

## **Supporting Information**

### **The Fate of Aryl/Amido Complexes of Rh(III) Supported by a POCOP Pincer Ligand: C-N Reductive Elimination, $\beta$ -Hydrogen Elimination, and Relevance to Catalysis**

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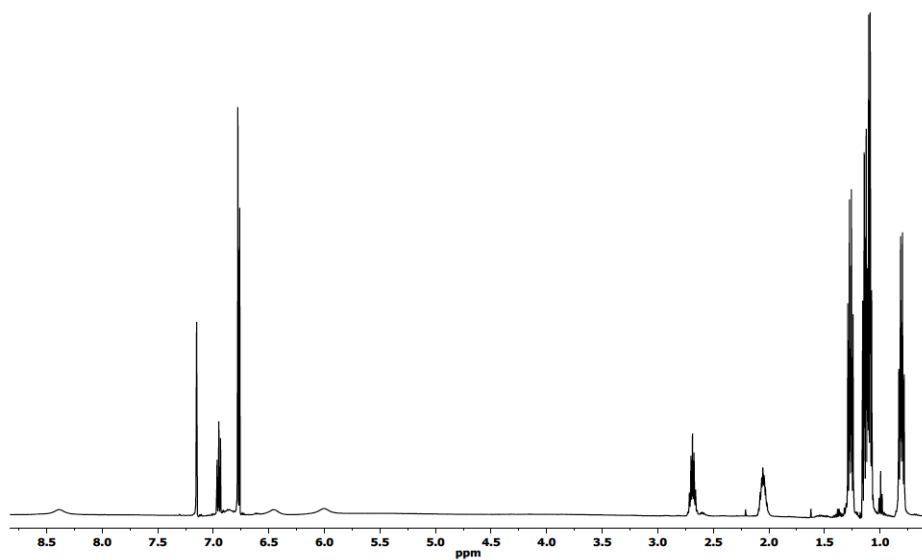
[ozero@chem.tamu.edu](mailto:ozero@chem.tamu.edu)

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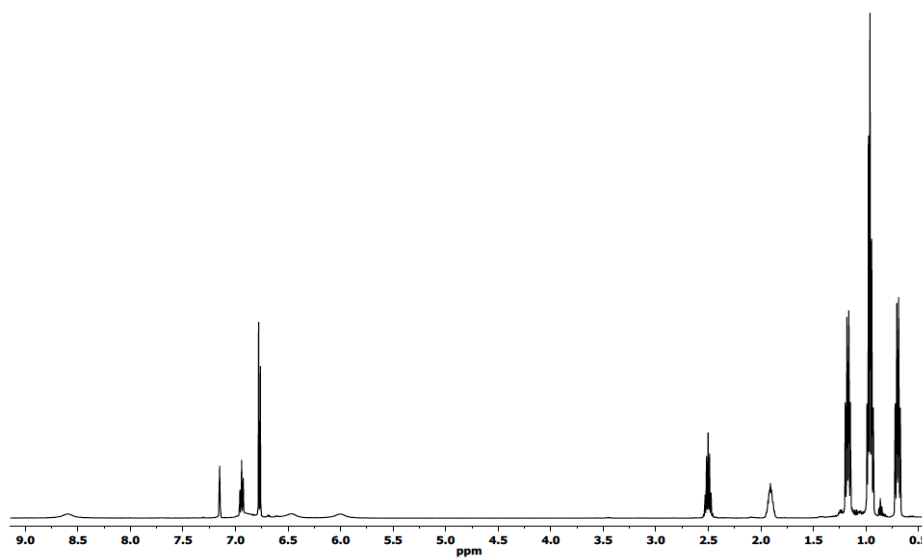
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**General Considerations.** Unless otherwise specified, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, THF, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system (Innovative Technology Pure Solv MD-5 Solvent Purification System) and stored over molecular sieves in an Ar-filled glove box. C<sub>6</sub>D<sub>6</sub> and hexanes were dried over and distilled from NaK/Ph<sub>2</sub>CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. Fluorobenzene was dried with and then distilled or vacuum transferred from CaH<sub>2</sub>. (POCOP)Rh(H)(Cl)<sup>1</sup> (**1**) was synthesized according to published procedures. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian NMRS 500 (<sup>1</sup>H NMR, 499.686 MHz; <sup>13</sup>C NMR, 125.659 MHz, <sup>31</sup>P NMR, 202.298 MHz, <sup>19</sup>F NMR, 470.111 MHz) spectrometer. For <sup>1</sup>H and <sup>13</sup>C NMR spectra, the residual solvent peak was used as an internal reference. <sup>31</sup>P NMR spectra were referenced externally using 85% H<sub>3</sub>PO<sub>4</sub> at δ 0 ppm. <sup>19</sup>F NMR spectra were referenced externally using 1.0 M CF<sub>3</sub>CO<sub>2</sub>H in CDCl<sub>3</sub> at -78.5 ppm. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ).

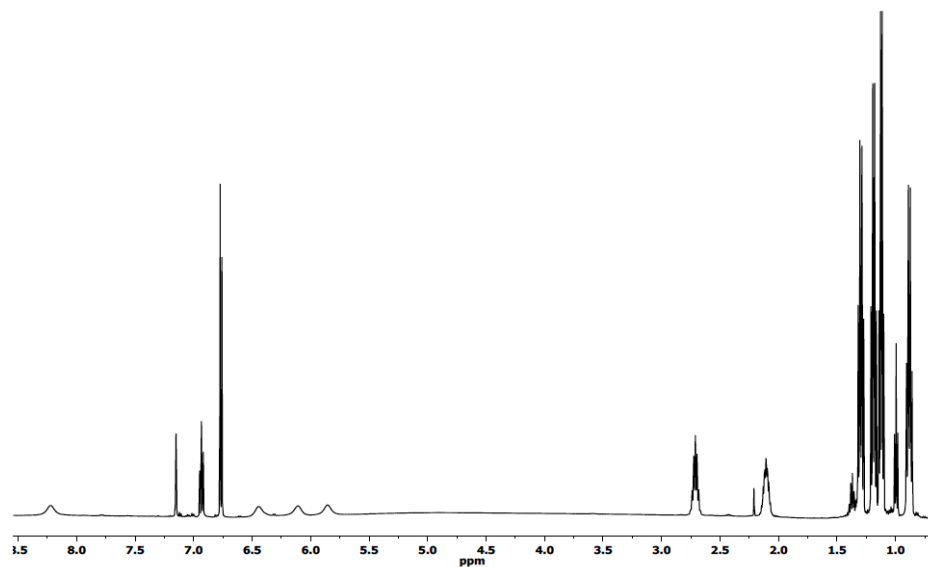
## I. $^1\text{H}$ NMR Spectra for Isolated Compounds\



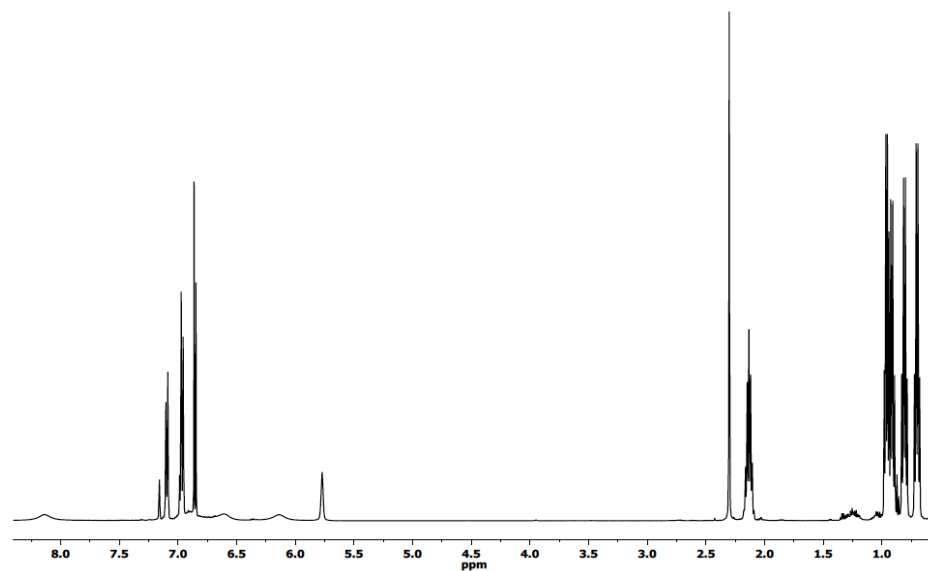
**Figure S1.**  $^1\text{H}$  NMR spectrum of  $(\text{POCOP})\text{Rh}(p\text{-C}_6\text{H}_4\text{CF}_3)(\text{Br})$  (**2**) in  $\text{C}_6\text{D}_6$ . Minor residual pentane.



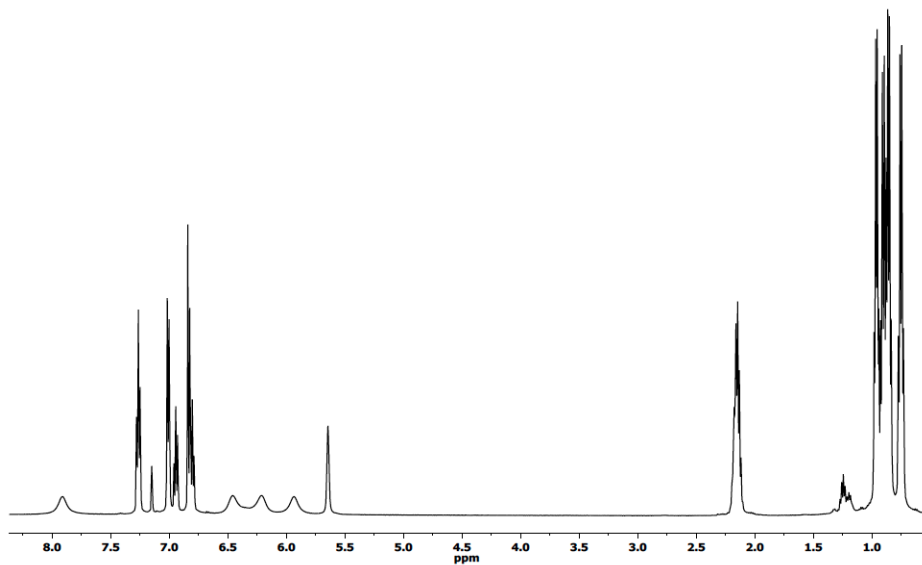
**Figure S2.**  $^1\text{H}$  NMR spectrum of  $(\text{POCOP})\text{Rh}(p\text{-C}_6\text{H}_4\text{CF}_3)(\text{Cl})$  (**3**) in  $\text{C}_6\text{D}_6$ . Minor residual pentane.



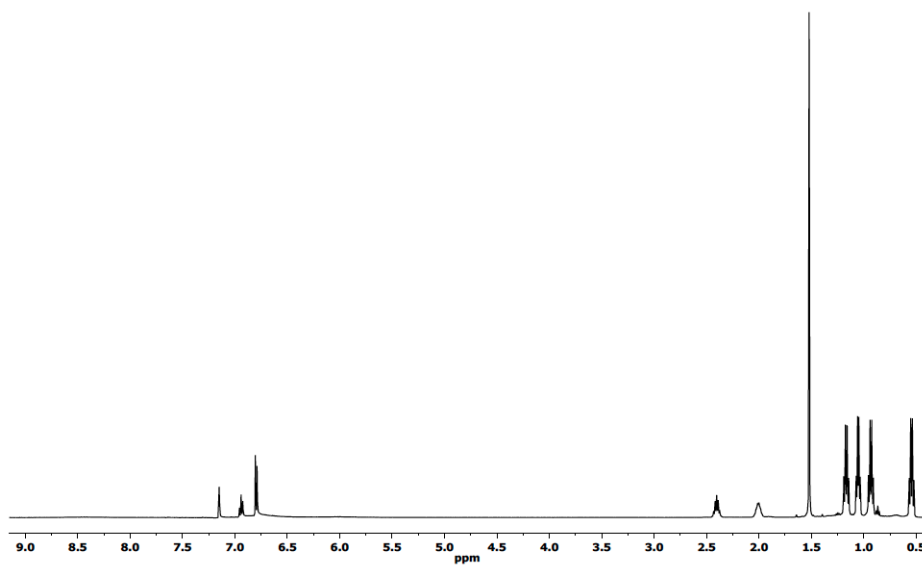
**Figure S3.**  $^1\text{H}$  NMR spectrum of  $(\text{POCOP})\text{Rh}(p\text{-C}_6\text{H}_4\text{F})(\text{Br})$  (**4**) in  $\text{C}_6\text{D}_6$ . Minor residual pentane and toluene.



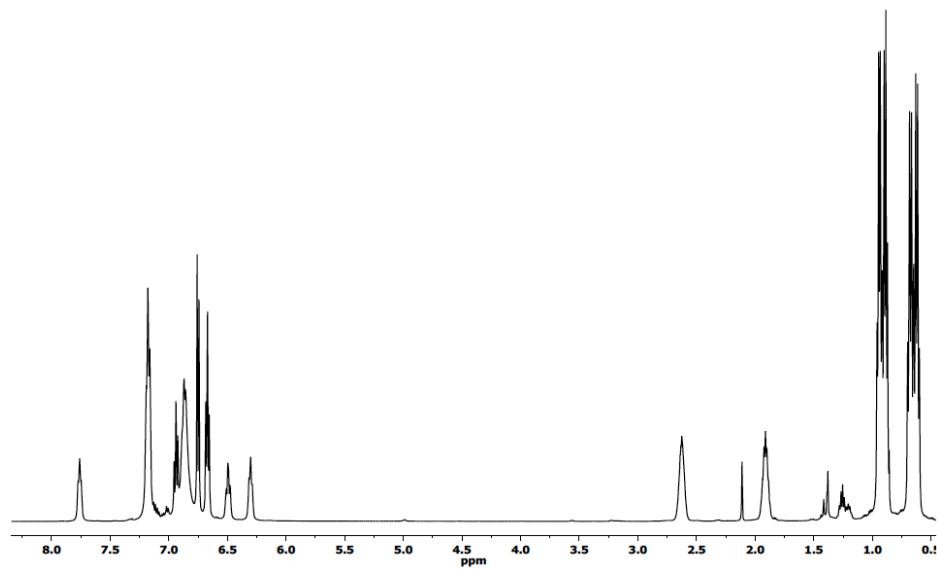
**Figure S4.**  $^1\text{H}$  NMR spectrum of  $(\text{POCOP})\text{Rh}(p\text{-C}_6\text{H}_4\text{CF}_3)(p\text{-NH}(\text{C}_6\text{H}_4\text{Me}))$  (**5**) in  $\text{C}_6\text{D}_6$ . Minor residual pentane.



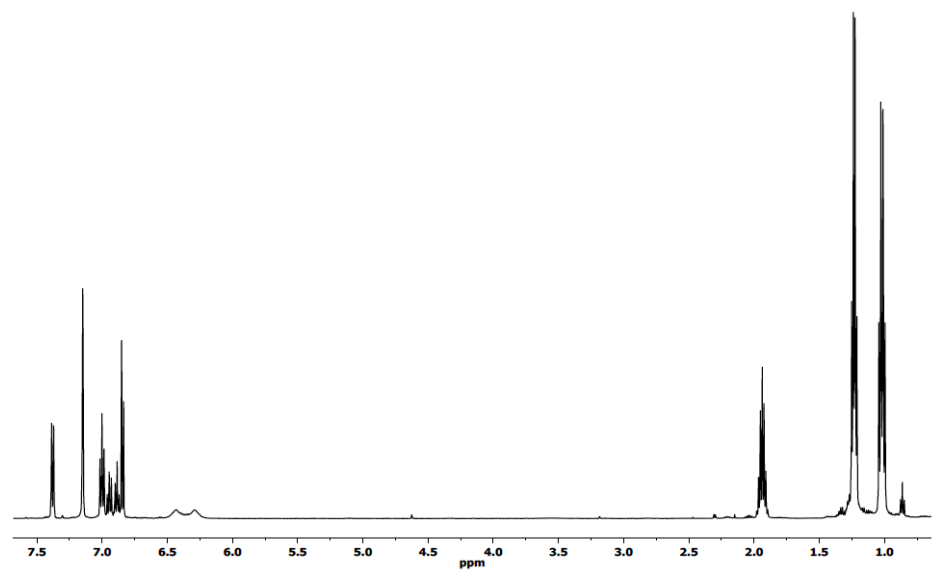
**Figure S5.**  $^1\text{H}$  NMR spectrum of  $(\text{POCOP})\text{Rh}(p\text{-C}_6\text{H}_4\text{F})(\text{NH}(\text{C}_6\text{H}_5))$  (**6**) in  $\text{C}_6\text{D}_6$ . Minor residual pentane.



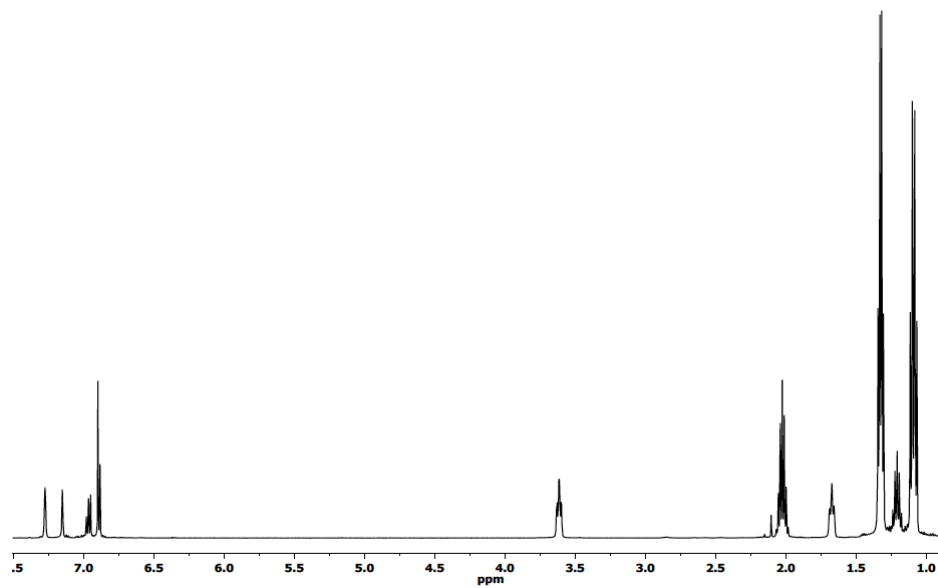
**Figure S6.**  $^1\text{H}$  NMR spectrum of  $(\text{POCOP})\text{Rh}(p\text{-C}_6\text{H}_4\text{CF}_3)(\text{O}(\text{CH}_3)_3)$  (**7**) in  $\text{C}_6\text{D}_6$ . Resonances corresponding to  $p\text{-C}_6\text{H}_4\text{CF}_3$  protons are broad in the baseline.



**Figure S7.** <sup>1</sup>H NMR spectrum of (POCOP)Rh(*p*-C<sub>6</sub>H<sub>4</sub>F)(NPh<sub>2</sub>) (**8**) in C<sub>6</sub>D<sub>6</sub>. Minor residual pentane and toluene. Also, minor residual NaO<sup>t</sup>Bu (1.34 ppm).



**Figure S8.** <sup>1</sup>H NMR spectrum of (POCOP)Rh(N(Ph)CH<sub>2</sub>) (**9**) in C<sub>6</sub>D<sub>6</sub>.



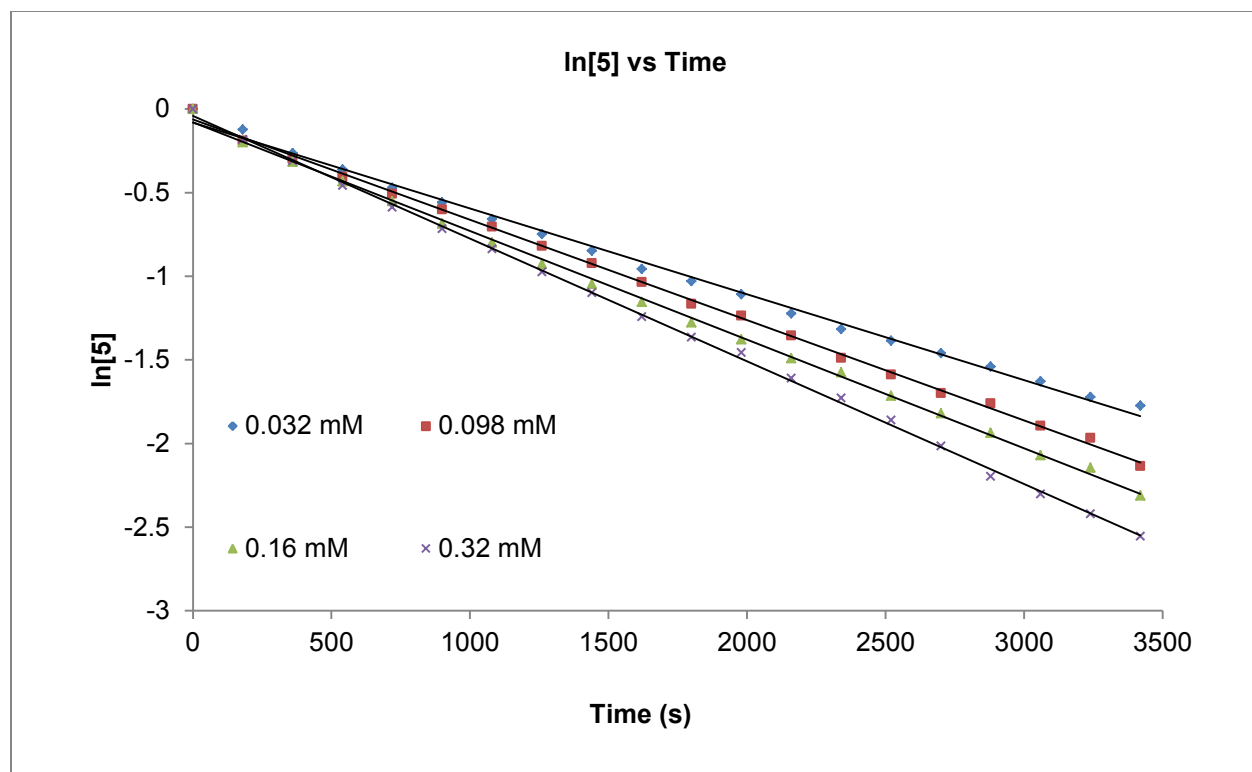
**Figure S9.**  $^1\text{H}$  NMR spectrum of  $(\text{POCOP})\text{Rh}(\text{C}_4\text{H}_7\text{N})$  (**10**) in  $\text{C}_6\text{D}_6$ .



### III. Kinetic Analysis

**Kinetic study of the C-N reductive elimination of NH(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)(p-C<sub>6</sub>H<sub>4</sub>Me) from (POCOP)Rh(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)(p-NH(C<sub>6</sub>H<sub>4</sub>Me)) (**5**).** (POCOP)Rh(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)(p-NH(C<sub>6</sub>H<sub>4</sub>Me)) (**5**) (11 mg, 0.016 mmol) was treated with p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br (four different experiments for four different concentrations of p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br: 2.3 μL, 0.016 mmol, 0.032 mM; 6.8 μL, 0.049 mmol, 0.098 mM; 11 μL, 0.081 mmol, 0.16 mM; 23 μL, 0.16 mmol, 0.32 mM) in toluene in a J. Young NMR tube. C<sub>6</sub>H<sub>5</sub>F (5.0 μL, 0.053 mmol) was added to each sample to act as an internal standard. The sample was inserted into the NMR probe, which was preheated to 105 °C. The disappearance of **5** was monitored by <sup>19</sup>F NMR at regular intervals for at least three half-lives.

Over the course of the reaction **5** (-62.3 ppm) was converted to (POCOP)Rh(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)(Br) (**2**) (-62.6 ppm) and free NH(p-NH(C<sub>6</sub>H<sub>4</sub>Me))(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>) (-61.7 ppm). Minor additional signals (-61.0 ppm and -62.4 ppm) were also observed during the kinetic studies; however, these signals disappeared for the reactions that were monitored to completion resulting in the final spectrum exclusively displaying signals for **2**, free NH(p-NH(C<sub>6</sub>H<sub>4</sub>Me))(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), and the remaining excess p-BrC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>.



**Figure S10.** Plot of  $\ln[5]$  vs time for the measurement of the rate constant for the C-N elimination of  $\text{NH}(\text{p-C}_6\text{H}_4\text{CF}_3)(\text{p-C}_6\text{H}_4\text{Me})$  at  $105\text{ }^\circ\text{C}$  for four different concentrations of  $\text{p-CF}_3\text{C}_6\text{H}_4\text{Br}$  (0.032 mM, 0.098 mM, 0.16 mM, and 0.32 mM) in toluene.

Rate constants:

$5.1(2) \times 10^{-4}$  for 0.032 mM

$6.0(1) \times 10^{-4}$  for 0.098 mM

$6.5(1) \times 10^{-4}$  for 0.16 mM

$7.3(1) \times 10^{-4}$  for 0.63 mM

Average  $t_{1/2} \approx 19$  min

**Note on the error calculation.** The errors in the values of the rate constants were taken to be twice the standard deviation ( $\sigma$ ) calculated using the LINEST function in the statistical analysis in MS excel.

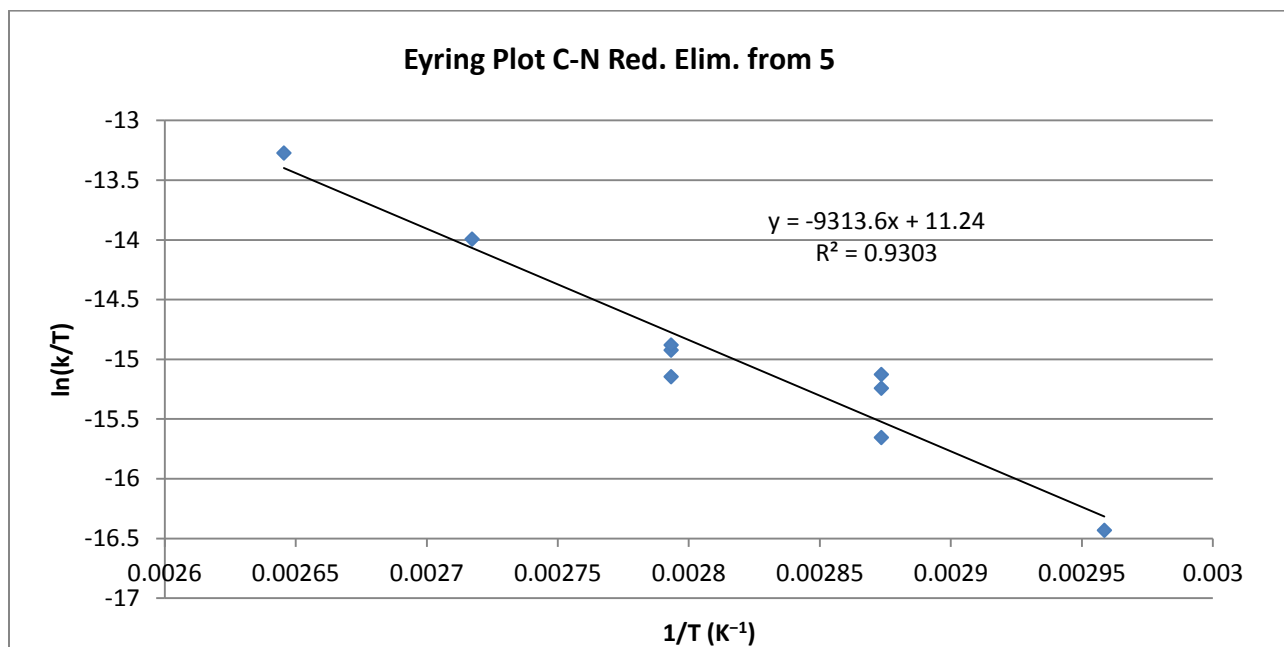
**Note on the temperature measurement.** The temperature inside the NMR probe was determined to be 95.2 °C via a chemical shift thermometer (neat ethylene glycol). Assume an uncertainty of 1 °C for this type of temperature measurements.

**Determination of activation parameters via Eyring plot.** **5** (11 mg, 0.016 mmol) was treated with p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br (6.8 μL, 0.049 mmol, 0.098 mM) in toluene in a J. Young NMR tube. C<sub>6</sub>H<sub>5</sub>F (5.0 μL, 0.053) was added to each sample to act as an internal standard. The sample was inserted into the NMR probe, which was preheated (to five different temperatures: 105 °C, 95 °C, 85 °C, 75 °C, and 65 °C). The reactions were monitored for a minimum of three half-lives. Over the course of the reaction **5** was converted to **2**. The rates of C-N reductive elimination from **5** at the different temperatures were determined by analysis of the disappearance of **5** by <sup>19</sup>F NMR (Table S1). An Eyring plot (Figure S11) was used to obtain the enthalpy and entropy of activation,  $\Delta H^\ddagger = 18.5(7)$  kcal/mol and  $\Delta S^\ddagger = -25(2)$  eu, respectively.

**Note on the error calculation for the Eyring plot.** The temperature inside the NMR probe was determined via a chemical shift thermometer (neat ethylene glycol). Assume an uncertainty of 1 °C for this type of temperature measurements. Errors in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were determined using the error propagation formulas presented by Girolami et al.<sup>2</sup>

**Table S1.** Rates of C-N reductive elimination for (POCOP)Rh(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)(p-NH(C<sub>6</sub>H<sub>4</sub>Me)) from 75 °C - 105 °C and corresponding Eyring plot parameters.

<i>T</i> (°C)	<i>T</i> (K)	<i>Rate</i> (s <sup>-1</sup> )	<i>ln</i> ( <i>k</i> / <i>T</i> )	<i>1/T</i> (K <sup>-1</sup> )
105	378	6.50 × 10 <sup>-4</sup>	-13.3	2.64 × 10 <sup>-3</sup>
95	368	3.08 × 10 <sup>-4</sup>	-14.0	2.71 × 10 <sup>-3</sup>
85	358	1.23 × 10 <sup>-4</sup>	-14.9	2.79 × 10 <sup>-3</sup>
75	348	8.36 × 10 <sup>-5</sup>	-15.2	2.87 × 10 <sup>-3</sup>
65	338	2.47 × 10 <sup>-5</sup>	-16.4	2.96 × 10 <sup>-3</sup>



**Figure S11.** Eyring plot for the C-N reductive elimination from **5**.

## IV. Catalytic Reactions

**Catalytic coupling reaction of *p*-FC<sub>6</sub>H<sub>4</sub>Br and NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) with 1 as catalyst. 1** (3.3 mg, 0.0068 mmol) was combined with *p*-FC<sub>6</sub>H<sub>4</sub>Br (25 μL, 0.23 mmol), NaO<sup>t</sup>Pent (38 mg, 0.34 mmol), NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) (25 μL, 0.27 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (5.0 μL, 0.041 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by <sup>19</sup>F NMR revealed NH(*p*-C<sub>6</sub>H<sub>4</sub>F)(C<sub>6</sub>H<sub>5</sub>) (32%), C<sub>6</sub>H<sub>5</sub>F (10%), and *p*-FC<sub>6</sub>H<sub>4</sub>Br (58%).

**Catalytic coupling reaction of *p*-FC<sub>6</sub>H<sub>4</sub>Br and *p*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) with 1 as catalyst. 1** (3.3 mg, 0.0068 mmol) was combined with *p*-FC<sub>6</sub>H<sub>4</sub>Br (25 μL, 0.23 mmol), NaO<sup>t</sup>Pent (38 mg, 0.34 mmol), *p*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) (29 mg, 0.27 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (5.0 μL, 0.041 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by <sup>19</sup>F NMR revealed NH(*p*-C<sub>6</sub>H<sub>4</sub>F)(C<sub>6</sub>H<sub>5</sub>) (46%), C<sub>6</sub>H<sub>5</sub>F (11%), and *p*-FC<sub>6</sub>H<sub>4</sub>Br (43%).

**Catalytic coupling reaction of *p*-FC<sub>6</sub>H<sub>4</sub>Br and *o*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) with 1 as catalyst. 1** (3.3 mg, 0.0068 mmol) was combined with *p*-FC<sub>6</sub>H<sub>4</sub>Br (25 μL, 0.23 mmol), NaO<sup>t</sup>Pent (38 mg, 0.34 mmol), *o*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) (29 μL, 0.27 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (5.0 μL, 0.041 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by <sup>19</sup>F NMR revealed NH(*p*-C<sub>6</sub>H<sub>4</sub>F)(C<sub>6</sub>H<sub>5</sub>) (33%), C<sub>6</sub>H<sub>5</sub>F (10%), and *p*-FC<sub>6</sub>H<sub>4</sub>Br (57%).

**Catalytic coupling reaction of *p*-FC<sub>6</sub>H<sub>4</sub>Cl and NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) with 1 as catalyst. 1** (3.4 mg, 0.0071 mmol) was combined with *p*-FC<sub>6</sub>H<sub>4</sub>Cl (25 μL, 0.23 mmol), NaO<sup>t</sup>Pent (38 mg, 0.35 mmol), NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) (26 μL, 0.28 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (5.0 μL, 0.041 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by <sup>19</sup>F NMR revealed NH(*p*-C<sub>6</sub>H<sub>4</sub>F)(C<sub>6</sub>H<sub>5</sub>) (20%), C<sub>6</sub>H<sub>5</sub>F (8%), and *p*-FC<sub>6</sub>H<sub>4</sub>Cl (72%).

**Catalytic coupling reaction of *p*-FC<sub>6</sub>H<sub>4</sub>Cl and *p*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) with 1 as catalyst. 1** (3.4 mg, 0.0071 mmol) was combined with *p*-FC<sub>6</sub>H<sub>4</sub>Cl (25 μL, 0.23 mmol), NaO<sup>t</sup>Pent (38 mg, 0.35 mmol), *p*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) (30 mg, 0.28 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (5.0 μL, 0.041 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by <sup>19</sup>F NMR revealed NH(*p*-C<sub>6</sub>H<sub>4</sub>F)(*p*-C<sub>6</sub>H<sub>4</sub>Me) (27%), C<sub>6</sub>H<sub>5</sub>F (8%), and *p*-FC<sub>6</sub>H<sub>4</sub>Cl (65%).

**Catalytic coupling reaction of *p*-FC<sub>6</sub>H<sub>4</sub>Cl and *o*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) with 1 as catalyst. 1** (3.4 mg, 0.0071 mmol) was combined with *p*-FC<sub>6</sub>H<sub>4</sub>Cl (25 μL, 0.23 mmol), NaO<sup>t</sup>Pent (38 mg, 0.35 mmol), *o*-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me) (30 μL, 0.28 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (5.0 μL, 0.041 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by <sup>19</sup>F NMR revealed NH(*p*-C<sub>6</sub>H<sub>4</sub>F)(*o*-C<sub>6</sub>H<sub>4</sub>Me) (22%), C<sub>6</sub>H<sub>5</sub>F (9%), and *p*-FC<sub>6</sub>H<sub>4</sub>Cl (69%).

**Catalytic coupling reaction of *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br and NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) with 1 as catalyst. 1** (2.7 mg, 0.0054 mmol) was combined with *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br (25 μL, 0.18 mmol), NaO<sup>t</sup>Pent (30 mg, 0.27 mmol), NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) (20 μL, 0.22 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>F (10 μL,

0.11 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by  $^{19}\text{F}$  NMR revealed no conversion from  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$ .

**Catalytic coupling reaction of  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$  and  $p\text{-NH}_2(\text{C}_6\text{H}_4\text{Me})$  with **1** as catalyst.**

**1** (2.7 mg, 0.0054 mmol) was combined with  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$  (25  $\mu\text{L}$ , 0.18 mmol),  $\text{NaO}^t\text{Pent}$  (30 mg, 0.27 mmol),  $p\text{-NH}_2(\text{C}_6\text{H}_4\text{Me})$  (23 mg, 0.22 mmol), and partially dissolved in toluene.  $\text{C}_6\text{H}_5\text{F}$  (10  $\mu\text{L}$ , 0.11 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by  $^{19}\text{F}$  NMR revealed no conversion from  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$ .

**Catalytic coupling reaction of  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$  and  $o\text{-NH}_2(\text{C}_6\text{H}_4\text{Me})$  with **1** as catalyst.**

**1** (2.7 mg, 0.0054 mmol) was combined with  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$  (25  $\mu\text{L}$ , 0.18 mmol),  $\text{NaO}^t\text{Pent}$  (30 mg, 0.27 mmol),  $o\text{-NH}_2(\text{C}_6\text{H}_4\text{Me})$  (23  $\mu\text{L}$ , 0.22 mmol), and partially dissolved in toluene.  $\text{C}_6\text{H}_5\text{F}$  (10  $\mu\text{L}$ , 0.11 mmol) was added to the reaction to act as an internal standard. The reaction mixture immediately turned dark purple. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by  $^{19}\text{F}$  NMR revealed no conversion from  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$ .

**Control catalytic reaction using  $[(\text{cod})\text{RhCl}]_2$ .**  $[(\text{cod})\text{RhCl}]_2$  (1.7 mg, 0.0068 mmol Rh) was combined with  $p\text{-FC}_6\text{H}_4\text{Br}$  (25  $\mu\text{L}$ , 0.23 mmol),  $\text{NaO}^t\text{Pent}$  (38 mg, 0.34 mmol),  $\text{NH}_2(\text{C}_6\text{H}_5)$  (25  $\mu\text{L}$ , 0.27 mmol), and partially dissolved in toluene.  $\text{C}_6\text{H}_5\text{CF}_3$  (5.0  $\mu\text{L}$ , 0.041 mmol) was added to the reaction to act as an internal standard. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by  $^{19}\text{F}$  NMR revealed no new products and no change in the concentration of  $p\text{-FC}_6\text{H}_4\text{Br}$ .

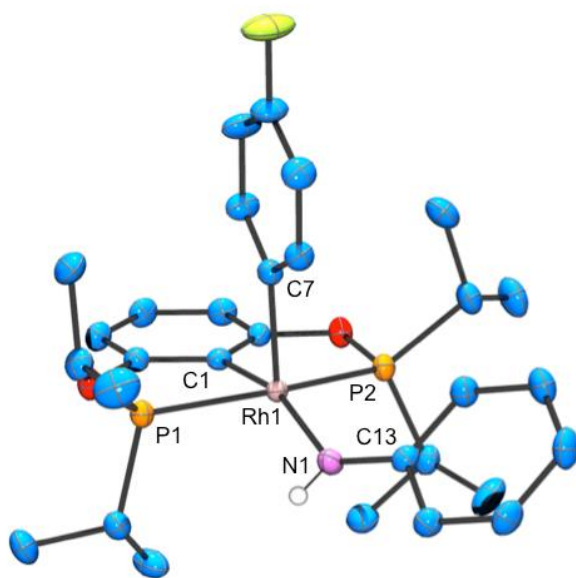
**Control catalytic reaction using  $[(\text{cod})\text{RhCl}]_2/\text{PCy}_3$ .**  $[(\text{cod})\text{RhCl}]_2$  (1.7 mg, 0.0068 mmol Rh) was combined with  $\text{PCy}_3$  (4.0 mg, 0.014 mmol),  $p\text{-FC}_6\text{H}_4\text{Br}$  (25  $\mu\text{L}$ , 0.23 mmol),

NaO<sup>t</sup>Pent (38 mg, 0.34 mmol), NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) (25 μL, 0.27 mmol), and partially dissolved in toluene. C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (5.0 μL, 0.041 mmol) was added to the reaction to act as an internal standard. The reaction was heated at 115 °C for 48 h. Analysis of the reaction by <sup>19</sup>F NMR revealed no new products and no change in the concentration of *p*-FC<sub>6</sub>H<sub>4</sub>Br.



#### IV. X-ray Crystallography

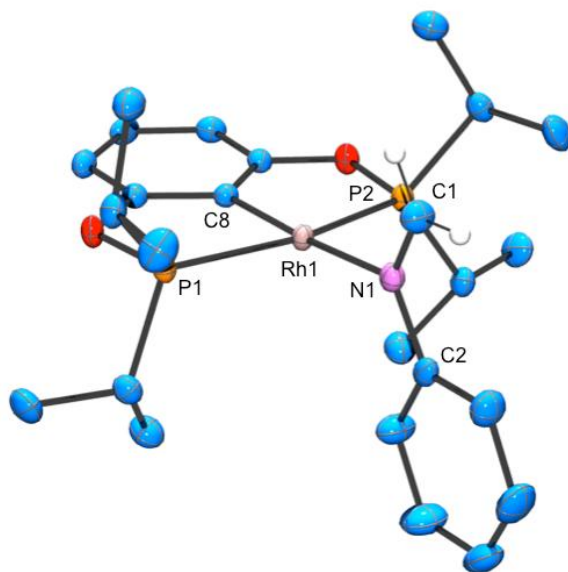
**X-Ray data collection, solution, and refinement for (POCOP)Rh(*p*-C<sub>6</sub>H<sub>4</sub>F)(NH(C<sub>6</sub>H<sub>5</sub>)) (6).** A single purple crystal of suitable size and quality (0.05 × 0.06 × 0.12 mm) was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop and placed in a cold stream of nitrogen (110 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube,  $K_{\alpha} = 0.71073 \text{ \AA}$ ). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.<sup>3</sup> An absorption correction was applied using SADABS.<sup>4</sup> The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . The structure was solved in the orthorhombic *Pbca* space group using XS<sup>5</sup> (incorporated in X-Seed). This symmetry was confirmed by PLATON.<sup>6</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on  $F^2$ ) to convergence.



**Figure S12.** POV-Ray rendition of the ORTEP drawing (50% thermal ellipsoids) of (POCOP)Rh(*p*-C<sub>6</sub>H<sub>4</sub>F)(NH(C<sub>6</sub>H<sub>5</sub>)) (**6**) showing selected atom labeling. Hydrogen atoms are omitted for clarity except for the N-H. Selected bond distances (Å) and angles (°): Rh1-P1, 2.3218(6); Rh1-P2, 2.2891(6); Rh1-C1, 2.019(2); Rh1-C7, 2.012(2); Rh1-N1, 2.076(2); P1-Rh1-P2, 157.79(2); C1-Rh1-N1, 162.38(7); Rh1-N1-C13, 135.3(1).

**X-Ray data collection, solution, and refinement for (POCOP)Rh(N(Ph)CH<sub>2</sub>) (**9**).** A single orange crystal of suitable size and quality (0.6 × 0.9 × 0.05 mm) was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop and placed in a cold stream of nitrogen (110 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K<sub>α</sub> = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.<sup>3</sup> An absorption correction was applied using SADABS.<sup>4</sup> The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F<sup>2</sup>. The structure was solved in the monoclinic P 2<sub>1</sub>/m space group using XS<sup>5</sup> (incorporated in X-Seed). Half of the structure was symmetry generated across the central mirror plane. This

symmetry was confirmed by PLATON.<sup>6</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on  $F^2$ ) to convergence.



**Figure S13.** POV-Ray rendition of the ORTEP drawing (50% thermal ellipsoids) of (POCOP)Rh(*p*-C<sub>6</sub>H<sub>4</sub>F)(N(Ph)CH<sub>2</sub>) (**9**) showing selected atom labeling. Hydrogen atoms are omitted for clarity except for the N-H. Selected bond distances (Å) and angles (°): Rh1-P1, 2.245(1); Rh1-N1, 2.166(3); Rh1-C8, 1.993(3); N1-C1, 1.272(3); N1-C2, 1.440(3); P1-Rh1-P2, 158.40(2); C8-Rh1-N1, 176.13(9); C1-N1-C2, 119.9(2).

## VI. Computational Details

All computations were carried out with the Gaussian09 program.<sup>7</sup> All of the geometries were fully optimized in toluene solvent via the PCM model<sup>8</sup> at the M06<sup>9</sup> level of theory. The Stuttgart basis set and the associated effective core potential (ECP) was used for Rh atom, and an all-electron 6-311G(d,p) basis set was used for the other atoms. The harmonic vibrational frequency calculations were performed to ensure that either a minimum or first-order saddle point was obtained.

## VII. References

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