**Selective, Catalytic Carbon-Carbon Bond Activation and Functionalization
Promoted by Late Transition Metal Catalysts.**

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Supporting Information: Results for the catalytic hydrogenation of $^t\text{PrCH}_2\text{OSiMe}_3$ as a function of metal catalyst and all experimental procedures (7 pages).

Entry	Catalyst ^a	% Product ^b	tof ^c
1	(PPh ₃) ₄ Pd	37	1.01
2	(PPh ₃) ₃ RhCl	35	0.98
3	[(COE) ₂ IrCl] ₂ ^c	38	1.05
4	[(COD)RhCl] ₂ ^c	50	1.39
5	[(COD)IrCl] ₂	25	0.69
6	(COD)PtCl ₂	20	0.55
7	(PPh ₃) ₂ Rh(CO)Cl	9.4	0.26

^a. 2.75 mM catalyst and 0.138 M substrate in anhydrous toluene. ^b. Determined by GC at 18 hours. ^c. turnover frequency in moles per hour^d. COE = cyclooctene, COD = 1,5-cyclooctadiene.

Table S1. Catalytic hydrogenation of ^tPrCH₂OSiMe₃.

Experimental Procedures

General Considerations. All reactions were carried out under an atmosphere of purified nitrogen unless stated otherwise. Solvents for all catalytic reactions were purified using methods described previously. Hydrogen was purified via passage through a column of activated 4 Å molecular sieves and RidoxTM. The transition metal complexes were purchased from the following vendors: (PPh₃)₃RhCl, Pd(PPh₄)₄ and [(COD)RhCl]₂ were purchased from Strem Chemical, (COD)PtCl₂ from Alfa Aesar and [(COE)₂IrCl]₂ and [(COD)IrCl]₂ were prepared according to literature procedures.¹ Unless otherwise noted, all other chemicals were purchased from Acros Organics and were used as received.

NMR spectroscopy was performed on a Varian INOVA 400 spectrometer operating at 399.860 MHz for ¹H and 125.89 MHz for ¹³C and spectra were referenced to the residual solvent (¹H) or solvent (¹³C) peak. ³¹P NMR spectroscopy was recorded on a Varian VXR 400 operating at 202.67 MHz and spectra were referenced to neat H₃PO₄. Catalytic reactions were assayed via gas chromatography by comparison to authentic samples. Gas chromatography was performed on a Hewlett Packard 6890 gas

chromatograph equipped with an HP1909 phenylmethylsilicone capillary column with an injector temperature of 220 °C and a detector temperature of 150 °C. The method used for separating starting material from product used an oven temperature of 50 °C with a ramp rate of 1 °C per minute to a final temperature of 60 °C.

General Procedure for Catalytic Hydrogenation: Catalyst Screening. A thick walled glass vessel was charged with 0.011 mmol of catalyst, a stir bar, and 4 mL of dry toluene. Via microsyringe, 100 μ L (0.552 mmol) of (cyclopropylmethoxy)trimethylsilane was added from a 5.52 M in toluene stock solution. The vessel was then evacuated on a high vacuum line and one atmosphere of dihydrogen was added at 77 K. The contents of the vessel were thawed and the reaction mixture heated at 130 °C for 18 hours. Periodically, aliquots were removed from the vessel and assayed via gas chromatography. The product of the reaction was assayed by comparison to an authentic sample of $\text{Me}_2\text{CHCH}_2\text{OSiMe}_3$, prepared via standard protection Me_3SiCl of $\text{Me}_2\text{CHCH}_2\text{OH}$.

General Procedure for Catalytic Hydrogenation: Substrate Screening. A thick walled glass vessel was charged with 10 mg (0.011 mmol) of $(\text{PPh}_3)_3\text{RhCl}$, a stir bar, and 4 mL of dry toluene. Via syringe, 0.552 mmol of the desired substrate was added to the reaction mixture. The vessel was evacuated on the vacuum line and 1 atmosphere of H_2 was added at 77 K. The reaction mixture was heated to 130 °C for 18 hours and aliquots were removed periodically and the progress of the reaction was assayed via gas chromatography or NMR spectroscopy. Products were identified by comparison to authentic samples.

General Procedure for Catalytic Olefination. A 6 mL vial was charged with 5 mg (0.0055 mmol) of $(\text{PPh}_3)_3\text{RhCl}$, a stir bar, and 2 mL of toluene. The vial was capped with a septum top and outside of the drybox, 0.276 mmol of the desired substrate was added via syringe. The cap with septum was secured with a piece of copper wire and heated in to 130 °C. Aliquots were periodically removed via syringe and analyzed by gas chromatography and NMR spectroscopy. Products were identified by comparison to authentic samples.

Synthesis of Substrates

Cyclopropylmethoxytrimethylsilane. Modified from a previously reported literature procedure as follows.² A 250 mL Schlenk flask was charged with 35 mL of 1.6 M (55.6 mmol) *n*-BuLi in hexane and an additional 100 mL of diethyl ether and a rubber septum attached. The flask was attached to a Schlenk line and 5.00 grams (55.6 mmol) of cyclopropylcarbinol were added via syringe at 0 °C. Upon addition, a voluminous white solid formed. The reaction mixture was stirred for 1 hour after which time, 6.0 grams (55.6 mmol) Me_3SiCl was added via syringe. After several hours, the flask was opened, the LiCl filtered out through Celite, and the diethyl ether was removed under reduced pressure. The product was then distilled to produce 5.25 g (65 %) of a clear liquid that was identified by comparison to literature data.²

Preparation of ${}^i\text{PrCH}_2\text{OPPh}_2$. This molecule was prepared identically to ${}^i\text{PrCH}_2\text{OSiMe}_3$ with 3.00 g of cyclopropylcarbinol, 26 mL of *n*-BuLi and 4.15 grams

(41.6 mmol) chlorodiphenylphosphine. The clear liquid product was purified via vacuum distillation at 90 °C (10^{-3} torr) yielding 8.82 g (83%) of the desired compound. ^1H (benzene- d_6): δ = 0.096 (d, 7.5 Hz, 2H, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 0.26 (d, 7.2 Hz, 2H, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 0.992 (sept, 2 Hz, 1H, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 3.61 (m, 2H, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 7.06 (m, 2H, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 7.13 (m, 1H, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 7.66 (m, 2H, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$). ^{13}C (benzene- d_6): δ = 3.6 ($^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 12.75 ($^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 74.95 (d, 24 Hz, $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 128.50 (d, 8.7 Hz, m- $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 129.28 (p- $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 130.36 (d, 27.7 Hz, o- $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$), 143.28 (d, 28.6 Hz, ipso- $^{\text{c}}\text{PrCH}_2\text{OPPh}_2$). ^{31}P (benzene- d_6): δ = 117.62. MS: $[\text{M}]^+ = 255 \text{ M/Z}$.

Preparation of $^{\text{c}}\text{PrCH}_2\text{OC(O)CH}_3$. This molecule was prepared identically to $^{\text{c}}\text{PrCH}_2\text{OSiMe}_3$ with 1.50 g of cyclopropylcarbinol, 13 mL of *n*-BuLi and 1.70 grams of acetyl chloride. The product was purified via vacuum distillation yielding 2.1 g (88 %) of the desired product which was identified by comparison to spectroscopic data reported previously.³

Preparation of $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. In the dry box, a 250 mL round bottom flask was charged with 1.50 grams (65 mmol) of sodium metal and approximately 100 mL of diethyl ether. The flask was capped with a rubber septum and attached to a Schlenk line where 3.00 grams (41.6 mmol) of cyclopropylcarbinol were added. The reaction mixture was stirred and a voluminous white solid formed. After 16 hours, 7.65 grams (41.6 mmol) of iodobutane was added. The reaction mixture was stirred for 3 hours and then was quenched by carefully pouring the mixture onto a saturated aqueous

solution of ammonium chloride. The aqueous layer was extracted with diethyl ether, the organic layers combined, dried over MgSO_4 and the solvent removed via rotovap. The desired product was obtained as a clear liquid following distillation at $40\text{ }^\circ\text{C}$ (10^{-3} torr) yielding 0.60 g (26 %) of pure material. ^1H (benzene- d_6): $\delta = 0.084$ (d, 4.9 Hz, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.324 (d, 2.4 Hz, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.652 (t, 7.3 Hz, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.936 (m, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.11 (m, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42 (m, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.75 (t, 7.3 Hz, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.30 (d, 6.8 Hz, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C (benzene- d_6): $\delta = 2.95$ ($^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 6.66 ($^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.02 ($^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.73 ($^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 23.76 ($^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 35.64 ($^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 66.96 (s, $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

Preparation of $^{\text{c}}\text{PrCH}_2\text{OCH}_2\text{CH}_3$. This molecule was prepared according to a modified literature procedure.⁴ A 50 mL Schlenk flask was charged with 8.0 mL (0.0128 moles) of 1.6 M *n*-BuLi in hexane and an additional 20 mL of pentane was added. On the Schlenk line, the reaction mixture was stirred at 1.00 g (0.0138 moles) of cyclopropylcarbinol was added via syringe. A voluminous white solid formed and the pentane was removed *in vacuo*. Via syringe, 3.0 g of diethylsulfate was added and the flask was heated in an oil bath to $100\text{ }^\circ\text{C}$ for one hour. A short path distillation head was attached to the flask and 0.330 g (24 %) of the product was collected. Identification of the product was achieved by comparison to literature data.⁴

References

¹ a) Giordano, G.; Crabtree, R. H. *Inorg. Syn.* **1990**, 28, 88. b) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Syn.* **1974**, 15, 18.

² Ponaras, A. A.; Meah, M. Y. *Tett. Lett.* **1986**, 27, 4953.

³ Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, 81, 4256.

⁴ Bergstrom, C. G.; Siegel, S. *J. Am. Chem. Soc.* **1952**, 74, 145.