Electronic supplementary information

Mild partial deoxygenation of esters catalyzed by an oxazoline-coordinated rhodium silylene

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EXPERIMENTAL DETAILS

General Considerations. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Benzene, pentane, methylene chloride, and diethyl ether were dried and deoxygenated using an IT PureSolv system. Chloroform was heated to reflux over CaH₂, and then distilled before use. Bromobenzene and bromobenzene-d₅ were degassed under vacuum and stored with activated molecular sieves. Benzene-d₆ was stirred over Na/K alloy and then vacuum transferred. Compound 1 was synthesized according to the previously published work.¹ Tris(perfluorophenyl)borane was synthesized from boron trichloride and bromopentafluorobenzene.² Phenylsilane was synthesized by reduction of trichlorophenylsilane with LiAlH₄. Benzyldimethylsilane was purchased from Gelest and stored over 4 Å molecular sieves in the glovebox. Ethyl acetate was purchased from Fisher Scientific, distilled over K₂CO₃, and stored over 4 Å molecular sieves in the glovebox. Commercial esters, amides, ketones and aldehydes were degassed and stored in the glovebox. Liquid samples were stored over 4 Å molecular sieves.

¹H, ¹³C{¹H}, and ¹¹B NMR spectra were collected on a Varian MR 400 MHz spectrometer or an Avance II 600 MHz NMR spectrometer. ¹⁵N NMR chemical shifts were determined by ¹H–¹⁵N HMBC experiments on an Avance II 600 MHz NMR spectrometer or a Bruker Avance II 700 MHz spectrometer with a Bruker Z-gradient inverse TXI ¹H/¹³C/¹⁵N 5 mm cryoprobe. ¹⁵N chemical shifts were originally referenced to an external liquid NH₃ standard and
[\{\kappa^3-\text{N}_2\text{Si}_C\text{-PhB}(\text{Ox}^{\text{Me}2})(\text{Ox}^{\text{Me}2}\text{SiPh})\text{Im}^{\text{Mes}})\text{Rh(H)CO}]\text{[HB(C\text{F}\text{3})_3]} \quad (2).

Tris(perfluorophenyl)borane (0.0895 g, 0.175 mmol) and \{PhB(\text{Ox}^{\text{Me}2})_2\text{Im}^{\text{Mes}}\}\text{Rh(H)SiH}_2\text{Ph})\text{CO (0.124 g, 0.175 mmol) were mixed in benzene (5 mL). Dark brown oily precipitate formed in a few minutes, and the solution was then stirred at room temperature for another 3 h. The top layer, a transparent brown solution, was decanted, and the oil was then washed with benzene (2 × 5 mL) and pentane (5 mL), and dried under vacuum to give the product as black solid (0.184 g, 0.151 mmol, 86.3%). \text{^1H NMR (bromobenzene-\text{d}_5, 400 MHz): } \delta 7.65 (\text{d}, \text{ }^3\text{J}_{\text{HH}} = 6.8 \text{ Hz, } 2 \text{ H, } \text{o-BC}_6\text{H}_3), 7.43 (\text{m}, 4 \text{ H, C}_6\text{H}_5), 7.14 (\text{m}, 2 \text{ H, C}_6\text{H}_5), 6.81 (\text{d}, \text{ }^3\text{J}_{\text{HH}} = 6.8 \text{ Hz, } 2 \text{ H, } \text{o-SiC}_6\text{H}_5), 6.72 (\text{s}, 1 \text{ H, } \text{m-C}_6\text{H}_2\text{Me}_3), 6.64 (\text{s}, 1 \text{ H, } \text{m-C}_6\text{H}_2\text{Me}_3), 6.34 (\text{d}, \text{ }^3\text{J}_{\text{HH}} = 2.0 \text{ Hz, } 1 \text{ H, } \text{4,5H-N}_2\text{C}_3\text{H}_2\text{Mes}), 6.25 (\text{d}, \text{ }^3\text{J}_{\text{HH}} = 2.0 \text{ Hz, } 1 \text{ H, } \text{4,5H-N}_2\text{C}_3\text{H}_2\text{Mes}), 5.15 (\text{vt}, \text{ }^1\text{J}_{\text{SiH}} = 234.0 \text{ Hz, } 1 \text{ H, SiH}), 3.89 (\text{m}, 3 \text{ H, } \text{CNCMe}_2\text{CH}_2\text{O}), 3.80 (\text{d}, \text{ }^2\text{J}_{\text{HH}} = 9.6 \text{ Hz, } 1 \text{ H, } \text{CNCMe}_2\text{CH}_2\text{O}), 2.06 (\text{s}, 3 \text{ H, } \text{p-C}_6\text{H}_2\text{Me}_3), 1.68 (\text{s}, 3 \text{ H, } \text{o-C}_6\text{H}_2\text{Me}_3), 1.10 (\text{s}, 3 \text{ H, } \text{CNCMe}_2\text{CH}_2\text{O}), 1.07 (\text{s}, 3 \text{ H, } \text{CNCMe}_2\text{CH}_2\text{O}), 1.04 (\text{s}, 3 \text{ H, } \text{CNCMe}_2\text{CH}_2\text{O}), 0.76 (\text{s}, 3 \text{ H, } \text{o-C}_6\text{H}_2\text{Me}_3), 0.68 (\text{s}, 3 \text{ H, } \text{CNCMe}_2\text{CH}_2\text{O}), -12.92 (\text{dd}, \text{ }^1\text{J}_{\text{RHH}} = 20.0 \text{ Hz, } \text{ }^3\text{J}_{\text{HH}} = 4.0 \text{ Hz, } 1 \text{ H, RhH}). \text{^13C\{^1H\} NMR (bromobenzene-\text{d}_5, 150 MHz): } \delta 186.33 (\text{d}, \text{ }^1\text{J}_{\text{RHC}} = 51 \text{ Hz, } \text{2C-N}_2\text{C}_3\text{H}_2\text{Mes}), 169.23 (\text{d}, \text{ }^1\text{J}_{\text{RHC}} = 37.5 \text{ Hz, CO}), 148 (\text{br, C}_6\text{F}_5), 147 (\text{br, C}_6\text{F}_5), 138.06 (\text{p-C}_6\text{H}_2\text{Me}_3), 137.6 (\text{br, ipso-C}_6\text{H}_5), 136.4 (\text{br, C}_6\text{F}_5), 136.0 (\text{br, ipso-C}_6\text{H}_5), 135 (\text{br, C}_6\text{F}_5), 133.89 (\text{o-BC}_6\text{H}_3), 133.76 (\text{ipso-C}_6\text{H}_2\text{Me}_3), 133.38 (\text{o-SiC}_6\text{H}_5), 132.91 (\text{o-C}_6\text{H}_2\text{Me}_3), 131.73 (\text{o-C}_6\text{H}_2\text{Me}_3), 128.36 (2 \text{ m-C}_6\text{H}_2\text{Me}_3, overlapped with C\text{d}_2\text{Br}), 127.03 (\text{C}_6\text{H}_3), 126.85 (\text{C}_6\text{H}_3), 126.68 (\text{C}_6\text{H}_3), 126.52 (\text{C}_6\text{H}_3), 125.18 (4,5C-N_2\text{C}_3\text{H}_2\text{Mes, overlapped with C\text{d}_2\text{Br}}), 122.92 (4,5C-N_2\text{C}_3\text{H}_2\text{Mes}), 80.68 (\text{CNCMe}_2\text{CH}_2\text{O}), 78.95 (\text{CNCMe}_2\text{CH}_2\text{O}), 68.39 (\text{CNCMe}_2\text{CH}_2\text{O}), 66.94 (\text{CNCMe}_2\text{CH}_2\text{O}), 26.98 (\text{CNCMe}_2\text{CH}_2\text{O}), 26.43 (\text{CNCMe}_2\text{CH}_2\text{O}), 25.04 (\text{CNCMe}_2\text{CH}_2\text{O}), 23.21 (\text{CNCMe}_2\text{CH}_2\text{O}),
19.63 (p-C₆H₂Me₃), 18.26 (o-C₆H₂Me₃), 15.12 (o-C₆H₂Me₃). ¹¹B NMR (bromobenzene-d₅, 192 MHz): δ −7.9 (PhB(OxMe₂)(OxMe₂-SiHPh)ImMe), −25 (br, HB(C₆F₅)₃). ¹⁵N {¹¹H} NMR (bromobenzene-d₅, 61 MHz): δ −167.7 (CN(Rh)CMe₂CH₂O), −180.7 (N₂C₃H₂Mes), −183.1 (N₂C₃H₂Mes), −199.5 (CN(SiHPh)CMe₂CH₂O). ¹⁹F NMR (bromobenzene-d₅, 545 MHz): δ −132.08 (o-C₆F₅), −162.79 (p-C₆F₅), −165.72 (m-C₆F₅). ²⁹Si NMR (bromobenzene-d₅, 119 MHz): δ 6.5 (¹JRSSi = 42 Hz). IR (KBr, cm⁻¹): 3398 w, 2972 w, 2928 w, 2859 w, 2386 w, 2162 w, 2076 s, 2016 m, 2000 br, 1652 m, 1639 m, 1560 m, 1508 s, 1464 s, 1373 m, 1301 m, 1274 m, 1209 m, 1184 m, 1162 m, 1110 s, 1075 s, 968 s, 852 m, 827 m, 750 w, 738 w, 705 w, 681 w, 639 w, 567 w. EIMS (positive ion mode): 707.2 M⁺, 679.2 M⁺-CO, 629.2 M⁺-C₇H₆O, 601.2 M⁺-SiC₂H₆O, 471.3 M⁺-RhSiC₇H₂O. EIMS (negative ion mode): 512.9 HB(C₆F₅)₃⁻. Anal. Calcd for C₅₃H₃₂B₂F₁₅N₃O₃RhSi: C, 52.16; H, 3.47; N, 4.59. Found: C, 51.45; H, 3.20; N, 4.55. Mp, 89-91 °C.

**Figure S1.** A ¹H NMR spectrum of 2 acquired in bromobenzene-d₅. The acquisition window extended from −40 to 14 ppm, and no signals were detected in the region not shown.
Figure S2. $^{13}$C-{$^1$H} NMR spectrum of 2 acquired in bromobenzene-$d_5$. 
Figure S3. $^1$H-$^{15}$N HMBC spectrum of 2 acquired in bromobenzene-$d_5$ on a Bruker Avance 700 spectrometer using a Bruker Z-gradient inverse TXI $^1$H/$^{13}$C/$^{15}$N 5 mm cryoprobe. Inset: a $^1$H-$^{15}$N HMBC experiment acquired on a Bruker Avance 600 spectrometer with an inverse BB probe. The F1 axis is the $^{15}$N dimension, and F2 is the $^1$H dimension. The spectrum is machine-calibrated to NH$_3$ as the standard, and the reported chemical shift values are adjusted to the nitromethane scale. Crosspeaks at ~203 ppm from minor contaminants in the above spectrum appeared at longer acquisition times required to observed N-Si-H correlations, and result from more efficient polarization transfer from oxazoline methyl groups to N than the two-bond correlation through silicon.
Figure S4. A $^1$H–$^{29}$Si HSQC experiment on 2 acquired in bromobenzene-$d_5$ with tetrakis(trimethylsilyl)silane as an internal standard.
**Figure S5.** $^{29}\text{Si}\{^1\text{H}\}$ INEPT spectrum showing the $^1J_{\text{RhSi}}$ coupling. The upfield signal is from tetrakis(trimethylsilyl)silane, added as an internal standard.
The $^1\text{H} \rightarrow ^{29}\text{Si}$ cross-polarization magic angle spinning (CPMAS) and $^1\text{H}$ MAS spectra of 2 were acquired on a 600 MHz Varian spectrometer equipped with a 1.6-mm FastMAS$^\text{TM}$ T3 probe. The rotor was packed in a glove box to provide protection from air and moisture contamination and was spun using dry nitrogen gas. The experimental parameters are given in figure captions, where $\nu_R$ is the MAS rate, $\nu_{RF}(X)$ is the magnitude of the RF magnetic field applied to X spins, $\tau_{CP}$ is the cross-polarization time, $\tau_{RD}$ is the recycle delay, and NS is the number of scans.

**Figure S6.** The $^1\text{H} \rightarrow ^{29}\text{Si}$ CPMAS spectrum of 2 acquired using the following experimental parameters: $\nu_R = 20$ kHz, $\nu_{RF}(\text{H}) = 100$ kHz during the excitation pulse, $\nu_{RF}(\text{H}) = 50$ kHz during CP, $\nu_{RF}(\text{H}) = 80$ kHz during TPPM heteronuclear decoupling, $\nu_{RF}(\text{Si}) = 70$ kHz during CP, $\tau_{CP} = 1$ ms, $\tau_{RD} = 3$ s, and NS = 8000.
Figure S7. The $^1$H MAS spectrum of 2 acquired using the following experimental parameters: $v_R = 20$ kHz, $v_{RF}(H) = 100$ kHz, $\tau_{RD} = 3$ s, and $NS = 4$.

Figure S8. $^{19}$F NMR spectrum of 2 acquired in bromobenzene-$d_5$. 
Figure S9. $^{11}$B NMR spectrum of 2 acquired in bromobenzene-$d_5$. 
Figure S10. High resolution mass spectrum of 2 acquired in bromobenzene and positive ion mode.

Figure S11. High resolution mass spectrum of 2 acquired in bromobenzene and negative ion mode.
**Description of Catalytic Experiments.**

**exo-2-Methoxybicyclo[2.2.1]heptane.** A methylene chloride solution of 2 (0.0150 g, 0.0123 mmol, 10 mL) was added to a mixture of exo-2-norbornylformate (1.60 mL, 12.0 mmol) and phenylsilane (3.10 mL, 25.1 mmol). The solution was stirred at room temperature for 24 h and then filtered through a short plug of celite (5 mL). The celite was washed with methylene chloride (2 × 5 mL), the clear and colorless filtrates were combined, and the mixture was purified by distillation. The product was distilled at 167 °C (760 mmHg) as a colorless liquid (0.740 g, 5.86 mmol, 48.8%). The experimental 1H and 13C{1H} NMR spectra matched those reported in the literature.3

1H NMR (chloroform-d, 600 MHz): δ 3.27 (s, 3 H, OMe), 3.25 (m, 1 H, 2H-C7H9), 2.34 (m, 1 H, 4H-C7H9), 2.24 (m, 1 H, 1H-C7H9), 1.56 (m, 2 H, 6,7H-C7H9), 1.50 (d, 1 H, 3H-C7H9), 1.43 (m, 1 H, 5H-C7H9), 1.35 (m, 1 H, 7H-C7H9), 1.09 (m, 1 H, 3H-C7H9), 1.05 (m, 1 H, 5H-C7H9), 0.98 (m, 1 H, 6H-C7H9). 13C{1H} NMR (chloroform-d, 150 MHz): δ 84.39 (2C-C6H9), 56.01 (OMe), 40.06 (4C-C7H9), 39.49 (7C-C7H9), 35.30 (1C-C7H9), 34.90 (3C-C7H9), 28.67 (5C-C7H9), 24.77 (6C-C7H9). EI MS: C8H14O m/z 126 (M+).

**Diethyl ether.** A chloroform-d solution of 2 (0.0002 g, 0.000164 mmol, 0.5 mL) was added to a mixture of ethyl acetate (16.0 µL, 0.164 mmol), phenylsilane (40.5 µL, 0.328 mmol), and Si(SiMe3)4 (0.314 M) as an internal standard. The reaction's progress was monitored with 1H NMR spectroscopy, and all of the ethyl acetate was consumed after 0.5 h to give the product in 70.0% yield. The NMR spectra matched those acquired using an authentic sample of diethyl ether. 1H NMR (chloroform-d, 600 MHz): δ 3.51 (q, 3JHH = 7.2 Hz, 4 H, CH2CH3), 1.24 (t, 3JHH = 7.2 Hz, 6 H, CH2CH3).

**1-Bromo-6-ethoxyhexane.** A chloroform solution of 2 (0.0150 g, 0.0123 mmol) was added to ethyl 6-bromohexanoate (0.218 mL, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was heated to 80 °C for 72 h and filtered through a short plug of celite (5 mL). The celite was extracted with chloroform (2 × 3 mL), the colorless filtrates were combined, and the mixture was separated by distillation. The product was distilled at 101 °C (10 mmHg) as a colorless liquid (0.193 g, 0.923 mmol, 75.0%). The experimental spectra matched the literature report.4

1H NMR (chloroform-d, 600 MHz): δ 3.48 (q, 3JHH = 6.6 Hz, 2 H, OCH2CH3), 3.42 (m, 4 H, BrCH2(CH2)4CH2OEt), 1.88 (m, 2 H, BrCH2CH2(CH2)4OEt), 1.57 (m, 2 H, Br(CH2)4CH2CH2OEt), 1.47 (m, 2 H, Br(CH2)3CH2(CH2)2OEt), 1.39 (m, 2 H,
Br(CH₂)₂CH₂(CH₂)₃OEt, 1.21 (t, 3J HH = 6.6 Hz, 3 H, OCH₂CH₂). ¹³C¹H NMR (chloroform-d, 150 MHz): δ 70.63 (Br(CH₂)₂CH₂OEt), 66.27 (OCH₂CH₂), 34.05 (BrCH₂(CH₂)₃OEt), 32.90 (BrCH₂CH₂(CH₂)₄OEt), 29.78 (BrCH₂CH₂CH₂CH₂OEt), 28.18 (BrCH₂CH₂CH₂CH₂CH₂OEt), 25.59 (Br(CH₂)₂CH₂CH₂CH₂OEt), 15.38 (OCH₂CH₂). EIMS: C₁₈H₁₇BrO m/z 209 (M⁺).

2-(2-Ethoxyethyl) thiophene. A 3 mL chloroform solution of 2 (0.0150 g, 0.0123 mmol) was added to ethyl 2-thiopheneacetate (0.184 mL, 1.23 mmol) and phenylsilane (3.1 mL, 25.1 mmol). The reaction mixture was heated to 60 °C for 24 h and filtered through a short plug of celite (5 mL). The celite was extracted with chloroform (2 × 3 mL), the colorless filtrates were combined, and the mixture was separated by distillation. The product distilled at 69 °C (10 mmHg) as a colorless liquid (0.0958 g, 0.613 mmol, 49.8%). The spectra of the isolated material matched the literature report.⁵¹H NMR (chloroform-d, 600 MHz): δ 7.15 (d, 3J HH = 4.8 Hz, 1 H, 5H-C₄H₃S), 6.94 (t, 3J HH = 4.2 Hz, 1 H, 4H-C₄H₃S), 6.86 (d, 3J HH = 3.0 Hz, 1 H, 3J HHH = 3.0 Hz, 3H-C₄H₃S), 3.68 (t, 3J HH = 7.2 Hz, 2 H, CH₂CH₂OEt), 3.54 (q, 3J HH = 7.2 Hz, 2 H, OCH₂CH₃), 3.11 (t, 3J HH = 7.2 Hz, 2 H, CH₂CH₂OEt), 1.24 (t, 3J HH = 7.2 Hz, 3 H, OCH₂CH₂). ¹³C¹H NMR (chloroform-d, 150 MHz): δ 141.52 (2C-C₄H₃S), 126.78 (3C-C₄H₃S), 125.15 (4C-C₄H₃S), 123.70 (5C-C₄H₃S), 71.31 (CH₂CH₂OEt), 66.44 (OCH₂CH₂), 30.67 (CH₂CH₂OEt), 15.32 (OCH₂CH₂). EIMS: C₁₈H₁₂OS m/z 156 (M⁺).

(Z)-1-Methoxyoctadec-9-ene. Compound 2 (0.0150 g, 0.0123 mmol) dissolved in chloroform (3 mL) was added to methyl oleate (0.417 mL, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was heated to 60 °C for 72 h and filtered through a short plug of celite (5 mL). The celite was extracted with chloroform (3 mL × 2), the colorless filtrates were combined, and the mixture was separated by distillation. The product distilled at 200 °C (0.1 mmHg) as a colorless liquid (0.215 g, 0.761 mmol, 61.9%) to give a substance with NMR spectroscopic properties that matched the literature report.⁶¹H NMR (chloroform-d, 600 MHz): δ 5.36 (m, 2 H, CH=CH), 3.37 (t, 3J HH = 6.6 Hz, 2 H, CH₂OCH₂), 3.34 (s, 3 H, OMe), 2.03 (m, 4 H, CH₂CH=CHCH₂), 1.57 (m, 2 H, CH₂CH₂OCH₂), 1.3 (br, 22 H, CH₃(CH₂)₆CH₂CH=CHCH₂(CH₂)₅CH₂CH₂OCH₂), 0.89 (t, 3J HH = 6.6 Hz, 3 H, CH₃(CH₂)₇CH=CH(CH₂)₈OCH₂). ¹³C¹H NMR (chloroform-d, 150 MHz): δ 130.08 (cis-CH=CH), 130.00 (cis-CH=CH), 73.13 (CH₂OCH₂), 58.69 (OMe), 32.07 (CH₃CH₂CH₂), 29.93-29.33 (CH₃CH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₃OCH₂), 27.37 (CH₂CH=CHCH₂), 26.30
(CH₂CH=CHCH₂), 22.84 (CH₃CH₂CH=CH(CH₂)₈OMe), 14.27 (CH₃(CH₂)₃CH=CH(CH₂)₈OMe). EIMS: C₁₉H₃₈O m/z 283 (M⁺).

(E)-5-Methoxypent-2-ene. A chloroform-d solution of 2 (0.0010 g, 0.000819 mmol) was added to methyl trans-3-pentenoate (10.0 µL, 0.0815 mmol), phenylsilane (20.2 µL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The solution was heated to 80 °C, and the conversion of ester to ether was monitored with ¹H NMR spectroscopy. The ester was completely consumed after 24 h to give the product in 64.9% yield.

¹H NMR (chloroform-d, 600 MHz): δ 5.48–5.53 (m, 2 H, CH=CH), 3.42 (t, 3 JHH = 10.2 Hz, 2 H, CH₂OMe), 3.37 (s, 3 H, OMe), 2.31 (m, 2 H, CH₂CH₂OMe), 1.69 (m, 3 H, CH₃CH=CH).

Tetrahydrofuran. A methylene chloride solution (3 mL) of 2 (0.0150 g, 0.0123 mmol) was added to γ-butyrolactone (0.100 mL, 1.30 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The resulting mixture was stirred at room temperature for 8 h and filtered through a short plug of celite (5 mL). The product was distilled at 65 °C (760 mmHg) to give a sample of THF (0.0520 g, 0.721 mmol, 55.4%) that matched authentic samples of tetrahydrofuran by ¹H and ¹³C{¹H} NMR spectroscopy.

¹H NMR (chloroform-d, 600 MHz): δ 3.7 (br, 4 H, 2,5H-C₄H₈O), 1.8 (br, 4 H, 3,4H-C₄H₈O). ¹³C{¹H} NMR (chloroform-d, 150 MHz): δ 68.08 (2,5C-C₄H₈O), 25.73 (3,4C-C₄H₈O). EIMS: C₄H₈O m/z 72 (M⁺).

1,1,1-Trifluoro-2-(2,2,2-trifluoroethoxy)ethane. A chloroform-d solution (0.5 mL) of 2 (0.0010 g, 0.000819 mmol) was added to trifluoroacetic anhydride (5.7 µL, 0.041 mmol), phenylsilane (20.2 µL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The reaction progress was monitored using ¹H NMR spectroscopy which indicated the anhydride was consumed after 6 h and provides the ether in 50.1% yield. ¹H NMR (chloroform-d, 600 MHz): δ 3.84 (q, 3 JHF = 8.0 Hz, CH₂). ¹³C{¹H} NMR (chloroform-d, 150 MHz): δ 124.10 (q, JCF = 277.5 Hz, CH₂CF₃), 63.51 (q, JCF = 36.0 Hz, CH₂CF₃). ¹⁹F NMR (chloroform-d, 376 MHz): δ −76.36 (t, 3 JHF = 8.6 Hz, CF₃).

Trimethylamine. A chloroform-d solution (0.5 mL) of 2 (0.0010 g, 0.000819 mmol) was added to N,N-dimethylformamide (6.3 µL, 0.0814 mmol), phenylsilane (20.2 µL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The solution was heated to 80 °C, and the progress was monitored through ¹H NMR. All amide was consumed after 3 h to give 85.4% yield of
NMe₃. The spectra matched the literature report.⁹ ¹H NMR (chloroform-ê, 600 MHz): δ 2.24 (s, Me). ¹³C{¹H} NMR (chloroform-ê, 150 MHz): δ 47.84 (Me).

**N,N-Dimethylbenzylamine chloride.** A chloroform solution (3 mL) of 2 (0.0150 g, 0.0123 mmol) was added to N,N-dimethylbenzamide (0.183 g, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was heated to 80 °C for 24 h and filtered through a short plug of celite (5 mL). The celite was washed with diethyl ether (2 × 3 mL), the extracts were combined, and a diethyl ether solution of hydrochloric acid (2.0 M, 5 mL) was added. The solvent was evaporated from the slightly cloudy solution, and the residual white solid was washed with diethyl ether (3 × 5 mL) and dried under vacuum to give the product as a white solid (0.168 g, 0.979 mmol, 79.6%). The NMR spectra of this material matched the literature report.

¹H NMR (chloroform-ê, 600 MHz): δ 12.8 (br, 1 H, NH), 7.6 (br, 2 H, C₆H₅), 7.5 (br, 3 H, C₆H₅), 4.17 (s, 2 H, C₂H₂Ph), 2.75 (s, 6 H, Me).

¹³C{¹H} NMR (chloroform-ê, 150 MHz): δ 131.20 (C₆H₅), 130.41 (C₆H₅), 129.59 (C₆H₅), 128.51 (C₆H₅), 61.39 (C₂H₂Ph), 42.29 (Me). EIMS: C₉H₁₄N m/z 135 (M⁺-Cl). For N,N-dimethyl-1-phenylmethanamine, a chloroform-ê solution (0.5 mL) of 2 (0.0010 g, 0.000819 mmol) was added to N,N-dimethylbenzamide (0.0122 g, 0.0818 mmol), phenylsilane (20.2 µL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The solution was heated to 80 °C, and the reaction progress was monitored using ¹H NMR spectroscopy which indicated the amide was consumed after 24 h (86.3%). ¹H NMR (chloroform-ê, 600 MHz): δ 7.31-7.20 (m, 5 H, C₆H₅), 3.37 (s, 2 H, CH₂), 2.20 (s, 6 H, Me).

**Ethylbenzene.** A methylene chloride solution (3 mL) of 2 (0.0150 g, 0.0123 mmol) was added to a mixture of acetophenone (0.140 mL, 1.20 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was stirred at room temperature for 7 h and filtered through a short plug of celite (5 mL), which was extracted with methylene chloride (2 × 3 mL). The colorless filtrates were combined, and the mixture was separated by distillation. The product was distilled at 132 °C (760 mmHg) as a colorless liquid (0.0739 g, 0.696 mmol, 58.0%). The spectra matched those acquired from an authentic sample of ethylbenzene. ¹H NMR (chloroform-ê, 600 MHz): δ 7.34 (m, 2 H, C₆H₅), 7.23 (m, 3 H, C₆H₅), 2.70 (m, 2 H, CH₂CH₃), 1.30 (m, 3 H, CH₂CH₃). ¹³C{¹H} NMR (chloroform-ê, 150 MHz): δ 144.38 (ipso-C₆H₅), 128.44 (m-C₆H₅), 127.99 (o-C₆H₅), 125.72 (p-C₆H₅), 29.03 (CH₂CH₃), 15.76 (CH₂CH₃). EIMS: C₈H₁₀ m/z 106 (M⁺).
2-Ethyl-1,3-dimethoxybenzene. A methylene chloride solution (3 mL) of 2 (0.0150 g, 0.0123 mmol) was added to a mixture of 2',6'-dimethoxyacetophenone (0.220 g, 1.22 mmol) and phenylsilane (3.10 mL, 25.1 mmol). The reaction mixture was stirred at room temperature for 24 h and then was filtered through a short plug of celite (5 mL). The celite was extracted with methylene chloride (2 × 3 mL), the colorless filtrates were combined, and the product was isolate through column chromatography (ethyl acetate:hexane = 1:9, Rf = 0.85) as a white solid (0.112 g, 0.674 mmol, 55.2%). The NMR spectra of the isolated material matched the literature report.\(^{11}\)

\[\begin{align*}
^1H \text{ NMR (chloroform-} d, 600 \text{ MHz): } \delta 7.13 (t, J_{HH} = 8.4 \text{ Hz}, 1 \text{ H, } 5H-C_6H_3), 6.56 (d, J_{HH} = 8.4 \text{ Hz}, 2 \text{ H, } 4,6H-C_6H_3), 3.83 (s, 6 \text{ H, OMe}), 2.68 (q, J_{HH} = 7.2 \text{ Hz}, 2 \text{ H, CH}_2CH_3), 1.10 (t, J_{HH} = 7.2 \text{ Hz}, 3 \text{ H, CH}_2CH_3). \end{align*}\]

\[\begin{align*}
^13C\{^1H\} \text{ NMR (chloroform-} d, 150 \text{ MHz): } \delta 158.27 (1,3C-1,3C\text{-C}_6H_3), 126.55 (5C-5C\text{-C}_6H_3), 121.07 (2C-1,3C\text{-C}_6H_3), 103.91 (4,6C-4,6C\text{-C}_6H_3), 55.88 (\text{OMe}), 16.43 (\text{CH}_2CH_3), 13.93 (\text{CH}_2CH_3). \text{ EIIMS: C}_{10}H_{14}O_2 \text{ m/z 166 (M)}. \end{align*}\]

1,3,5-Trimethoxy-2-methylbenzene. A methylene chloride solution of cationic rhodium complex 1 (0.0150 g, 0.0123 mmol, 3 mL) was added to 2,4,6-trimethoxybenzaldehyde (0.241 g, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was stirred at room temperature for 7 h and filtered through a short plug of celite (5 mL). The celite was washed with methylene chloride (2 × 3 mL), the colorless filtrates were combined, and the mixture was purified by distillation. The product was distilled at 74 °C (0.1 mmHg) as a colorless liquid (0.107 g, 0.587 mmol, 47.8%). The spectra matched the literature report.\(^{12}\)

\[\begin{align*}
^1H \text{ NMR (chloroform-} d, 600 \text{ MHz): } \delta 6.15 (s, 2 \text{ H, C}_6H_2), 3.82 (s, 9 \text{ H, OMe}), 2.03 (s, 3 \text{ H, Me}). \end{align*}\]

\[\begin{align*}
^13C\{^1H\} \text{ NMR (chloroform-} d, 150 \text{ MHz): } \delta 159.07 (5C\text{-C}_6H_2), 158.95 (1,3C\text{-C}_6H_3), 106.94 (2C\text{-C}_6H_2), 90.68 (4,6C\text{-C}_6H_3), 55.86 (1,3\text{-OMe}), 55.52 (5\text{-OMe}), 7.80 (\text{Me}). \text{ EIIMS: C}_{10}H_{14}O_3 \text{ m/z 182 (M)}. \end{align*}\]

1,3-Dimethoxy-2-methylbenzene. A chloroform-\(d\) solution (0.5 mL) of 2 (0.0010 g, 0.000819 mmol) was added to 2,6-dimethoxybenzaldehyde (0.0136 g, 0.0818 mmol), phenylsilane (20.2 µL, 0.163 mmol), and Si(SiMe\(_3\))\(_4\) (0.314 M) as an internal standard. The progress was monitored through \(^1H\) NMR, and all aldehyde was consumed after 4 h to give the hydrocarbon in 77% yield. The products spectra matched the literature report.\(^{11}\)

\[\begin{align*}
^1H \text{ NMR (chloroform-} d, 600 \text{ MHz): } \delta 7.15 (t, J_{HH} = 8.4 \text{ Hz}, 1 \text{ H, } 5H-C_6H_3), 6.57 (d, J_{HH} = 8.4 \text{ Hz}, 2 \text{ H, } 4,6H-C_6H_3), 3.85 (s, 6 \text{ H, OMe}), 2.14 (s, 3 \text{ H, Me}). \end{align*}\]

\[\begin{align*}
^13C \text{ NMR (chloroform-} d, 150 \text{ MHz): } \delta 158.53 (1,3C\text{-C}_6H_3), 128.41 \text{ and 128.01 (C}_6H_3). \end{align*}\]
(5C-C₆H₃), 114.67 (2C-C₆H₃), 103.67 (4,6C-C₆H₃), 55.86 (OMe), 8.27 (Me). EIMS: C₉H₁₂O₂ m/z 152 (M⁺).

**Computational Details.** Structure optimizations were performed in TURBOMOLE¹³ using B3LYP¹⁴ density functional theory. The Stuttgart 1997 relativistic small core basis set plus effective core potential (ECP)¹⁵ was used for Rh, and the 6-311G(d,p) basis set¹⁶ was used for all other atoms. NMR calculations were performed in NWChem¹⁷ using the gauge independent atomic orbital method.¹⁸ The same level of theory and basis sets were used as for the structure optimizations except an all electron basis, ATZP¹⁹ was used for Rh. NMR results for both the ATZP and Stuttgart (with ECP) basis sets are reported below.

**Table S1.** Comparison of calculated and experimental NMR chemical shifts, with ATZP basis set on Rh.

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<th>expt (ppm)</th>
<th>difference</th>
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**Table S2.** Comparison of calculated and experimental NMR chemical shifts, with Stuttgart basis set and ECP on Rh.

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**Table S3.** Reference compounds and shieldings used in calculated NMR shifts.

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Energy: -6803.357051 hartree (ATZP basis on Rh)
**Table S5.** Coordinates (Å) for Optimized geometry of [{PhB(OxMe2)2ImMes}RhH(SiHPh)CO]+ (2-A).

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Table S6. Coordinates (Å) for optimized geometry of \([\kappa^3-N, Si, C-PhB(OxMe2)(OxMe2SiHPh)Im^\text{Mes}]\)Rh(H)CO\(^+\) (2-B).

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**Figure S12.** $^1$H NMR spectrum of benzyl(1-ethoxyethoxy)dimethylsilane from the hydrosilylation reaction of ethyl acetate and benzyldimethylsilane catalyzed by 2.
Figure S13. $^{13}$C{$^{1}$H} NMR spectrum of benzyl(1-ethoxyethoxy)dimethylsilane from the hydrosilylation reaction of ethyl acetate and benzyl[dimethylsilane catalyzed by 2.
Figure S14. Gas chromatogram of benzyl(1-ethoxyethoxy)dimethylsilane from the hydrosilylation reaction of ethyl acetate and benzyltrimethylsilane catalyzed by 2. Retention time: 8.24 min. Fragmentation: 238.1 (M⁺), 193.1 (M⁺-OCH₂CH₃), 147.1 (M⁺-OCH(CH₃)OCH₂CH₃).
Figure S15. $^1$H NMR spectrum of hexadecyl methyl ether from the deoxygenation reaction of methyl palmitate with phenylsilane catalyzed by 2.
Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of hexadecyl methyl ether from the deoxygenation reaction of methyl palmitate with phenylsilane catalyzed by 2.
Figure S17. Gas chromatogram of hexadecyl methyl ether from the deoxygenation reaction of methyl palmitate with phenylsilane catalyzed by 2. Retention time: 9.58 min. Fragmentation: 255.2 (M⁺), 224.2 (M⁺-OCH₃).
Figure S18. $^1$H NMR spectrum of exo-2-methoxybicyclo[2.2.1]heptane from the deoxygenation reaction of exo-2-norbornylformate with phenylsilane catalyzed by 2.
Figure S19. $^{13}$C-$^1$H NMR spectrum of exo-2-methoxybicyclo[2.2.1]heptane from the deoxygenation reaction of exo-2-norbornylformate with phenylsilane catalyzed by 2.
Figure S20. GC chromatograph of *exo*-2-methoxybicyclo[2.2.1]heptane from the deoxygenation reaction of *exo*-2-norbornylformate with phenylsilane catalyzed by 2. Retention time: 3.46 min. Fragmentation: 126.1 (M$^+$), 111.1 (M$^+$-CH$_3$), 97.0 (M$^+$-OCH$_3$).
Figure S21. $^1$H NMR spectrum of 1-bromo-6-ethoxyhexane from the deoxygenation reaction of ethyl 6-bromohexanoate with phenylsilane catalyzed by 2. The product was purified by distillation, and GC analysis (Figure S22) confirms the isolated materials is a single product.
Figure S22. $^{13}$C\{1H\} NMR spectrum of 1-bromo-6-ethoxyhexane from the deoxygenation reaction of ethyl 6-bromohexanoate with phenylsilane catalyzed by 2.
**Figure S23.** Gas chromatogram of 1-bromo-6-ethoxyhexane from the deoxygenation reaction of ethyl 6-bromohexanoate with phenylsilane catalyzed by 2. Retention time: 6.12 min. Fragmentation: 209.1 (M⁺), 164.0 (M⁺-OCH₂CH₃), 83.1 (M⁺-OCH₂CH₃-Br).
Figure S24. $^1$H NMR spectrum of 2-(2-ethoxyethyl)thiophene from the deoxygenation reaction of ethyl 2-thiopheneacetate with phenylsilane catalyzed by 2.
**Figure S25.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-(2-ethoxyethyl)thiophene from the deoxygenation reaction of ethyl 2-thiopheneacetate with phenylsilane catalyzed by 2.
Figure S26. Gas chromatogram of 2-(2-ethoxyethyl)thiophene from the deoxygenation reaction of ethyl 2-thiopheneacetate with phenylsilane catalyzed by 2. Retention time: 5.43 min. Fragmentation: 156.1 (M+), 59.0 (M−CH₂C₆H₅S).
Figure S27. $^1$H NMR spectrum of (Z)-1-methoxyoctadec-9-ene from the deoxygenation reaction of methyl oleate with phenylsilane catalyzed by 2.
Figure S28. $^{13}$C {$^{1}$H} NMR spectrum of (Z)-1-methoxyoctadec-9-ene from the deoxygenation reaction of methyl oleate with phenylsilane catalyzed by 2.
Figure S29. GC chromatograph of (Z)-1-methoxyoctadec-9-ene from the deoxygenation reaction of methyl oleate with phenylsilane catalyzed by 2. Retention time: 10.32 min. Fragmentation: 282.3 (M+), 251.3 (M+-OCH3).
Figure S30. $^1$H NMR spectrum of 2-ethyl-1,3-dimethoxybenzene from the deoxygenation reaction of 2',6'-dimethoxyacetophenone with phenylsilane catalyzed by 2.
Figure S31. $^{13}$C\{H\} NMR spectrum of 2-ethyl-1,3-dimethoxybenzene from the deoxygenation reaction of 2',6'-dimethoxyacetophenone with phenylsilane catalyzed by 2.
Figure S32. Gas chromatogram of 2-ethyl-1,3-dimethoxybenzene from the deoxygenation reaction of 2',6'-dimethoxyacetophenone with phenylsilane catalyzed by 2. Retention time: 6.66 min. Fragmentation: 166.1 (M+), 151.1 (M+-CH₃), 91.1 (M+-CH₃-OCH₃-OCH₃).
**Figure S33.** $^1$H NMR spectrum of 1,3,5-trimethoxy-2-methylbenzene from the deoxygenation reaction of 2,4,6-trimethoxybenzaldehyde with phenylsilane catalyzed by 2. The product is isolated by distillation and its purity is confirmed by GC (see Figure S34 below).
Figure S34. $^{13}\text{C}^{1}\text{H}$ NMR spectrum of 1,3,5-trimethoxy-2-methylbenzene from the deoxygenation reaction of 2,4,6-trimethoxybenzaldehyde with phenylsilane catalyzed by 2.
**Figure S35.** GC chromatograph of 1,3,5-trimethoxy-2-methylbenzene from the deoxygenation reaction of 2,4,6-trimethoxybenzaldehyde with phenylsilane catalyzed by 2. Retention time: 7.90 min. Fragmentation: 182.1 (M⁺), 167.1 (M⁺-CH₃), 151.1 (M⁺-OCH₃).
References.