

## Supporting Information

### Hydrogenation and Hydrosilylation of Nitrous Oxide Homogeneously

#### Catalyzed by a Metal Complex

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**Materials:** THF and toluene were distilled freshly over sodium and kept over 4Å MS. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. Complexes **5**,<sup>1</sup> **6**,<sup>2</sup> **13**,<sup>3</sup> and **15**<sup>1</sup> were prepared according to the known literature.<sup>1-3</sup> The precursors for **8**,<sup>4</sup> **10**,<sup>5</sup> **11**,<sup>6</sup> and **12**<sup>7</sup> were prepared according to the known literature. All reactions were carried out with stirring bar under an atmosphere of purified nitrogen in a Braun glovebox equipped or using standard Schlenk techniques. Reaction temperatures were reported as the temperatures of the oil bath. Nuclear magnetic resonance spectra (<sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>31</sup>P NMR) were recorded with a Bruker-300 MHz spectrometer (300 MHz, <sup>1</sup>H at 300 MHz, <sup>13</sup>C at 75 MHz, and <sup>31</sup>P at 121 MHz) or Bruker-400 MHz spectrometer (400 MHz, <sup>1</sup>H at 400 MHz, <sup>13</sup>C at 101 MHz). Chemical shifts are reported in parts per million (ppm, δ). In <sup>1</sup>H NMR, the chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. In <sup>13</sup>C{<sup>1</sup>H} NMR measurements, the signals of deuterated solvents were used as a reference. <sup>31</sup>P NMR chemical shifts are reported in parts per million downfield from H<sub>3</sub>PO<sub>4</sub> and referenced to an external 85% solution of phosphoric acid in D<sub>2</sub>O. Coupling constants were reported in Hertz (Hz). Data for <sup>1</sup>H NMR spectra were reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, coupling constant (Hz), and integration).

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**1. Table S1:  $^1\text{H}$  NMR of Ru–H bonds and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra data of complexes **5**, **14**, and **15** in THF<sup>a</sup>**

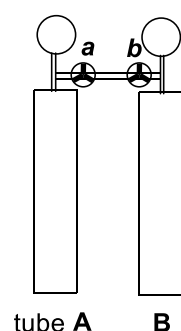
Entry	Complex	$^1\text{H}$ NMR for Ru-H	$^{31}\text{P}\{^1\text{H}\}$ NMR
1	<b>5</b>	-20.1 (t, $^2J_{\text{PH}} = 18.0$ Hz)	67.0 (d, $^2J_{\text{PP}} = 235.4$ Hz), 60.1 (d, $^2J_{\text{PP}} = 235.4$ Hz) <sup>b</sup>
2	<b>15</b>	-5.5 (t, $^2J_{\text{PH}} = 18.0$ Hz)	107.0 (s)
3	<b>14</b>	-14.7 (t, $^2J_{\text{PH}} = 18.0$ Hz)	74.0 (s)

<sup>a</sup> All the data were obtained in normal THF. Chemical shifts are reported in parts per million (ppm,  $\delta$ ) and are referenced to residual solvent (THF,  $\delta=3.58$  ppm for  $\text{CH}_2\text{O}$ , for  $^1\text{H}$  NMR) and external standard sample ( $\text{H}_3\text{PO}_4$ ,  $\delta=0$  ppm, for  $^{31}\text{P}$  NMR). <sup>b</sup> AB system centered at 67.0 and 60.1, respectively.

**2. Determination of solubility of  $\text{N}_2\text{O}$  in THF.**

To determine the solubility and total amount of  $\text{N}_2\text{O}$  in THF at rt (20 °C), the following experiments using two Fisher-Porter tubes have been done:

Two Fisher-Porter



The experiments are based on the balanced pressure between tube **A** and **B**

*Procedure* for **Exp. 1** and **2**: Two 90 mL of Fisher-Porter tubes **A** and **B** were connected and controlled by two cock valves **a** and **b**, in which tube **A** was pumped and kept in a vacuum while tube **B** was filled with high pressure of  $\text{N}_2\text{O}$ . After switching on cock valves **a** and **b**, the pressure of tube **A** reached the pressure as same as tube **B**. In **Exp. 1**, no THF was used in tube **A** as a control experiment. To be mentioned, due to the exist of the connecting tube between tube **A** and **B**, the amount decreasing in tube **B** was not equal to the amount increasing in tube **A**.

	Before switching on <b>a</b> and <b>b</b> :	After switching on <b>a</b> and <b>b</b> :
<b>Exp. 1</b>	Tube <b>A</b> : no THF under vacuum; Tube <b>B</b> : 105 psi of $\text{N}_2\text{O}$	Tube <b>A</b> and Tube <b>B</b> : 47 psi of $\text{N}_2\text{O}$
<b>Exp. 2</b>	Tube <b>A</b> : with 5 mL of THF under vacuum; Tube <b>B</b> : 105 psi of $\text{N}_2\text{O}$	Tube <b>A</b> and Tube <b>B</b> : 42.5 psi of $\text{N}_2\text{O}$

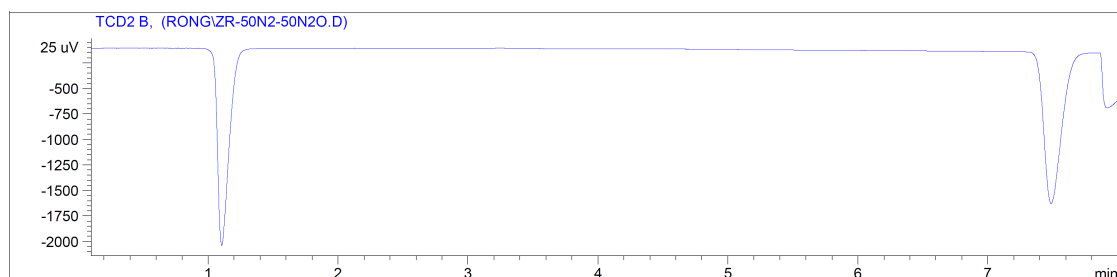
Based on **exp. 1**: the total volume of the system (including 2 Fisher-Porter tubes and 1 connecting tube) could be calculated:

$$* P_1V_1 = P_2V_{\text{total}}$$

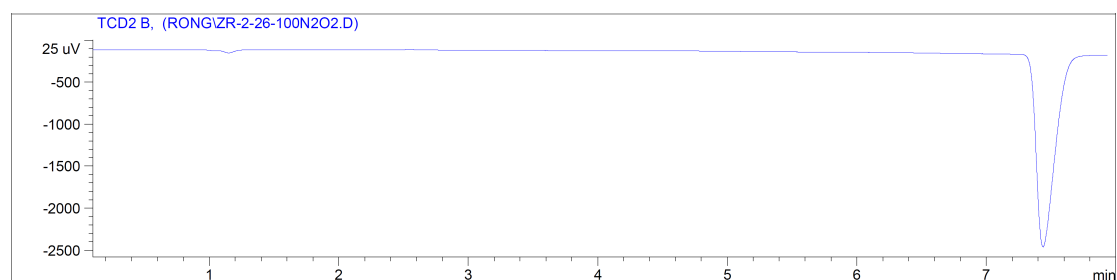


SUPPORT 45/60 CARBOXEN™ 1000, Packed Column. Inlets: 87 °C; Flow: 29.1; Oven: 35 °C, hold 2 min; 10 °C/min to 60 °C, hold 0 min; 30 °C/min to 200 °C. Carrier Gas: He. Detector: TCD 250 °C.

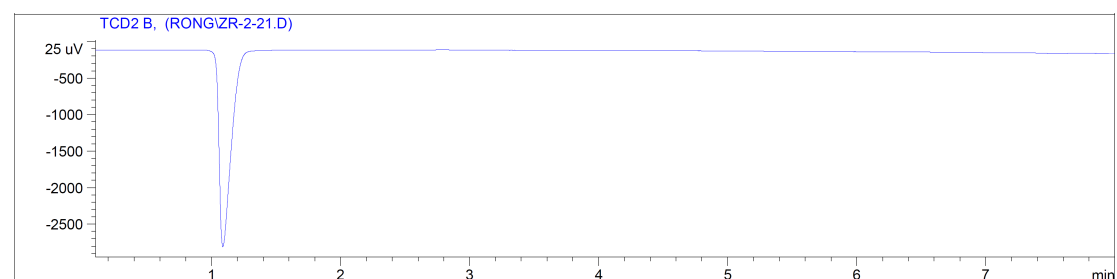
1) Control experiment: 50% N<sub>2</sub> + 50% N<sub>2</sub>O



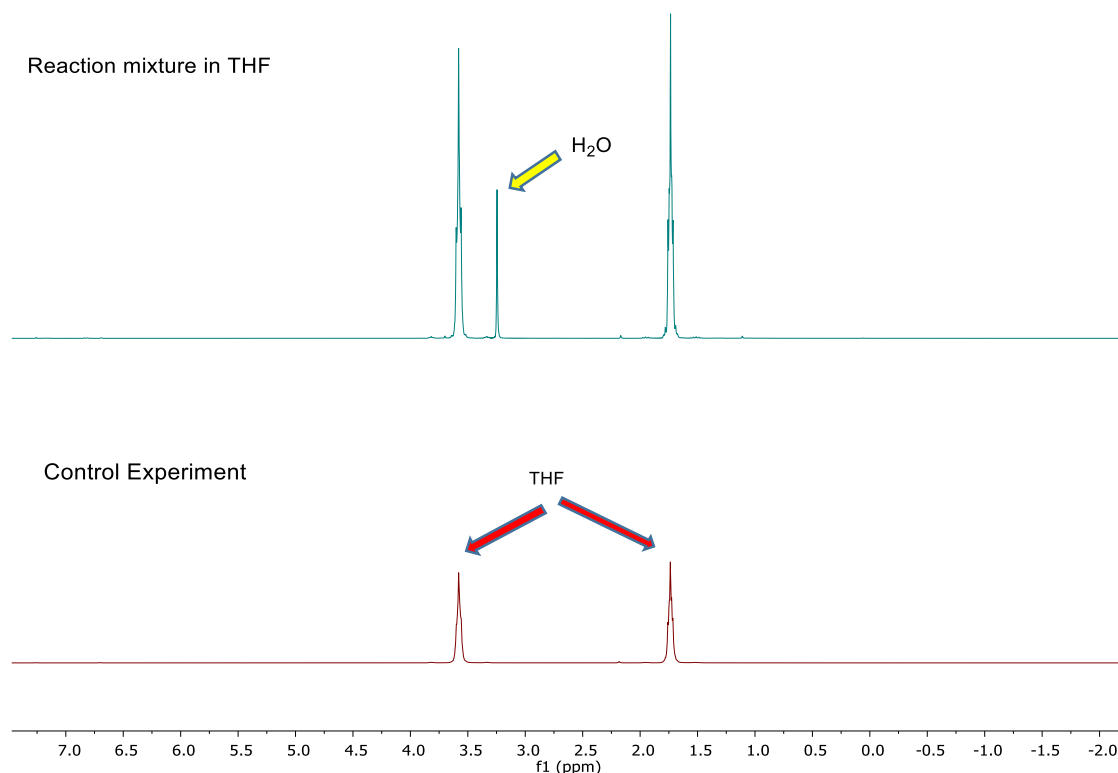
2) Control experiment: 100% N<sub>2</sub>O



3) Gas phase of final product: N<sub>2</sub>



**II. H<sub>2</sub>O determination by <sup>1</sup>H NMR:**



To quantify the amount of H<sub>2</sub>O, mesitylene was added as internal standard based on 9 methyl hydrogens of mesitylene with calibration.

**i. Calibration experiments:**

To a 20 mL vial were added mesitylene, THF, and H<sub>2</sub>O, and the resulting mixture was examined by <sup>1</sup>H NMR.

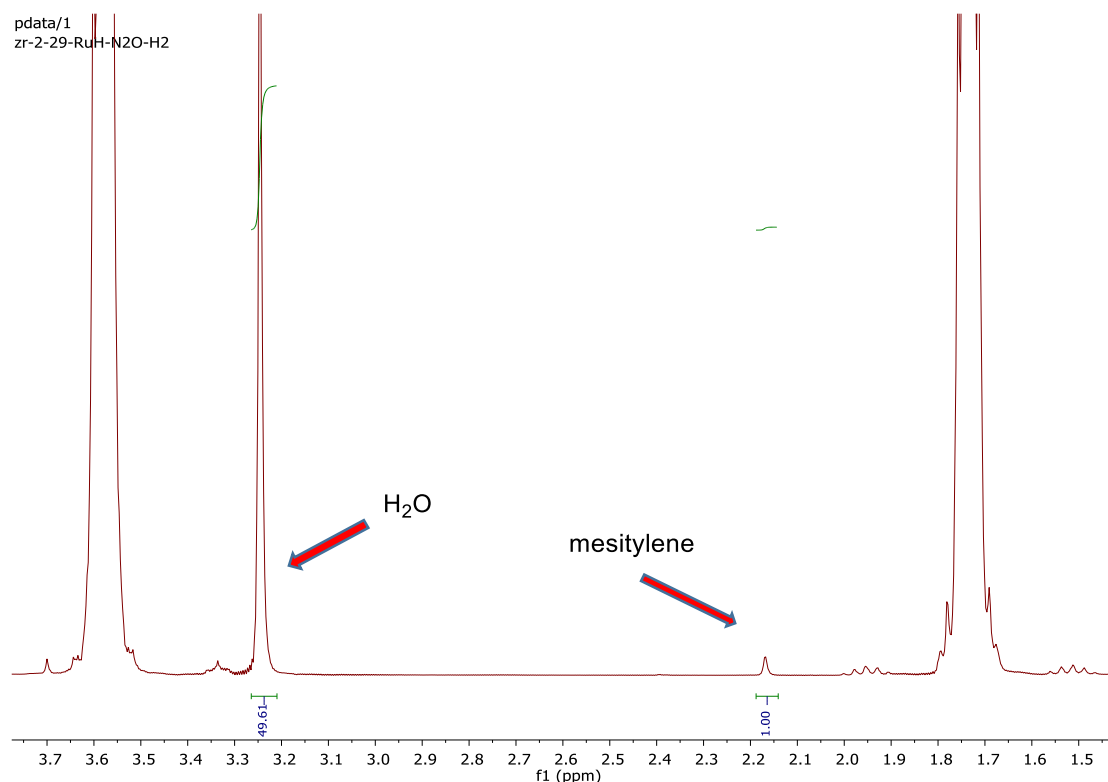
<sup>1</sup>H NMR conditions: Bruker-300 MHz spectrometer; d1 = 10 seconds, r1 = 1, and ns = 16.

Exp.	Mesitylene / mg	H <sub>2</sub> O / μL	(mmols H <sub>2</sub> O × 2) / (mmols mesitylene × 9)		Calibration
			Calculated	Observed	
1	9.7	10	1.53/1	1.97/1	1.53/1.97 = 0.777
2	5.5	20	5.39/1	7.12/1	5.39/7.12 = 0.757
3	11.3	30	3.93/1	4.84/1	3.93/4.84 = 0.812
4	8.3	50	8.93/1	11.68/1	8.93/11.68 = 0.762
5	7.9	70	13.13/1	16.47/1	13.13/16.47 = 0.797

Average of calibration numbers = 0.781

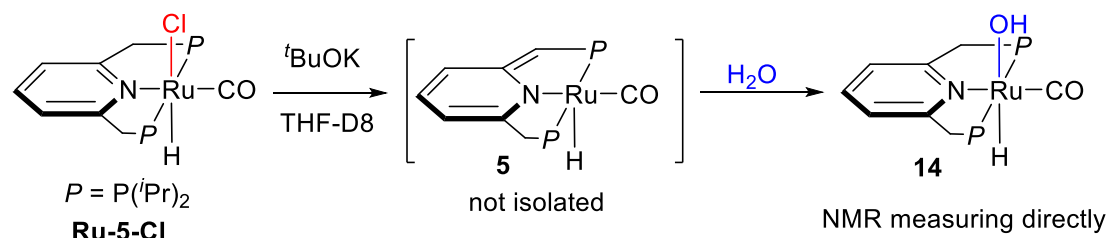
**ii. Determination of H<sub>2</sub>O amount in the reaction mixture:** 8.6 mg of mesitylene was added as internal standard into the reaction mixture, in which 13.0 mmol of N<sub>2</sub>O was used (see procedure on page S3). <sup>1</sup>H NMR analysis indicated that 12.5 mmol of H<sub>2</sub>O (96% yield based on N<sub>2</sub>O) was generated after calibration.

Yield of H<sub>2</sub>O = 12.5/13.0 = 96%



#### 4. Formation of complex **14**

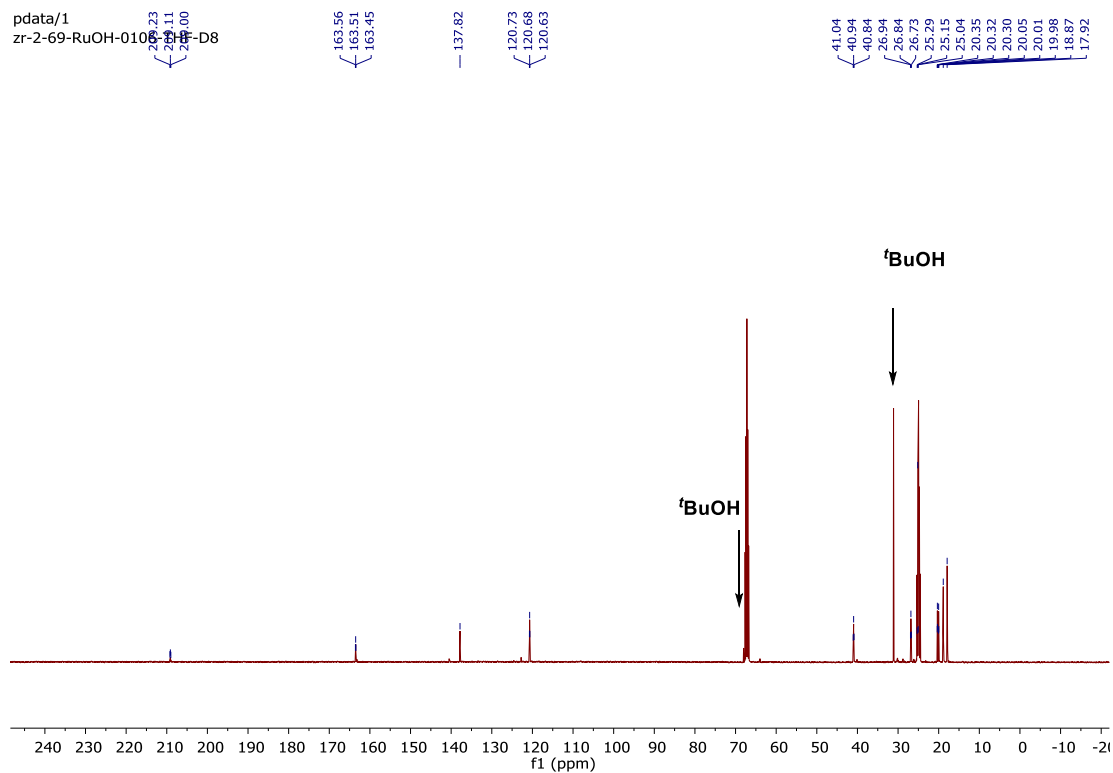
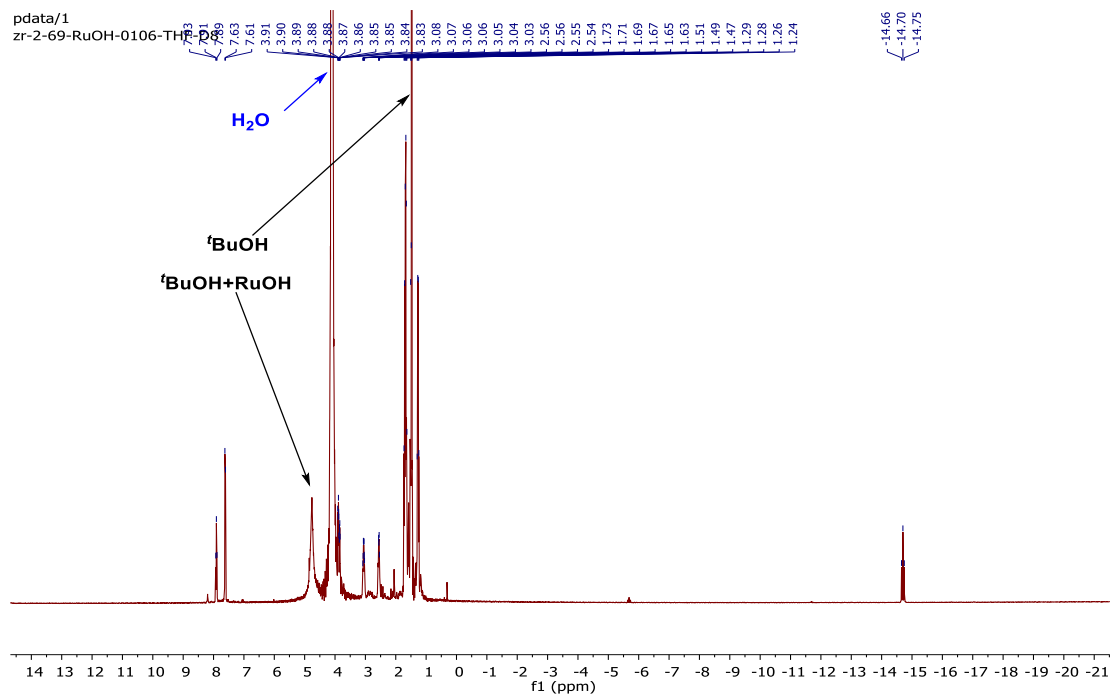
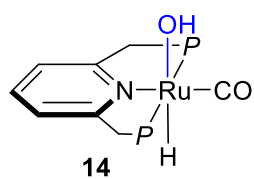
Complex **14** was prepared by deprotonation of complex (PNP)RuH(CO)Cl followed by addition of water in THF- $d_8$ . It is stable in the presence of excess water, and was characterized in situ.



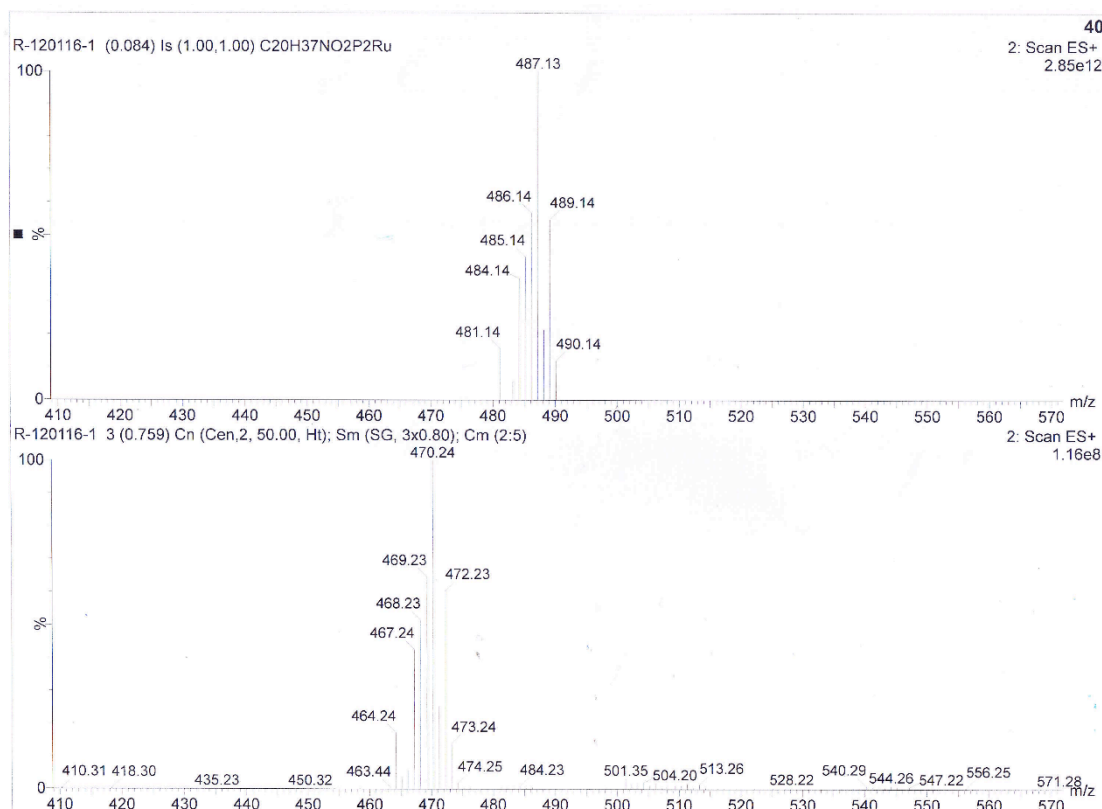
*Procedure:* To a dried NMR tube were added (PNP)RuHCl(CO) **Ru-5-Cl** (10.3 mg, 0.02 mmol),  $t\text{BuOK}$  (2.7 mg, 1.2 equiv, 0.024 mmol), and THF- $d_8$  (0.7 mL) in a glovebox. The resulting mixture was shaken at room temperature for 3 h to afford a solution of **5** in THF- $d_8$ .<sup>1</sup> After injection of 0.1 mL of  $\text{H}_2\text{O}$ , the mixture was shaken for an additional 15 min. Complex **14** was obtained according to NMR analysis, which was performed *in-situ* without further purification.

The solution is yellow;  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ )  $\delta$  7.91 (t,  $^3J_{\text{HH}} = 8.0$  Hz, 1H, Ar-H), 7.62 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, Ar-H), 3.90-3.82 (m,  $\text{CH}_2 \times 2$ ), 3.10-3.10 (m,  $\text{CH} \times 2$ ), 3.62-3.50 (m,  $\text{CH} \times 2$ ), 1.75-1.60 (m,  $\text{CH}_3 \times 2$ ), 1.55-1.40 (m,  $\text{CH}_3 \times 2$ ), -14.7 (t,  $^2J_{\text{HP}} = 18$  Hz, Ru-H);  $^{13}\text{C}$  NMR (101 MHz, THF- $d_8$ )  $\delta$  209.1 (t,  $^2J_{\text{CP}} = 11.7$  Hz, CO), 163.5 (t,  $^2J_{\text{CP}} = 5.6$  Hz, Py-C), 137.8 (s, Py-CH), 120.7 (t,  $^3J_{\text{CP}} = 5.0$  Hz, Py-CH), 40.9 (t,  $^1J_{\text{CP}} = 9.8$  Hz,  $\text{CH}_2$ ), 26.8 (t,  $^1J_{\text{CP}} = 10.9$  Hz, CH), 25.2 (t,  $^1J_{\text{CP}} = 12.5$  Hz, CH), 20.3 (t,  $^2J_{\text{CP}} = 2.6$  Hz,  $\text{CH}_3$ ), 20.0 (t,  $^2J_{\text{CP}} = 3.5$  Hz,  $\text{CH}_3$ ), 18.9 (s,  $\text{CH}_3$ ), 17.9 (s,  $\text{CH}_3$ ).

In-situ  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR of complex **14**

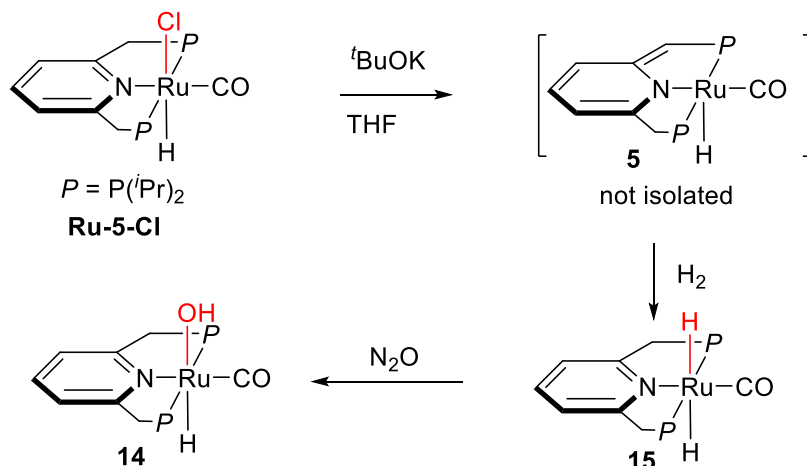


MS-ESI spectra for **14**: Upper: calculated data of **14** (C<sub>20</sub>H<sub>37</sub>NO<sub>2</sub>P<sub>2</sub>Ru); Lower: observed data for C<sub>20</sub>H<sub>36</sub>NOP<sub>2</sub>Ru, which corresponds to [M-OH]<sup>+</sup>.



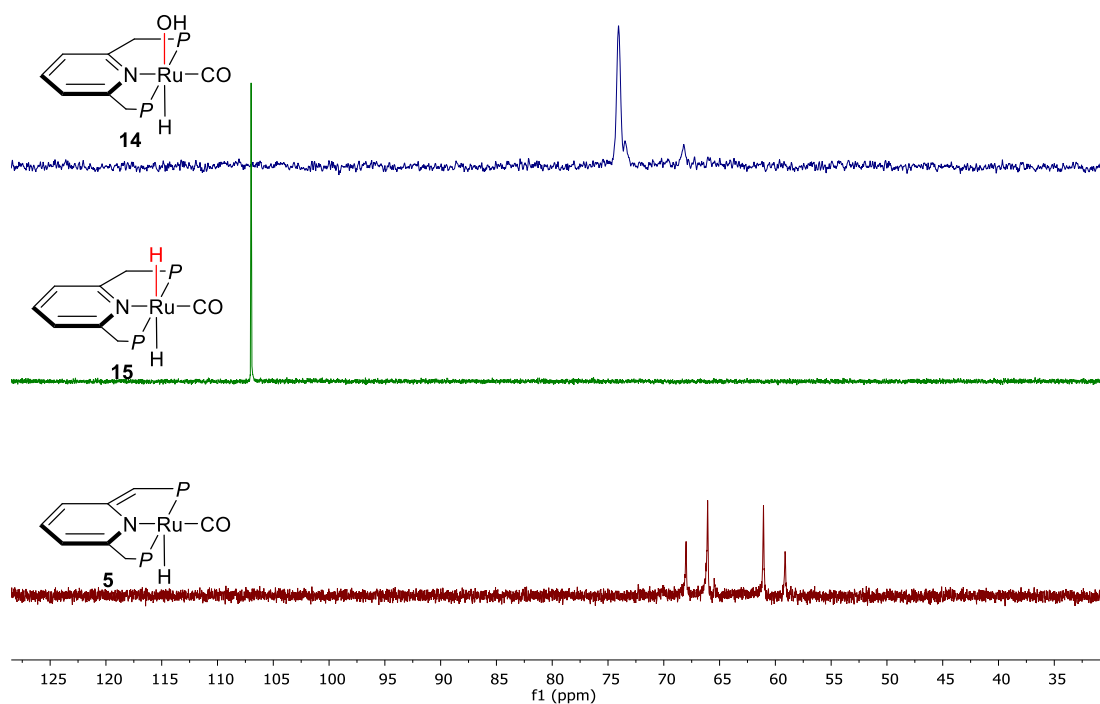
## 5. Mechanistic Studies.

### i. Reaction of **5** with H<sub>2</sub>, followed by N<sub>2</sub>O

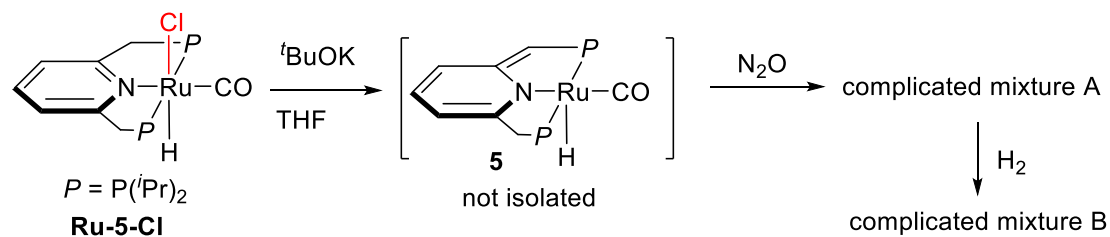


*Procedure:* To a dried 4 mL vial were added (PNP)RuHCl(CO) **Ru-5-Cl** (5.4 mg, 0.01 mmol), <sup>t</sup>BuOK (1.3 mg, 0.01 mmol), and THF (0.5 mL) in a glovebox. The resulting mixture was stirred at room temperature for 2 h to afford a solution of **5** in THF.<sup>1</sup> After transfer into a dried NMR tube, 0.25 mL of H<sub>2</sub> (1 equiv) was injected. The mixture was shaken for a few seconds. The orange color changed to light yellow, which corresponds to complex **15** according to NMR analysis. Then 0.5 mL of N<sub>2</sub>O (2 equiv) was injected. After 24 h, <sup>31</sup>P NMR analysis showed full conversion of complex **15** to complex **14**.

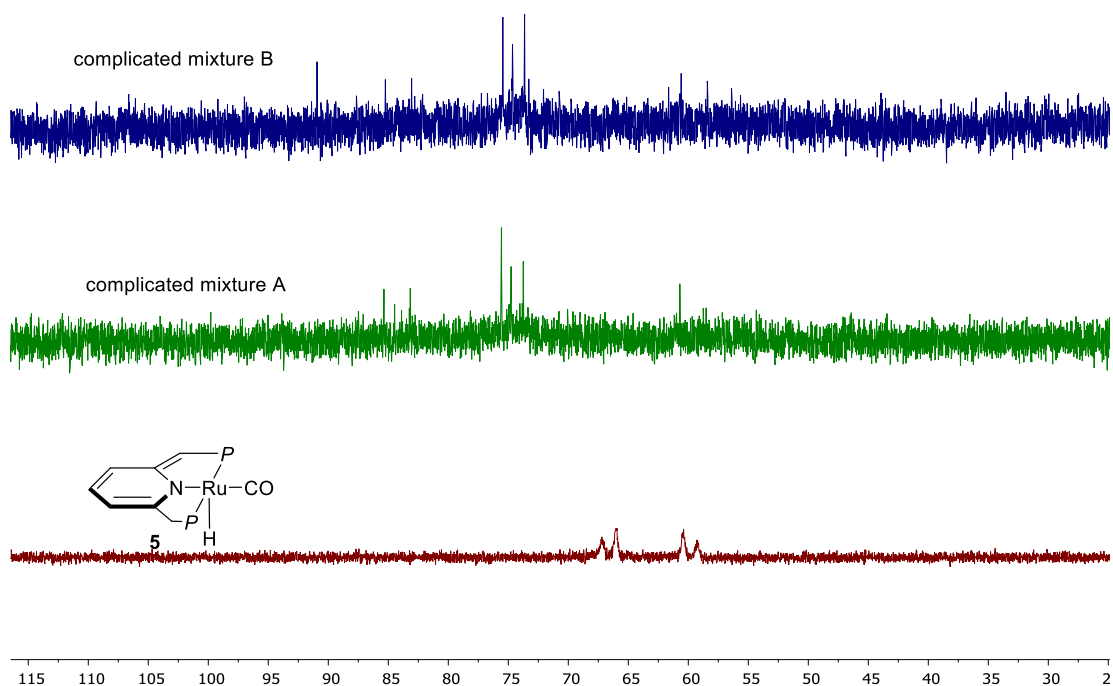




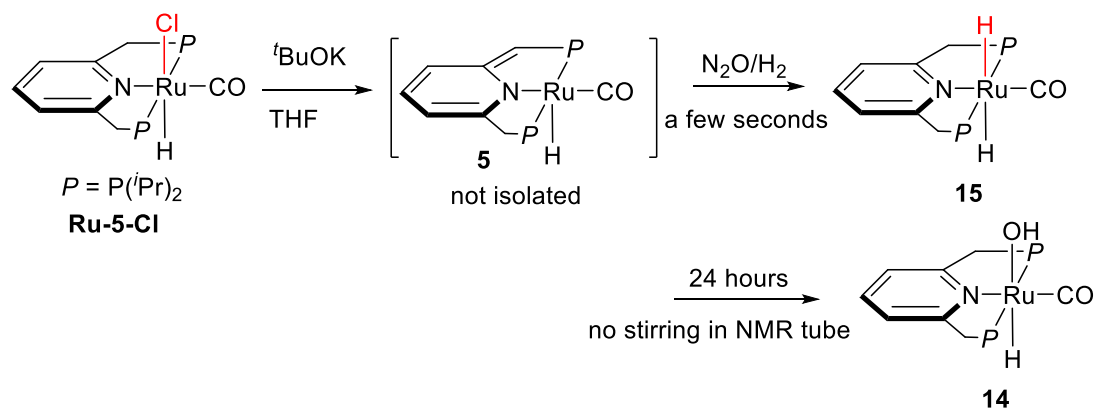
## ii. Reaction of 4 with N<sub>2</sub>O, followed by H<sub>2</sub>



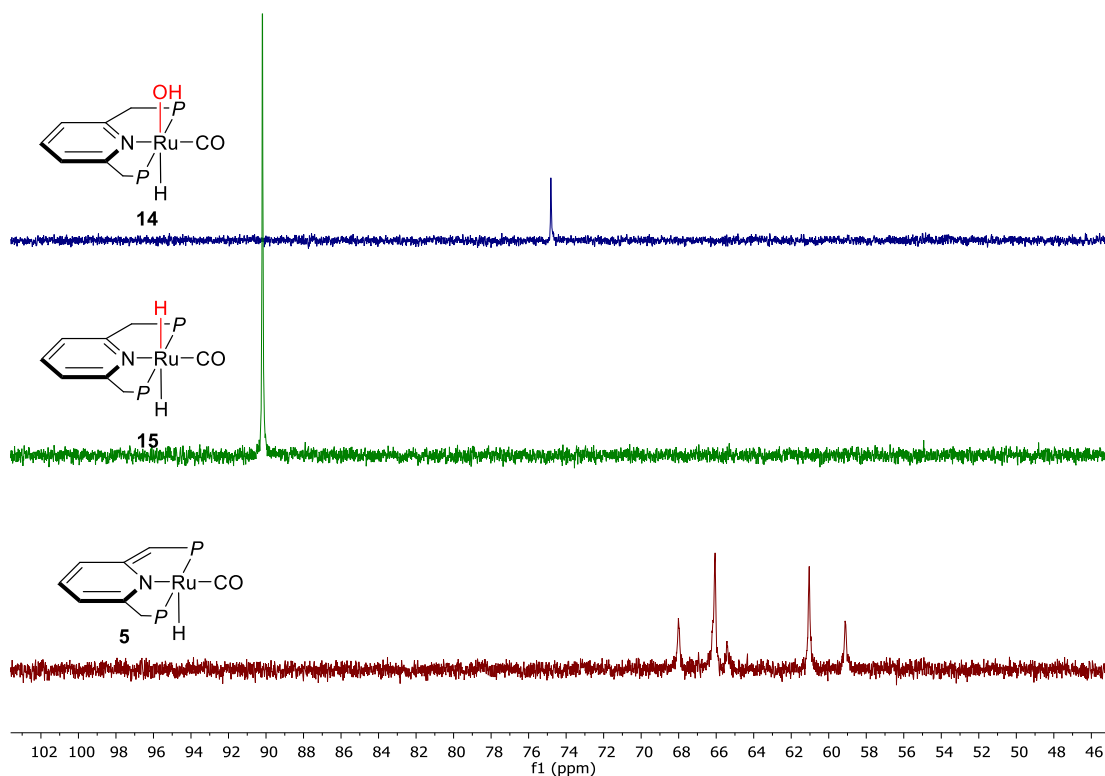
*Procedure:* To a dried 4 mL vial were added (PNP)RuHCl(CO) **Ru-5-Cl** (3.3 mg, 0.006 mmol), <sup>t</sup>BuOK (0.9 mg, 0.008 mmol), and THF (0.5 mL) in a glovebox. The resulting mixture was stirred at room temperature for 15 h to afford a solution of **5** in THF.<sup>1</sup> After transfer into a dried NMR tube, excess N<sub>2</sub>O was purged for changing the N<sub>2</sub> atmosphere to N<sub>2</sub>O. The mixture was shaken for an additional 2 h. A complicated mixture A was obtained according to <sup>31</sup>P NMR analysis. Changing the N<sub>2</sub>O atmosphere to H<sub>2</sub> by purging H<sub>2</sub> gas followed by shaking for another 24 h, afforded a complicated mixture B, which is almost the same as mixture A.



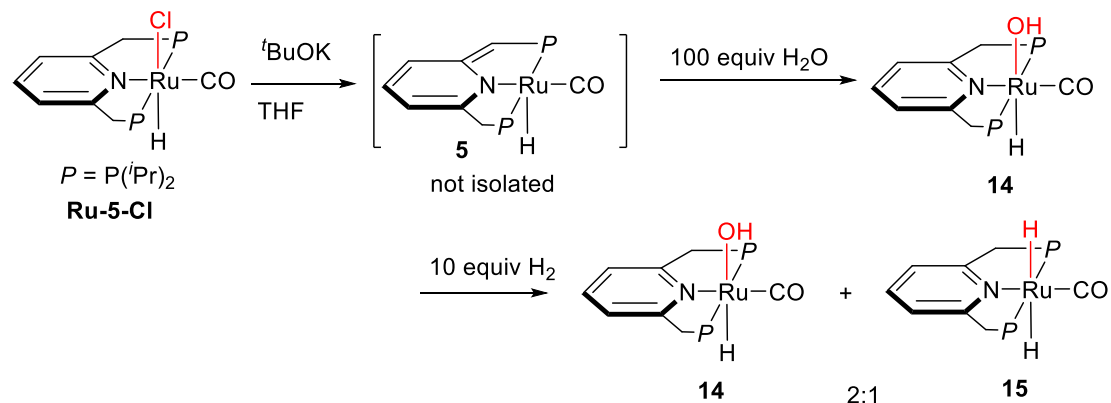
### iii. Reaction of **5** with $\text{N}_2\text{O}/\text{H}_2$



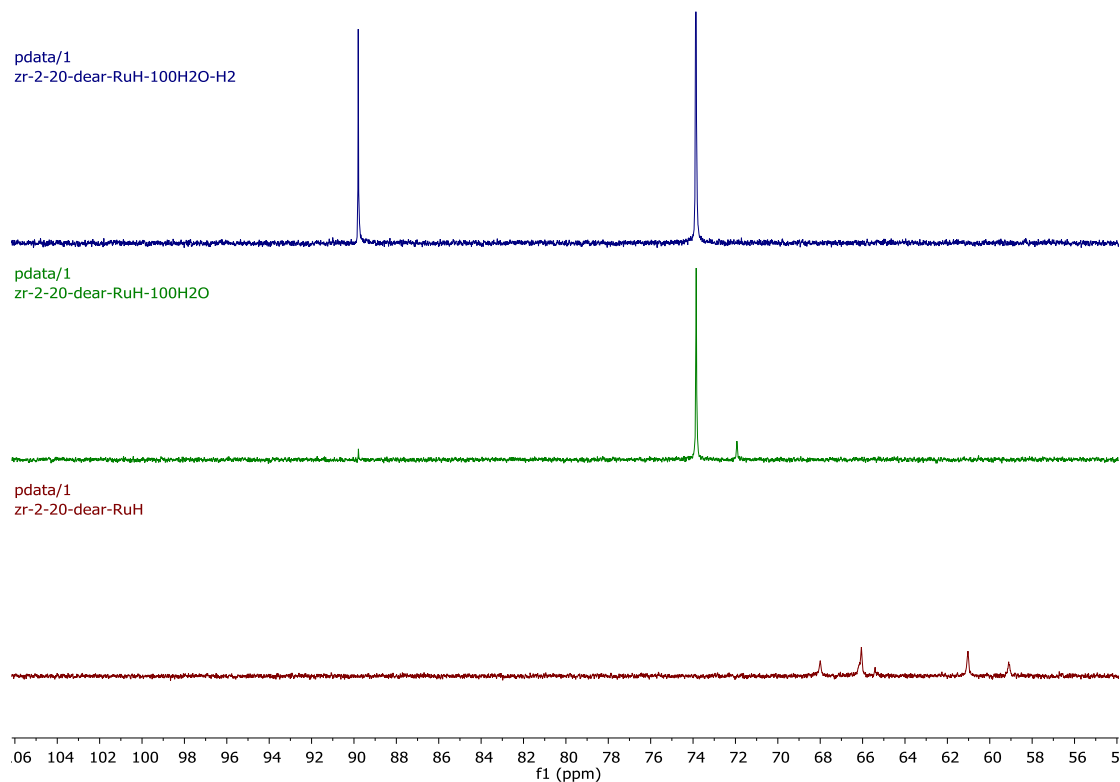
*Procedure:* To a dried 4 mL vial were added (PNP)RuHCl(CO) **Ru-5-Cl** (5.1 mg, 0.01 mmol),  $\text{tBuOK}$  (1.2 mg, 0.01 mmol), and THF (0.5 mL) in a glovebox. The resulting mixture was stirred at room temperature for 4 h to afford a solution of **5** in THF.<sup>1</sup> After transfer into a dried NMR tube, 0.5 mL of  $\text{N}_2\text{O}$  (2 equiv) and 0.5 mL of  $\text{H}_2$  (2 equiv) were injected immediately before shaking. The mixture was shaken for a few seconds. The orange color changed to be light yellow, which corresponds to complex **15** according to  $^{31}\text{P}$  NMR analysis. Only **15** was detected by  $^{31}\text{P}$  NMR. This experiment indicated that reacting **5** with  $\text{H}_2$  is much faster than its reaction with  $\text{N}_2\text{O}$ .



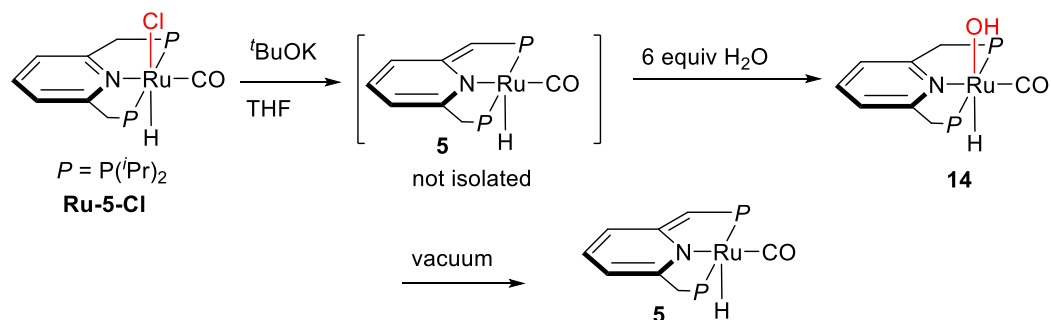
#### iv. Reaction of **14** with H<sub>2</sub>



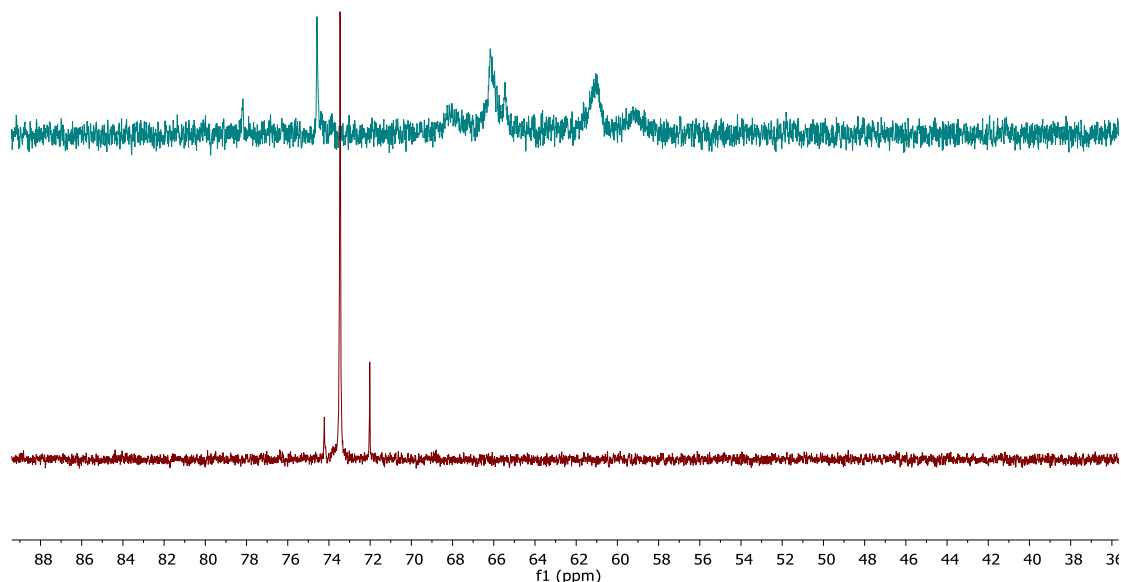
*Procedure:* To a dried 4 mL vial were added (PNP)RuHCl(CO) **Ru-5-Cl** (5.0 mg, 0.01 mmol), <sup>t</sup>BuOK (1.2 mg, 0.01 mmol), and THF (0.5 mL) in a glovebox. The resulting mixture was stirred at room temperature for 4 h to afford a solution of **5** in THF.<sup>1</sup> After transfer into a dried NMR tube, 18 μL of H<sub>2</sub>O (100 equiv) was added. The mixture was shaken for 30 mins and then excess H<sub>2</sub> was purged for changing the N<sub>2</sub> atmosphere to H<sub>2</sub> (the volume of gas phase in the NMR tube is about 2.5 mL, which corresponds to 10 equiv of H<sub>2</sub>). After shaking for 20 mins, both **14** and **15** were detected by <sup>31</sup>P NMR in a 2/1 ratio.



#### v. Dehydration of **14** under vacuum.



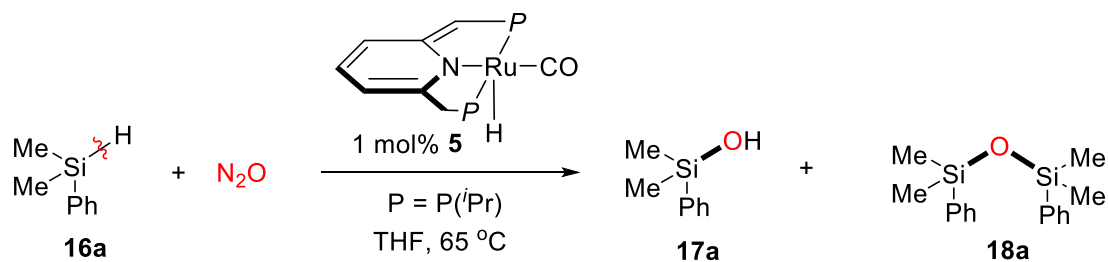
*Procedure:* To a dried 4 mL vial were added (PNP)RuHCl(CO) **Ru-5-Cl** (5.0 mg, 0.01 mmol), <sup>t</sup>BuOK (1.2 mg, 0.01 mmol), and THF (0.5 mL) in a glovebox. The resulting mixture was stirred at room temperature for 4 h to afford a solution of **5** in THF.<sup>1</sup> After transfer into a dried NMR tube, 1  $\mu$ L of H<sub>2</sub>O (6 equiv) was added. The mixture was shaken for 30 mins and then evaporated under vacuum for 24 h. Complex **5** was formed, as shown by <sup>31</sup>P NMR.



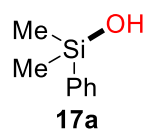
## 7. Catalytic oxidation of silanes with nitrous oxide

Silanol **17a** and **17b** are not stable, and they transform to the siloxanes **18a** and **18b** on GC, respectively. Thus, the corresponding yields all are based on the isolated yields obtained by flash chromatography.

Silanol **17c** is stable for the yield determination by GC. While **16c** is also stable on GC, the corresponding reaction with  $N_2O$  only afford silanol **17c**. No **18c** was observed.

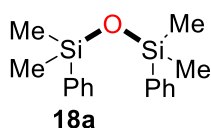


*Procedure:* To a 90 mL Fisher-Porter tube were added **Ru-5** (0.01 mmol),  $\text{PhMe}_2\text{SiH}$  (136.5 mg, 1 mmol), and THF (4 mL) in a glovebox. The Fisher-Porter tube was then refilled with 50 psi of  $N_2O$  and heated at 65 °C for 36 h. Upon reaction completion, the solution was concentration and flash chromatography (neutral  $\text{Al}_2\text{O}_3$ , eluent: hexane to hexane/ethyl acetate = 20/1 to 5/1) afforded compound **17a** (48.6 mg, 32%) and **18a** (92.9 mg, 64%).

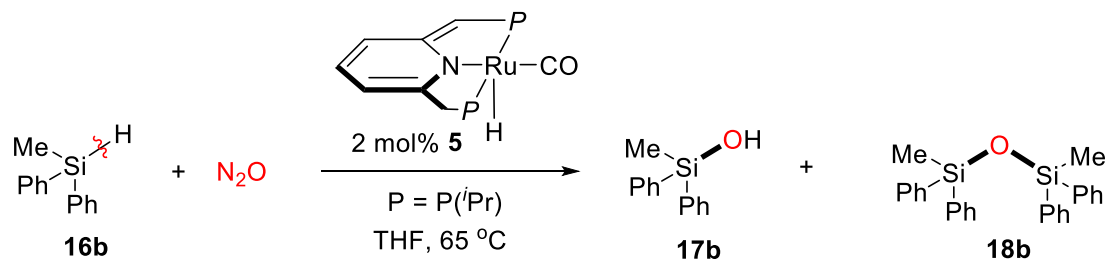


colorless liquid:<sup>8</sup>  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.50 (m, 2H), 7.50-7.22 (m, 3H), 2.63 (s,

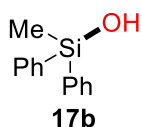
1H), 0.40 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.1, 133.0, 129.6, 127.8, -0.1.



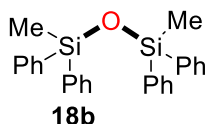
colorless liquid:<sup>9</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.65-7.41 (m, 4H), 7.40-7.16 (m, 6H), 0.27 (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.8, 133.0, 129.2, 127.7, 0.9.



*Procedure:* To a 90 mL Fisher-Porter tube were added **Ru-5** (0.01 mmol), Ph<sub>2</sub>MeSiH (100.4 mg, 0.5 mmol), and THF (4 mL) in glovebox. The Fisher-Porter tube was then refilled with 50 psi of N<sub>2</sub>O and heat at 65 °C for 66 h. Upon reaction completion, concentration and flash chromatograph (neutral Al<sub>2</sub>O<sub>3</sub>, eluent: hexane to hexane/ethyl acetate = 20/1 to 5/1) afforded compound **17b** (32.1 mg, 30%) and **18b** (47.2 mg, 46%).

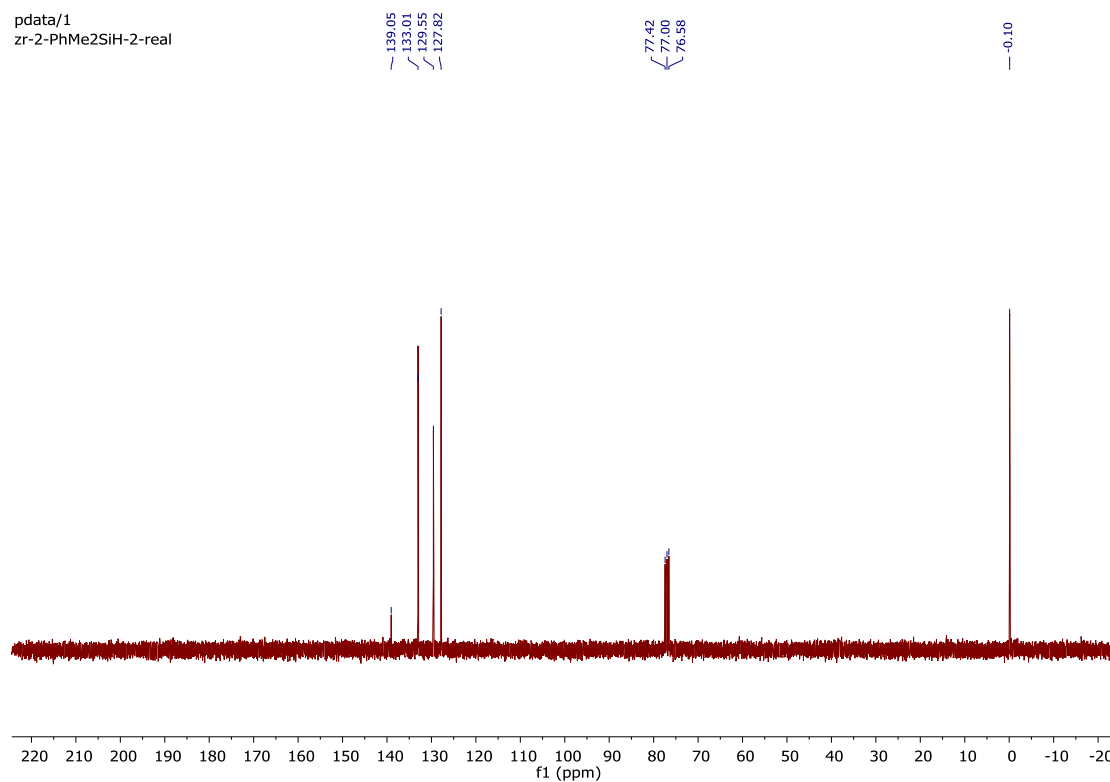
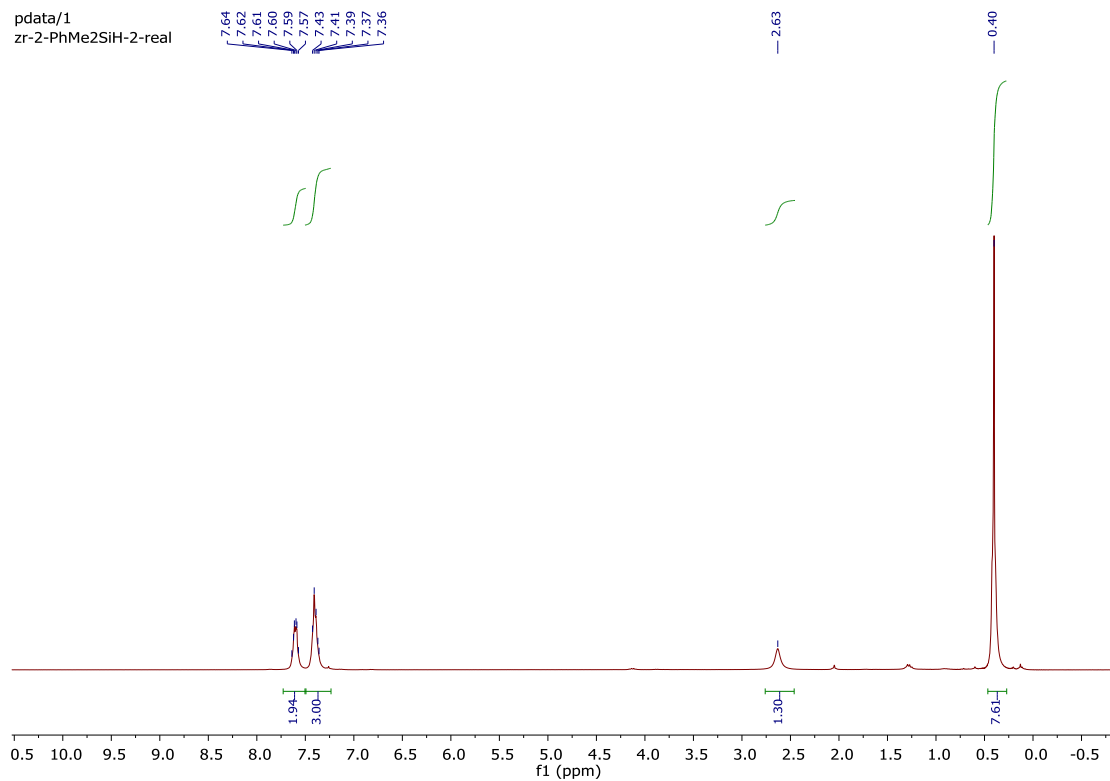
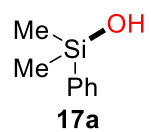


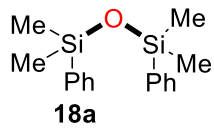
colorless liquid:<sup>8</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.82-7.50 (m, 4H), 7.50-7.28 (m, 6H), 2.16 (brs, 1H), 0.68 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.0, 133.9, 129.9, 127.9, -1.3.



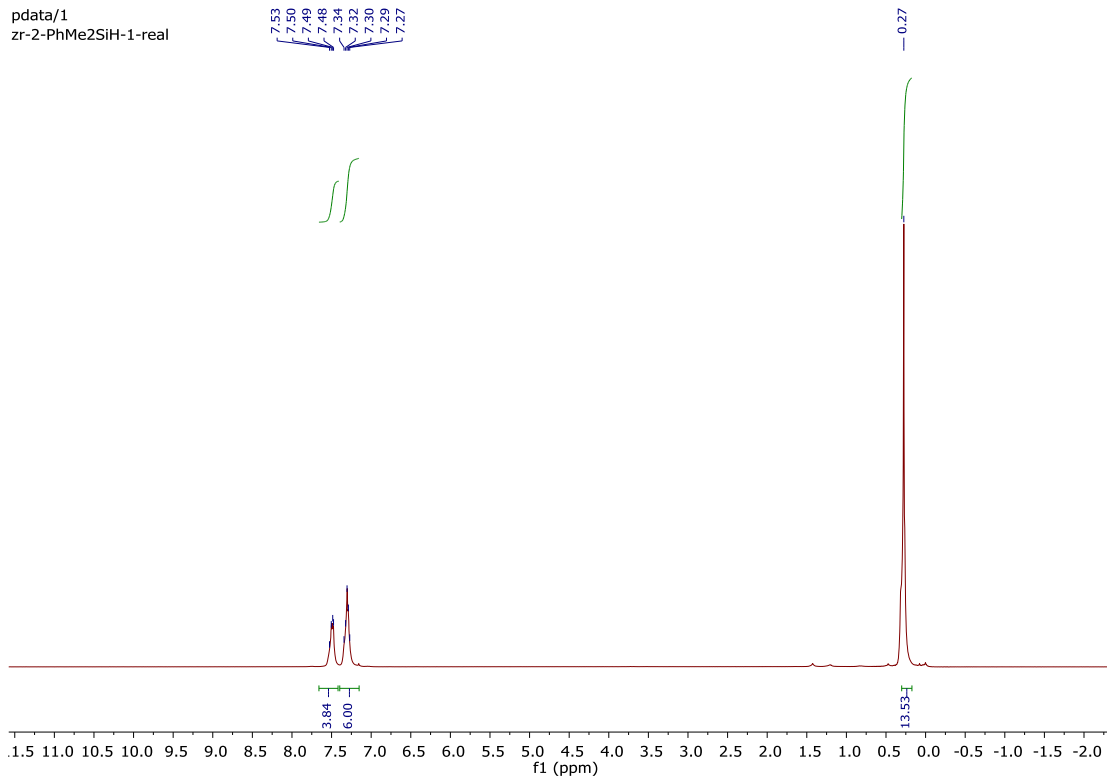
colorless liquid:<sup>9</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.75-7.50 (m, 4H), 7.50-7.24 (m, 6H), 0.63 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.5, 134.0, 129.6, 127.7, -0.6.

### 8. Spectra for catalytic oxidation of silane:

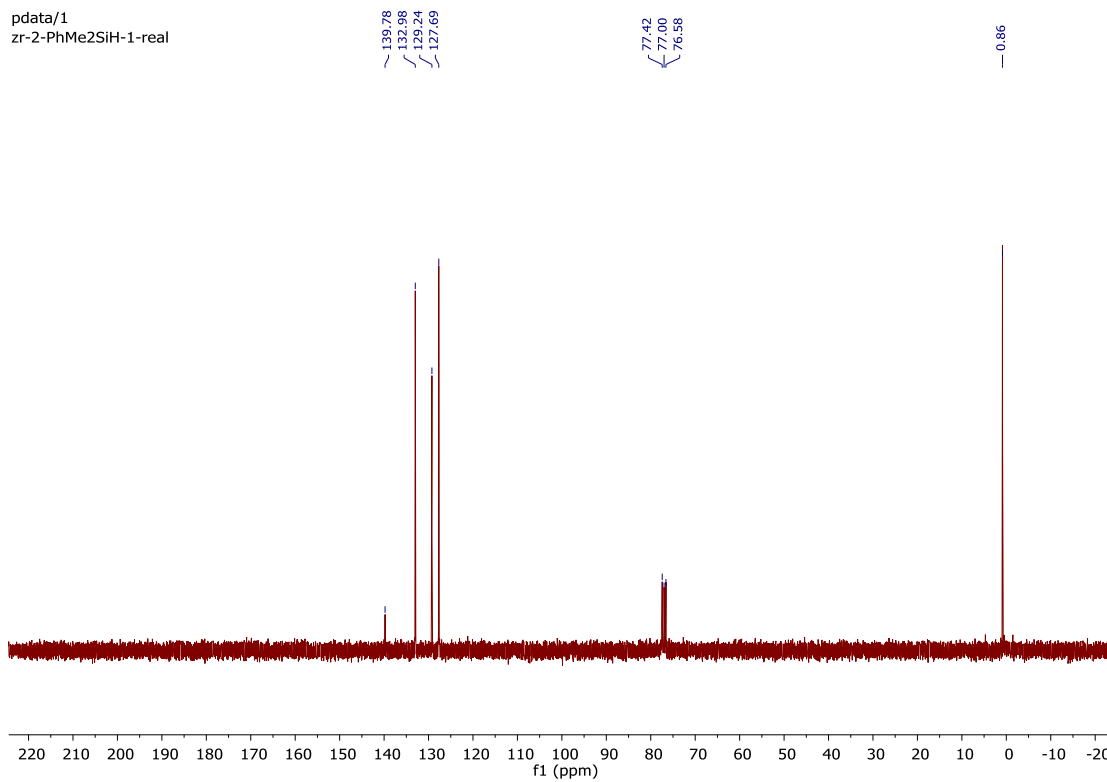




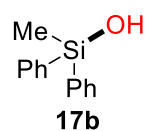
pdata/1  
zr-2-PhMe2SiH-1-real



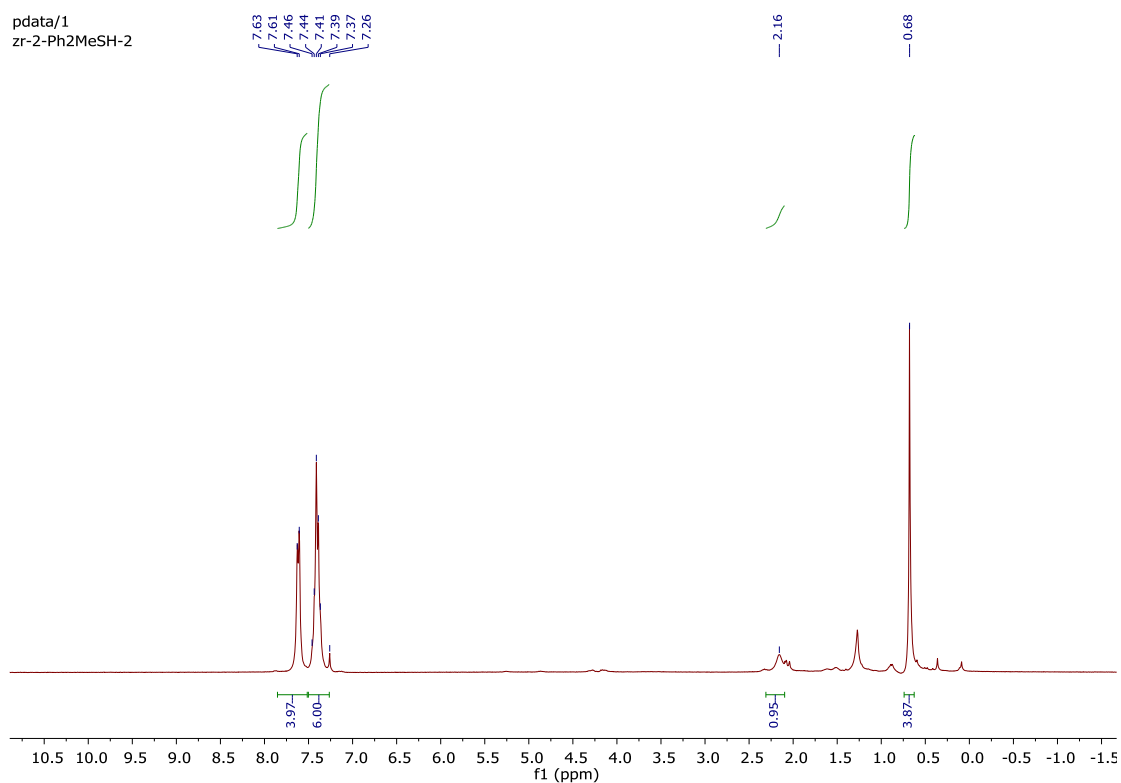
pdata/1  
zr-2-PhMe2SiH-1-real



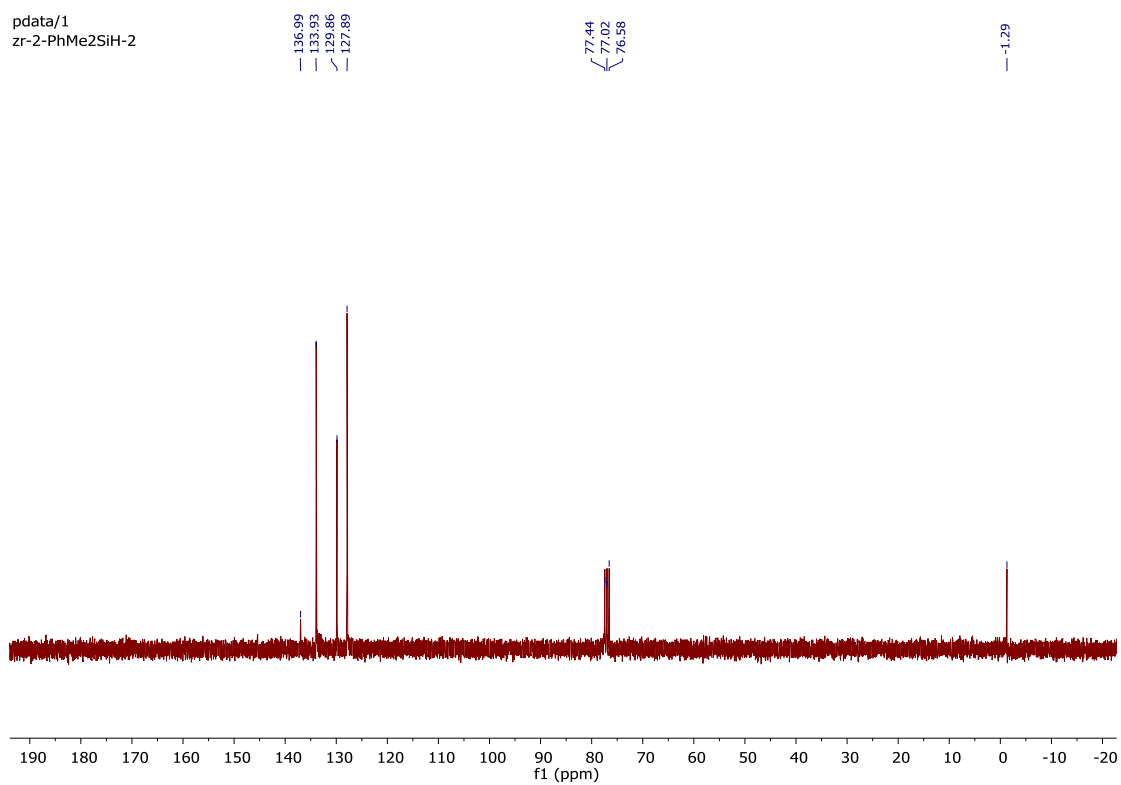


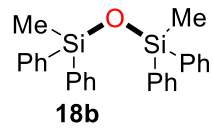


pdata/1  
zr-2-Ph2MeSH-2

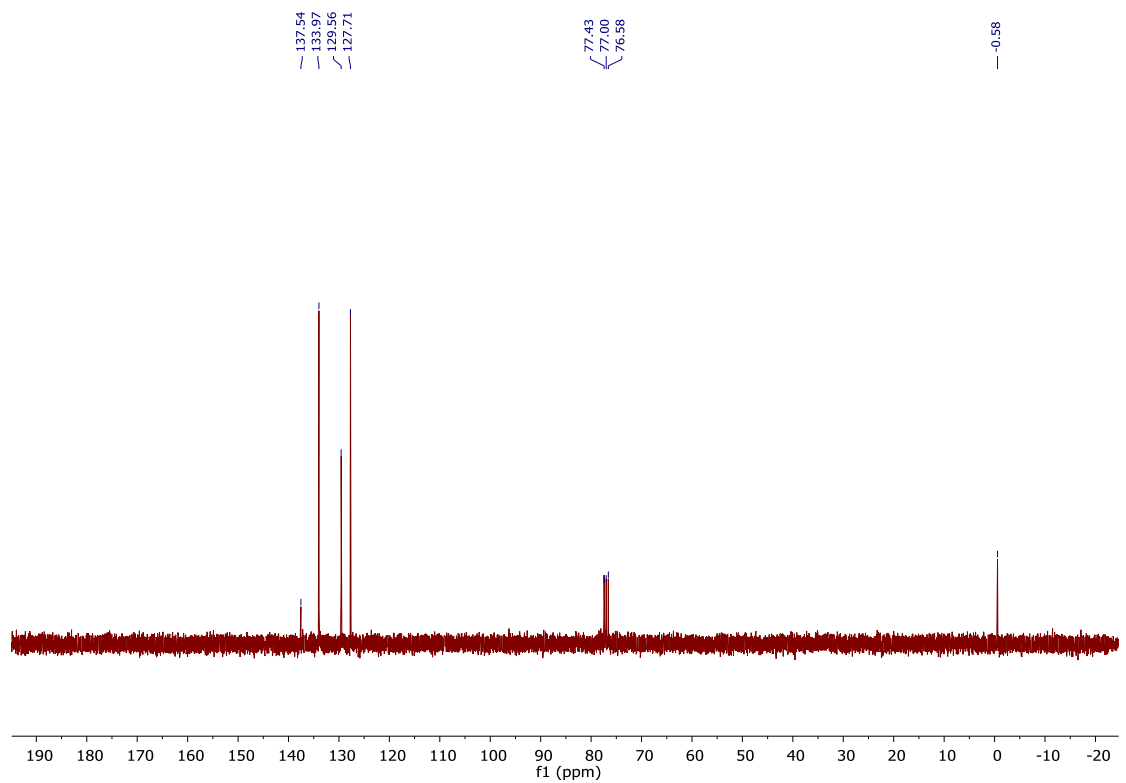
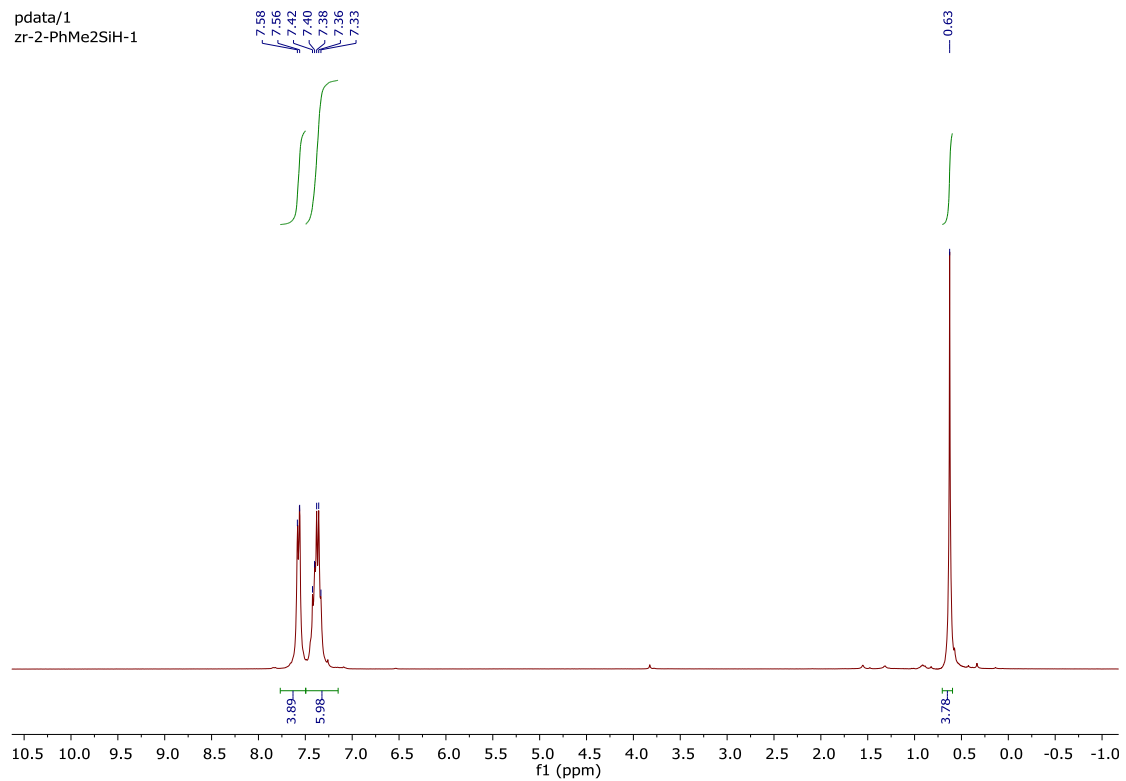


pdata/1  
zr-2-PhMe2SiH-2





pdata/1  
zr-2-PhMe2SiH-1



## 8. References:

1. Zhang, J.; Leitius, G.; Ben-David, Y.; Milstein, D. *Angew. Chem. Int. Ed.* **2006**, *45*, 1113-1115.
2. Zhang, J.; Leitius, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840-10841.
3. Gunanathan, C.; Milstein, D. *Angew. Chem. Int. Ed.* **2008**, *47*, 8661-8664.
4. Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 16756-16758.
5. Khaskin, E.; Iron, M. A.; Shimon, L. J. W.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 8542-8543.
6. Jia, G.; Lee, H. M.; Williams, I. D. *Organometallics* **1997**, *16*, 3941-3939.
7. Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *Organometallics* **2004**, *23*, 4026-4033.
8. The NMR spectra are matching with literature, see: John, J.; Gravel, E.; Hagege, A.; Li, H.; Gacoin, T.; Doris, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 7533-7536.
9. The NMR spectra match with literature reports, see: Motokura, K.; Naijo, M.; Yamaguchi, S.; Miyaji, A.; Baba, T. *Chem. Lett.* **2015**, *44*, 1464-1466.