; GC-MS (m/e) (%) 308 (M^+, 1) 281(1), 280(23), 279 (M^+-29, 100),

252(5), 249(8), 180(5), 103(5), 87(5), 75(15), 59(10). Anal Calcd. for $C_{19}H_{36}OSi$: C, 73.89; H, 11.76. Found: C, 73.73, H, 11.66.

(Z)-1-Triethylsilyl-2-formyl-4-oxa-1,6-heptadiene (5a): ^1H NMR ($CDCl_3$) δ 0.74 (q, J = 7.8 Hz, 6H), 0.97 (t, J = 7.8 Hz, 9H), 4.02 (dt, J = 5.6, 1.3 Hz, 2H), 4.21 (d, J = 1.7 Hz, 2H), 5.28 (m, 2H), 5.92 (m, 1H), 7.09 (t, J = 1.6 Hz, 1H), 9.78 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 5.26, 7.37, 67.86, 71.82, 117.14, 134.43, 148.36, 152.93, 192.77. GC-MS m/e (%) 211 (9.6), 169 (8), 155 (100), 141 (7), 127 (30), 113 (9), 99 (10), 87 (9), 75 (17). Anal. Calcd. for $C_{13}H_{24}O_2Si$: C, 64.95; H, 10.06. Found: C, 64.82; H, 9.92.

(Z)-1-Triethylsilyl-2-formyl-6-methyl-4-oxa-1,6-heptadiene (5b-1): ^1H NMR ($CDCl_3$) δ 0.74 (q, J= 8.1, 15.8 Hz, 6H), 0.97 (t, J= 8.1, 15.8 Hz, 9H), 1.74 (s, 3H), 3.92 (s, 1H), 4.18 (d, J= 1.6 Hz, 1H), 4.90 (s, 1H), 4.95 (s, 1H), 7.09 (s, 1H), 9,79 (s, 1H). ^{13}C NMR ($CDCl_3$) d 5.37, 7.40, 19.41, 67.84, 74.79, 96.17, 112.23, 141.99, 148.15, 192.66. Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30. Found: C, 65.90; H, 10.50.

(Z)-1-Dimethylphenylsilyl-2-formyl-6-methyl-4-oxa-1,6-heptadiene (5b-2): ^1H NMR ($CDCl_3$) δ 0.63 (s, 6H), 1.85 (s, 3H), 4.05 (s, 1H), 4.28 (d, J = 1.4 Hz, 1H), 5.01 (s, 1H), 5.08 (s, 1H), 7.48 (s, 1H), 9.88 (s, 1H). Anal. Calcd. for $C_{16}H_{22}O_2Si$: C, 70.03; H, 8.08. Found: C, 69.92; H, 8.20.

(Z,Z)-1,8-Bis(triethylsilyl)-2,7-bis(formyl)-1,7-octadiene (5c): ^1H NMR ($CDCl_3$) δ 0.67(q, J = 7.8 Hz, 12H), 0.93 (t, J = 7.8 Hz, 18H), 1.40 (bs, 4H), 2.30 (bs, 4H), 6.73 (s, 2H), 9.73 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 5.35, 7.32, 28.08, 31.62, 148.97, 157.35, 193.39, 193.36. Anal. Calcd for $C_{22}H_{42}O_2Si$: C, 66.94; H, 10.72. Found: C, 67.12; H, 10.85.

(Z)-5-Cyano-1-dimethylphenylsilyl-2-formyl-1-hexene (5d): ^1H NMR ($CDCl_3$) δ 0.50 (s, 6H), 1.75 (dt, J = 7.6, 7.1 Hz, 2H), 2.25 (t, J = 7.1 Hz, 2H), 2.45 (t, J = 7.6 Hz, 2H), 7.10 (s, 1H), 7.35 (m, 3H), 7.50 (m, 4H), 9.74 (s, 1H). ^{13}C NMR ($CDCl_3$) δ -0.20, 16.50, 24.80, 32.00, 119.82, 127.90, 129.20, 133.40, 137.85, 152.00, 154.15, 192.50. IR (neat) 2247 (νC≡N) , 1735, 1686 (νC=O), 1591 cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_4Si$: C, 69.99; H, 7.44, N, 5.44 Found: C, 69.81; H, 7.35, N, 5.40.

5-[(2-Dimethylphenylsilyl-1-formyl)ethenyl]pyrrolidinone (7): A dry 25 ml Schlenk flask equipped with a septum port and a magnetic stirring bar containing $Rh(acac)(CO)_2$ (13.5 mg, 0.052 mmol) was evacuated and thoroughly flushed with carbon monoxide. To the flask was added sequentially dry toluene (10 mL) and dimethylphenylsilane (1.21 mL, 7.87 mmol) via syringe. The mixture was stirred at room temperature for 10 min and added to **6** (715 mg, 6.56 mmol) in a 25 mL round bottomed flask via syringe under nitrogen. The reaction vessel was placed in autoclave, charged with carbon monoxide (20 atm), and the mixture was stirred at room temperature for 24 h. Then, the pressure was released and the solvent was removed under reduced pressure to give an orange oil, which was purified by chromatography on silica gel (EtOAc/hexanes = 4 / 1) to give **7** (1.74 g, 97%) as a white solid: m.p. 69-70°C; IR ($CHCl_3$) 3220, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.53 (s, 6H), 1.68-1.75 (m, 1H), 2.31 (t, J = 8.0 Hz, 2H), 2.46-2.55 (m, 1H), 4.62-4.66 (m, 1H), 6.42 (br.s, NH), 7.10 (s, 1H),

7.35-7.50 (m, 5H), 9.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 0.43, 28.08, 29.41, 53.56, 60.27, 128.27, 129.72, 133.43, 146.84, 155.96, 179.81, 192.01. Anal. Calcd. for $C_{15}H_{19}NO_2Si$: C, 65.91; H, 7.01; N, 5.13. Found: C, 65.80; H, 6.97; N, 4.92.

5-(1-Hydroxymethyl-2-dimethylphenylsilylethenyl)-2-pyrrolidinone: To a solution of **7** (0.90 g, 3.3 mmol) in ethanol-water (vol.: 1 / 1, 10 mL) was added $NaBH_4$ (0.12 g, 3.3 mmol) at 0 °C. The suspension was stirred overnight. The reaction mixture was extracted with ethyl acetate (40 mL x 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give the product (0.90 g, quant.) as a colorless oil: IR ($CHCl_3$) 3260, 1689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.33 (s, 6H), 1.86-2.02 (m, 2H), 1.90 (s, 1H), 2.30-2.43 (m, 2H), 4.02 (d, J = 12.6 Hz, 1H), 4.36 (t, J = 6.7 Hz, 1H), 5.81 (s, 1H), 6.50 (br s, 1H), 7.35-7.62 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.93, 27.94, 29.90, 58.36, 62.30, 124.22, 127.96, 129.10, 133.45, 139.00, 157.99, 179.80. Anal. Calcd. for $C_{15}H_{21}NO_2Si$: C, 65.42; H, 7.69; N, 5.09. Found: C, 65.36; H, 7.66; N, 5.02.

5-(1-Hydroxymethyl)-2-pyrrolidinone: To a solution of 5-(1-hydroxymethyl-2-dimethylphenylsilyl-ethenyl)-2-pyrrolidinone (180 mg, 0.65 mmol) in wet acetonitrile (2% water, 8 mL) was added freshly prepared *p*-toluenesulfinic acid (30 mg, 0.19 mmol). The mixture was stirred under reflux for 6 hr under nitrogen atmosphere. The solvent was removed under reduced pressure to give an oily residue which was chromatographed on silica gel (EtOAc/methanol = 5/1) to give the product (69 mg, 75%) as a white solid: m.p.. 99-100 °C; IR ($CDCl_3$) 3430, 3155, 1691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90-1.98 (m, 1H), 2.32-2.43 (m, 3H), 2.97 (t, J = 5.7 Hz, 1H), 4.14-4.18 (m, 2H), 4.29-4.34 (m, 1H), 5.11 (s, 1H), 5.16 (s, 1H), 6.87 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.49, 29.86, 56.18, 63.48, 111.04, 149.00, 178.61. Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.34; H, 7.65; N, 9.75.

5-(1-*tert*-Butyldimethylsiloxymethylethenyl)-2-pyrrolidinone (8): To a solution of 5-(1-hydroxymethyl)-2-pyrrolidinone (99 mg, 0.7 mmol) in DMF (1 mL) were added *tert*-butyldimethylsilyl chloride (116 mg, 0.77 mmol) and imidazole (119 mg, 1.75 mmol) at room temperature under nitrogen atmosphere. After the reaction mixture was stirred at room temperature for 9 hr, the solvent was removed under reduced pressure to give an oily residue. The residue was dissolved in ethyl acetate and washed with 10 % citric acid. The aqueous layer was extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give **8** (170 mg, 98%) as a colorless oil: IR ($CDCl_3$) 3432, 1693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 6H), 0.86 (s, 9H), 1.85-1.89 (m, 1H), 2.25-2.37 (m, 3H), 4.12 (s, 2H), 4.18-4.21 (m, 1H), 5.03 (s, 1H), 5.07 (s, 1H), 6.94 (br s, 1H), ^{13}C NMR ($CDCl_3$) δ -5.54, 18.19, 25.78, 27.56, 29.73, 55.83, 63.94, 109.45, 148.70, 178.38. Anal. Calcd. for $C_{13}H_{25}NO_2Si$: C, 61.13; H, 9.87; N, 5.48. Found: C, 61.33; H, 9.76; N, 5.37.

4-*tert*-Butyldimethylsiloxymethyl-2-ethoxy-1-azabicyclo[3.3.0]octane-8-one (9): A 25 mL round bottomed flask containing a solution of **8** (62 mg, 0.26 mmol) and $HRh(CO)(PPh_3)_3$ (2.4 mg, 2.6 X 10^{-3} mmol) in triethyl orthoformate (2 mL) was placed in a 300 mL stainless steel autoclave. The reaction mixture was stirred at 100 °C for 24 hr under carbon monoxide (50 atm) and hydrogen gas (50 atm). The gases were released, and

the solvent removed under reduced pressure to give a dark brown residue, which was chromatographed on silica gel (EtOAc/hexanes = 3/1) to give **9** (*syn /anti* = 2/1, 59 mg, 72%) as a colorless oil: IR (neat) 1682, 1086 cm^{-1}, ^1H NMR ($CDCl_3$) δ [0.035 (s), 0.043 (s)] (6H), [0.88 (s), 0.89 (s)] (9H), [1.180 (t, J = 7.1 Hz), 1.184 (t, J = 7.1 Hz)] (3H), 1.56-2.12 (m, 4H), 2.30-2.48 (m, 2H), 2.56-2.69 (m, 1H), 3.48-3.73 (m, 4H), [3.88 (q, J = 7.3 Hz), 4.24 (q, J = 7.4 Hz)] (1H), 5.14-5.22 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -5.60, -5.53, 15.01, 15.58, 18.13, 21.09, 25.78, 25.92, 33.69, 33.88, 37.44, 41.00, 48.79, 61.50, 62.56, 63.94, 64.28, 64.45, 83.92, 83.98, 176.25, 176.57. Anal. Calcd. for $C_{16}H_{31}NO_3Si$: C, 61.30; H, 9.97; N, 4.47. Found: C, 61.13; H, 9.97 N, 4.48.

The stereoisomers were separated by preparative scale HPLC on silica gel (3% 2-propanol in hexanes).

9a (*Syn* isomer): ^1H NMR ($CDCl_3$) δ 0.031 (s, 6H), 0.87 (s, 9H), 1.17 (t, J = 7.1 Hz, 3H), 1.97-2.14 (m, 4H), 2.46-2.64 (m, 2H), 2.67-2.73 (m, 1H), 3.48-3.67 (m, 4H), 4.28 (q, J = 7.6 Hz, 1H), 5.19 (dd, J = 3.3, 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -5.58, 14.94, 18.18, 21.41, 25.84, 34.06, 37.56, 40.85, 61.95, 62.60, 64.30, 83.85, 177.68.

9b (*Anti* isomer); ^1H NMR ($CDCl_3$) δ 0.043 (s, 6H), 089 (s, 9H), 1.18 (t, J = 7.1 Hz, 3H), 1.61-1.72 (m, 1H), 1.77-1.97 (m, 2H), 2.30-2.48 (m, 3H), 2.56-2.69 (m, 1H), 3.50-3.75 (m, 4H), 3.86 (q, J = 7.3 Hz, 1H), 5.20 (dd, J = 4.5, 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -5.49, 15.04, 18.16, 25.84, 26.00, 33.68, 37.52, 48.84, 63.86, 64.22, 64.51, 84.05, 176.57.

(±)-Isoretronecanol:[16a,b,c,d] To a solution of **9a** (135 mg, 0.43 mmol) in THF (5 mL) was added 1M tetrabutylammonium fluoride in THF (0.86 mL, 0.86 mmol) at 0 °C. The reaction mixture was stirred at 0°C for 1 hr and at room temperature for 1 hr. The solvent was removed at reduced pressure to give an oily residue which was chromatographed on silica gel pretreated with triethylamine (EtOAc –> EtOAc/methanol = 5/1) to give 4-hydroxymethyl-2-ethoxy-1-azabicyclo-[3.3.0]octane-8-one (*syn* isomer, 82.1 mg, 96%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.19 (t, J = 7.1 Hz, 3H), 1.75-1.80 (m, 1H), 1.98-2.17 (m, 3H), 2.36-2.46 (m, 2H), 2.54-2.66 (m, 2H), 3.55-3.74 (m, 4H), 4.27 (q, J = 7.4 Hz, 1H), 5.18-5.25 (m, 1H).

To a suspension of $LiAlH_4$ (45 mg, 1.2 mmol) in THF (4 mL) was added a solution of *syn*-4-hydroxymethyl-2-ethoxy-1-azabicyclo[3.3.0]octane-8-one (80 mg, 0.40 mmol) in THF at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 hr and refluxed for 15 hr. To the reaction mixture was carefully added water (0.045 mL), 15 % aqueous NaOH (0.045 mL), and water (0.14 mL) at 0 °C. After filtration of the resulting suspension, the solid residue was washed with ether. The combined filtrate was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give (±)-isoretronecanol (37 mg, 65%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.40-2.10 (m, 6H), 2.40-2.65 (m, 3H), 2.90-3.15 (m, 3H), 3.38-3.72 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 25.91, 26.52, 27.29, 44.19, 53 99, 55.55, 63.37, 66.27; MS-FAB (m/e) 142 (M+1). These spectral data matched with the literature values.[16a,b,c,d]

(±)-Trachelanthamidine:[16b,c] Trachelanthamidine was prepared in the same manner as that for (±)-isoretronecanol; **9b** (93 mg, 0.30 mmol) was converted to 4-hydroxymethyl-2-ethoxy-1-azabicyclo[3.3.0]octane-8-one (*anti* isomer, 57 mg, 96%): ^1H NMR ($CDCl_3$) δ 1.20 (t, J = 7.1 Hz, 3H), 1.75-1.80 (m, 2H), 1.97-2.04 (m, 1H), 2.36-2.51 (m, 4H), 2.54-2.72 (m, 1H), 3.55-3.75 (m, 4H), 3.90 (q, J = 7.3 Hz, 1H), 5.21 (dd, J = 3.9, 6.6 Hz, 1H).

The *anti* -isomer thus obtained (13 mg, 0.065 mmol) was then converted to (±)-trachelanthamidine (6.5 mg, 70%): ^{1}H NMR ($CDCl_3$) δ 1.35-2.12 (m, 6H), 2.53-2.71 (m, 1H), 2.79-3.14 (m, 4H), 3.60-3.83 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.6, 30.0, 31.8, 48.0, 54.4, 54.7, 65.0, 68.0; MS (m/e) (%) 141 (M^+, 33), 140 (20), 124 (20), 83 (100). These spectral data matched with the literature values.[16b,c]

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