**Intramolecular Endo-Dig Hydrosilylation Catalyzed by Ruthenium:
Evidence for a New Mechanistic Pathway**

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Supplemental Information

All reactions were performed under argon atmosphere unless otherwise indicated. Methylene chloride (CH_2Cl_2) was purified on an alumina column solvent purification system. Dimethylformamide (DMF) was purchased from Aldrich and used as received. Pyridine was distilled from calcium hydride. All other reagents were purchased and used as received. $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ was synthesized as described by Schenk.¹

Flash chromatography was performed with EM Science silica gel (0.040-0.063 μm grade) or 200 mesh Florisil (Aldrich). Analytical thin layer chromatography was performed with 0.2-mm coated commercial silica gel plates (E. Merck, DC Plastifolien, kieselgel 60 F₂₅₄).

Proton and broad-band decoupled ^{13}C nuclear magnetic resonance data were acquired on a Varian GEM-300, Mercury-400 or Unity Inova-500 spectrometer as indicated. Chemical shifts are reported in ppm relative to TMS or C_6D_6 as an internal standard.

Infrared (IR) data were recorded in sodium chloride plates on PerkinElmer Paragon 500 FT-IR spectrometer. Gas chromatographic and GC-MS analyses were performed on a Hewlett-Packard 6890 Series gas chromatograph with attached HP 5973 Series mass detection.

General Procedure for Intramolecular Hydrosilylation

(±)-(1R,2S)-(2,2-Dimethyl-3-(3-phenyl-propyl)-4a,5,6,7,8,8a-hexahydro-2H-benzo[e][1,2]oxasiline

A round-bottomed flask [Note: it is important to use a rather large flask to allow removal of the excess silane under vacuum without bumping] was charged with (±)-(1*S*,2*S*)-2-(5-phenyl-1-propynyl)-cyclohexanol (123 μ L, 0.50 mmol) under Ar at rt. To the neat alcohol was added 1,1,3,3-tetramethyldisilazane (270 μ L, 1.5 mmol) and the flask heated to 50 °C for 2 hr. Next, the flask was cooled to ambient temperature and placed under vacuum (c.a. 1 mmHg) for 45 min to remove the excess silazane. An Ar atmosphere was then re-introduced and the residue taken up in CH₂Cl₂ (1.0 mL). The flask was cooled to 0 °C and solid [Cp^{*}Ru(MeCN)₃]PF₆ (2.5 mg, 0.005 mmol) was added to the solution. The flask was allowed to warm to rt, and after 15 min, the solution was diluted with ether (5 mL) and filtered through a short plug of florisil, washing with additional ether (15 mL). The volatile components were then removed under reduced pressure and the resulting residue purified on a florisil column (eluent 30:1 pet. ether: ether) to afford 130 mg (85%) of the desired silacycle as a colorless oil. NMR analysis of all products (including cross-coupling product) shown indicated complete isomeric purity. A conservative estimate of $\geq 97:3$ isomeric purity for all products is in line with the uncertainty in NMR measurements.

¹H NMR (300 MHz, CDCl₃) δ 7.28 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.15-7.19 (m, 3H), 6.03 (s, 1H), 3.38 (ddd, *J* = 10.0, 10.0, 3.9 Hz, 1H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.10 (t, *J* = 7.3 Hz, 2H), 1.96 (m, 2H), 1.65-1.80 (m, 5H), 1.00-1.42 (m, 4H), 0.19 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 146.2, 142.5, 138.5, 128.4, 128.3, 125.7, 76.0, 44.7, 35.7, 35.0, 34.7, 32.0, 31.2, 25.8, 25.0, -0.7. IR (thin film) 3027 (w), 2930 (s), 2855, 1603 (w), 1496 (w), 1449, 1248, 1064, 948, 882, 828, 785 cm⁻¹. Anal. calc. for C₁₉H₂₈OSi: C, 75.94; H, 9.39; Found: C, 75.82; H, 9.30.

6-Ethyl-2,2,3-trimethyl-5,6-dihydro-2H-[1,2]oxasiline

R_f 0.59 (10:1 pet. ether: EtOAc). ¹H NMR (300 MHz, CDCl₃) δ 6.30 (m, 1H), 3.74 (m, 1H), 2.10 (m, 1H), 1.71 (d, *J* = 1.7 Hz, 3H), 1.43-1.62 (m, 2H), 0.92 (d, *J* = 7.4 Hz, 3H), 0.18 (s, 3H), 0.17 (s, 3H). ¹³C NMR (300 MHz, CDCl₃) δ 139.5, 134.8, 73.2, 35.5, 30.6, 20.2, 10.0, -1.8, -1.9. IR (thin film) 2963, 1614, 1440, 1253 cm⁻¹.

3-Heptyl-2,2,7-trimethyl-2,5,6,7-tetrahydro-[1,2]oxasilepine

¹H NMR (500 MHz, CDCl₃) δ 6.22 (t, *J* = 6.3 Hz, 1H), 4.02 (m, 1H), 2.42 (m, 1H), 2.14 (m, 1H), 2.05 (m, 1H), 1.99 (m, 1H), 1.74 (ddt, *J* = 14.2, 10.7, 3.7 Hz, 1H), 1.60 (m, 1H), 1.22-1.32 (m, 16H), 1.20 (d, *J* = 6.4 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.24 (s, 3H), 0.18 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 142.6, 140.4, 68.7, 36.9, 36.6, 31.9, 30.2, 29.6 (2), 29.5 (2), 29.3, 26.7, 23.9, 22.7, 14.1, 0.54, -1.0. Anal. calc. for C₁₇H₃₄OSi: C, 72.27; H, 12.13; Found: C, 72.37; H, 11.96.

6,6,7-Trimethyl-3,4,4a,6,9,9a-hexahydro-1H-5-oxa-6-sila-benzocyclohepten-2-one 2-ethylene ketal

R_f 0.48 (4:1 pet. ether: EtOAc). ¹H NMR (300 MHz, CDCl₃) δ 6.23 (m, 1H), 3.43-3.57 (m, 5H), 1.88-2.28 (m, 5H), 1.71 (s, 3H), 1.33-1.68 (m, 4H), 1.32 (s, 3H), 0.24 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 141.2, 138.2, 108.6, 78.8, 64.33, 64.28, 43.1, 42.0, 37.0, 33.7, 33.1, 22.3, 0.85, -1.1. IR (thin film) 2946 (s), 1622 (w), 1145, 1250, 1148 (s), 1119 (s), 1078 (s), 932, 825, 779 cm⁻¹. HRMS—EI (*m/z*): [M]⁺ calcd for C₁₄H₂₄O₃Si: 268.1495; found: 268.1496.

Ethyl 2,2-Dimethyl-3-pentyl-5,6-dihydro-2H-[1,2]oxasiline-6-carboxylate

R_f 0.29 (10:1 pet. ether: EtOAc). ¹H NMR (400 MHz, C₆D₆) δ 6.16 (m, 1H), 4.52 (dd, *J* = 7.5, 4.3 Hz, 1H), 3.94 (q, *J* = 7.2 Hz, 2H), 2.51 (m, 1H), 2.39 (m, 1H), 2.02 (m, 2H), 1.18-1.37 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.39 (s, 3H), 0.21 (s, 3H). ¹³C NMR (100 MHz, C₆D₆) δ 172.3, 141.4, 137.1, 71.3, 60.6, 35.7, 32.9, 31.9, 29.4, 22.8, 14.3, 14.2, 0.1, -0.3. IR (thin film) 2958, 2927, 1754, 1733 (w), 1251, 1188, 832, 784 cm⁻¹. Anal. calc. for C₁₄H₂₆O₃Si: C, 62.18; H, 9.69; Found: C, 62.28; H, 9.53.

3-Benzoyloxymethyl-2,2,5,5,7-pentamethyl-2,5,6,7-tetrahydro-[1,2]oxasilepine

R_f 0.41 (10:1 pet. ether: ether). ¹H NMR (400 MHz, C₆D₆) δ 7.31 (d, *J* = 6.9 Hz, 2H), 7.18 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.13 (d, *J* = 1.2 Hz, 1H), 4.33 (d, *J* = 11.9 Hz, 1H), 4.27 (q, *J* = 11.9 Hz, 1H), 4.21 (m, 1H), 4.13 (dd, *J* = 10.9, 1.5 Hz, 1H), 3.88 (dd, *J* = 10.9, 0.6 Hz, 1H), 1.98 (dd, *J* = 15.3, 10.8 Hz, 1H), 1.25 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.04 (s, 3H), 0.96 (s, 3H), 0.48 (s, 3H), 0.37 (s, 3H). ¹³C NMR (100 MHz, C₆D₆) δ 154.1, 139.1, 135.1, 128.5, 127.9, 127.6, 72.0, 67.3, 50.5, 37.4, 34.0, 27.2, 25.8, 3.7, -0.4. IR (thin film) 2962, 1618 (w), 1454, 1371, 1248, 1172, 1084, 830, 784 cm⁻¹. Anal. calc. for C₁₈H₂₈O₂Si: C, 71.00; H, 9.27; Found: C, 70.87; H, 9.12.

6-Benzoyloxymethyl-3-(tert-butyldimethylsilyloxymethyl)-2,2-dimethyl-5,6-dihydro-2H-[1,2]oxasiline

R_f 0.61 (80:20:1 pet. ether: EtOAc: MeOH). ¹H NMR (300 MHz, C₆D₆) δ 7.08-7.28 (m, 5H), 6.38 (m, 1H), 4.36 (d, *J* = 1.7 Hz, 2H), 4.22 (s, 2H), 4.17 (m, 1H), 3.57 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.38 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.19 (m, 2H), 0.96 (s, 9H), 0.34 (s, 3H), 0.33 (s, 3H), 0.04 (s, 6H). ¹³C NMR (75 MHz, C₆D₆) δ 140.5, 139.2, 137.7, 128.5, 127.8, 127.6, 75.1, 73.4, 70.8, 67.5, 33.0, 26.1, 18.5, -0.1, -0.2, -5.3. IR (thin film) 2957, 2857, 1615 (w), 1472, 1362, 1252, 1105, 835 cm⁻¹. Anal. calc. for C₂₁H₃₆O₃Si₂: C, 64.23; H, 9.24; Found: C, 64.13; H, 9.05.

2,2-Dimethyl-3-phenyl-1-oxa-2-sila-spiro[5.5]undec-3-ene

R_f 0.54 (20:1 pet. ether: ether). ¹H NMR (400 MHz, C₆D₆) δ 7.03-7.22 (m, 5H), 6.53 (t, *J* = 5.0 Hz, 1H), 2.13 (d, *J* = 5.0 Hz, 2H), 1.71-1.85 (m, 4H), 1.52 (m, 1H), 1.35 (m, 2H), 1.10-1.26 (m, 3H), 0.29 (s, 6H). ¹³C NMR (100 MHz, C₆D₆) δ 143.3, 141.5, 140.2, 128.8, 126.7, 126.5, 73.4, 41.5, 38.5, 26.4, 22.3, 1.3. IR (thin film) 3026 (w), 2933, 2859, 1596, 1491, 1444, 1251, 1010 cm⁻¹. Anal. calc. for C₁₇H₂₄OSi: C, 74.94; H, 8.88; Found: C, 74.76; H, 8.93.

2-Dimethylsilanyloxy-6,6,7-trimethyl-1,2,3,4,4a,6,9,9a-octahydro-5-oxa-6-sila-benzocycloheptene

¹H NMR (400 MHz, C₆D₆) δ 6.28 (m, 1H), 4.84 (sep, *J* = 2.7 Hz, 1H), 3.75 (m, 1H), 3.46 (ddd, *J* = 11.1, 11.1, 4.2 Hz, 1H), 2.34 (m, 1H), 2.19 (m, 1H), 2.05 (m, 1H), 1.99 (dd, *J* = 16.8, 7.6 Hz, 1H), 1.89 (m, 1H), 1.73 (s, 3H), 1.68 (m, 1H), 1.59 (dddd, *J* = 13.1, 3.4, 3.4, 3.4 Hz, 1H), 1.12 (m, 1H), 0.96 (ddd, *J* = 13.1, 13.1, 2.2 Hz, 1H), 0.87 (m, 1H), 0.36 (s, 3H), 0.27 (s, 3H), 0.11 (d, *J* = 2.7 Hz, 3H), 0.10 (d, *J* = 2.7 Hz, 3H). ¹³C NMR (100 MHz, C₆D₆) δ 141.7, 138.1, 79.6, 68.0, 40.7, 39.8, 37.4, 31.9, 30.3, 22.4, 0.9, -1.07, -1.13. IR (thin film) 2943, 2109, 1622 (w), 1444,

1252, 1124, 1037, 897 cm^{-1} . HRMS—EI (m/z): $[M]^+$ calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}_2$: 284.1628; found: 284.1624.

Vinylsilane oxidation:

*Synthesis of ($\pm$)-(1*R*,2*S*)-1-acetyloxy-2-(2-oxo-5-phenylpentyl)cyclohexane*

The vinyl silacycle (125 mg, 0.416 mmol) was taken up in DMF (4 mL) under air at rt. Solid KHF_2 (98 mg, 1.25 mmol) was added, followed by acetic anhydride (1.2 mL) and 30% aq. H_2O_2 (1 mL). After stirring for 14 hr at rt, sat. aq. NaHCO_3 (40 mL) was added and the mixture stirred for 10 min until bubbling ceased. The mixture was extracted with EtOAc (3 x 15 mL) and the organic extracts washed with brine (15 mL), dried over Na_2SO_4 , and concentrated *in vacuo*. The crude alcohol was then taken up in CH_2Cl_2 (2 mL) and treated with pyridine (134 μL , 1.66 mmol). After cooling to 0 $^\circ\text{C}$, acetyl chloride (59 μL , 0.83 mmol) was then added and the reaction mixture allowed to stir for 15 minutes. Sat. aq. Na_2SO_4 (15 mL) is then added, and the mixture extracted with EtOAc (3 x 15 mL). The extracts were washed with 0.5 M HCl (10 mL), sat. aq. Na_2SO_4 (10 mL), and brine (10 mL), then dried over Na_2SO_4 , and concentrated *in vacuo*. The crude product was then purified on silica gel (20:1, then 10:1 pet. ether: EtOAc) which provided 78 mg (62%) of the desired acetoxo ketone as a colorless oil.

R_f 0.44 (80:20:1 pet. ether: EtOAc: MeOH). ^1H NMR (500 MHz, CDCl_3) δ 7.27-7.30 (m, 2H), 7.16-7.21 (m, 3H), 4.43 (ddd, $J = 10.3, 10.3, 4.4$ Hz, 1H), 2.61 (t, $J = 6.6$ Hz, 2H), 2.48 (dd, $J = 16.2, 4.4$ Hz, 1H), 2.39 (t, $J = 7.4$ Hz, 2H), 2.16 (dd, $J = 16.2, 8.3$ Hz, 1H), 2.06 (m, 1H), 1.99 (s, 3H), 1.98 (m, 1H), 1.89 (m, 2H), 1.80 (m, 1H), 1.74 (m, 1H), 1.57-1.64 (m, 2H), 1.20-1.35 (m, 3H), 0.99 (dddd, $J = 12.2, 12.2, 12.2, 2.9$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 209.9, 170.8, 141.6, 128.44, 128.38, 126.0, 76.5, 46.2, 42.5, 38.2, 35.1, 31.8, 31.3, 25.2, 25.0, 24.5, 21.2. IR (thin film) 2935, 2859, 1732 (s), 1732 (s), 1713 (s), 1452, 1372, 1242 (s), 1030 cm^{-1} . Anal. calc. for $\text{C}_{19}\text{H}_{26}\text{O}_3$: C, 75.46; H, 8.67; Found: C, 75.29; H, 8.53.

Palladium-catalyzed Cross-coupling

Synthesis of (Z)-6-Phenyl-5-hepten-1-ol

5-Heptyne-2-ol (100 mg, 0.892 mmol) was subjected to the standard intramolecular hydrosilylation conditions above to afford 145 mg (96%) of the desired silacyle (145 mg, 96%) contaminated with small amounts of polymeric material after filtration through a small plug of Florisil. This material was used directly in the next reaction (^1H NMR (400 MHz, C_6D_6) δ 6.23 (m, 1H), 3.96 (m, 1H), 2.28 (m, 1H), 2.02 (m, 1H), 1.71 (d, $J = 1.5$ Hz, 3H), 1.54 (m, 2H), 1.15 (d, $J = 6.1$ Hz, 3H), 0.27 (s, 3H), 0.20 (s, 3H)).

The silacyle (35 mg, 0.20 mmol) was taken up in THF (0.40 mL) at rt under an Ar atmosphere. The solution was treated sequentially with iodobenzene (35 μL , 0.30 mmol) and then TBAF (0.40 mL, 0.40 mmol, 1.0 M in THF). Solid $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (9.5 mg, 0.005 mmol) was then introduced and the solution was brought to 55 $^\circ\text{C}$. After stirring for 6 hr, the solution was allowed to cool, and was then filtered through a short plug of silica, eluting with pure ether, and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (10:1, then 4:1 pet. ether: ether) to provide the desired trisubstituted olefin as a pale yellow oil (32.5 mg, 83 %).

^1H NMR (400 MHz, CDCl_3) δ 7.33 (dd, $J = 7.0, 7.0$ Hz, 2H), 7.24 (m, 1H), 7.17 (d, $J = 7.0$ Hz, 2H), 5.46 (td, $J = 7.3, 1.2$ Hz, 1H), 3.73 (m, 1H), 2.06 (m, 2H), 2.02 (s, 3H), 1.48 (m, 2H), 1.30 (br OH, 1H), 1.10 (d, $J = 6.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 136.8, 128.1, 127.9, 126.9, 126.5, 67.6, 39.4, 25.6, 25.4, 23.2. IR (thin film) 3358 (br, OH), 3022 (w), 2967 (s), 2926 (s), 1600 (w), 1435, 1374, 1130, 1080, 763, 701.

Crossover Experiment

5-Acetyloxy-1-pentyne (38 μL , 0.29 mmol) was taken up in CH_2Cl_2 (0.60 mL) at 0 $^\circ\text{C}$ under Ar. The solution was treated with equimolar amounts of $\text{HSi}(n\text{Pr})_3$ (47 μL , 0.23 mmol) and DSiEt_3 (36 μL , 0.23 mmol). The solution was next treated with solid $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ (1.3 mg, 0.0026 mmol) and the reaction vessel allowed to warm to rt. After 20 min, the alkyne was consumed as determined by TLC analysis, and the crude reaction mixture was filtered through a plug of Florisil, washing with ether. The crude solution thus obtained was analyzed directly by GC/MS. Peaks arising from $(n\text{Pr})_3\text{SiH}$ and Et_3SiD were of similar intensity, indicating that, as expected, the two very similar silanes reaction at comparable rates. GC/MS data is given in the figures at the end of the supporting information. Figure S1 shows a GC/MS trace from a typical hydrosilylation without deuterium incorporation with an MS for the major product peak. Figure S2 shows a similar GC/MS, this time demonstrating complete D incorporation upon use of Et_3SiD (note $[\text{M}+1]^+$, no M^+ peaks). Figure S3 shows results from the crossover experiment, with the two silane products clearly separating in the GC. S3 gives an MS for the first peak from hydrosilylation with Et_3SiD without any M^+ . Figure S4 shows the same GC trace, with MS data from the second peak resulting from $(n\text{Pr})_3\text{SiH}$.

Intermolecular Hydrosilylation of Terminal Alkyne Stereochemistry

2-triethylsilyl-5-acetyloxy-1-pentene-d²

5-Acetyloxy-1-pentyne (34 μL , 0.26 mmol) was taken up in CH_2Cl_2 (0.60 mL) at 0 $^\circ\text{C}$ under Ar. The solution was treated with DSiEt_3 (50 μL , 0.31 mmol, Aldrich, 97% D). The solution was next treated with solid $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ (2.6 mg, 0.0052 mmol) and the reaction vessel allowed to warm to rt. After 1 hr, the alkyne was consumed as determined by TLC analysis, and the crude reaction mixture was concentrated and applied directly to a silica gel column (eluent 20:1 pet. ether: ether) to afford the desired selectively deuterated vinylsilane. NMR analysis

indicated full deuterium incorporation at the trans position indicated in the reaction above. Isomeric purity is conservatively estimated at $\geq 97:3$. Relevant ^1H NMR: (300 MHz, CDCl_3) δ 5.65 (s, 1H, (*E*) proton trans to silicon, 1H) 5.33 (s, 1H, (*Z*) proton cis to silicon, 1H). The assignment of olefinic protons was made through nOe data:

References:

- (1) Steinmetz, B.; Schenk, W. A. *Organometallics* **1999**, *18*, 943-946.
- (2) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726-12727.

FigureS1. GC/MS of typical crude hydrosilylation reaction.

File : C:\HPCHEM\1\DATA\SAMPLE2.D
Operator : zach
Acquired : 22 Oct 01 8:38 am using AcqMethod GGAMBER
Instrument : GC/MS Ins
Sample Name:
Misc Info :
Vial Number: 1

X111-7 std (no D)

Figure S2. GC/MS of reaction with deuterated silane. No [M-1] peak indicates no scrambling with alkyne C-H of starting material.

File : C:\HPCHEM\1\DATA\SAMPLE1.D *XIII-7*
 Operator : zach
 Acquired : 20 Oct 01 5:36 pm using AcqMethod GGAMBER
 Instrument : GC/MS Ins
 Sample Name: drfii34b2
 Misc Info :
 Vial Number: 1

Figure S3. GC/MS trace of crossover experiment with expansion on MS of peak corresponding to DSiEt_3 product. Lack of $[\text{M}-1]$ peak indicates no crossover with competing $\text{HSi}(n\text{Pr})_3$.

Figure S4. Repeated GC/MS trace from fig. S3, with MS expansion on $\text{HSi}(n\text{Pr})_3$.