

Supporting Information

Iluc, V. M.; Fedorov, A.; Grubbs, R. H.

H/D Exchange Processes Catalyzed by an Iridium-Pincer Complex

Vlad M. Iluc, Alexey Fedorov, and Robert H. Grubbs*

*The Arnold and Mabel Beckman Laboratory of Chemical Synthesis,
Division of Chemistry and Chemical Engineering, California Institute of
Technology, Pasadena, California 91125*

*To whom correspondence should be addressed. E-mail: rhg@caltech.edu

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1. Experimental Section

General considerations. All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated by sparging with Ar gas and dried by passage through an activated alumina column.¹ (PNP)IrH₂ (**1**)² was prepared according to literature procedures. Other reagents were purchased from commercial vendors, degassed by three freeze-thaw cycles and used without further purification. NMR spectra were recorded on Varian Mercury 300 MHz, 500 MHz or 600 MHz spectrometers (74.5 MHz, 125 MHz and 150 MHz, respectively, for ¹³C). All NMR spectra were recorded in C₆D₆ or C₆D₁₂ and the chemical shifts are reported in ppm relative to the appropriate solvent. High-resolution mass spectra (EI and FAB) were acquired by the California Institute of Technology Mass Spectrometry Facility. The catalytic reactions were monitored by ¹H NMR spectroscopy and the conversions were quantified by integration of the substrate / product signals to an internal standard (a sealed capillary tube containing a standard dioxane solution in C₆D₆ or C₆D₁₂). Mesitylene was used as an internal standard in kinetic experiments. Deuterium incorporation was verified by ²H and ¹³C NMR spectroscopies and GC-MS.

Synthesis of [D₂]-1. A solution of (PNP)IrH₂ (**1**, 31 mg, 0.05 mmol) was heated in C₆D₆ in a sealed tube for 1 h at 80 °C. Removing the volatiles under reduced pressure yielded [D₂]-**1** in a quantitative yield as a red powder. For (PNP)IrD₂: ¹H NMR (300 MHz, C₆D₆) δ 7.83 (dt, *J* = 8.5, 2.0 Hz, 2H, *H*_{Ar}), 6.99 (dd, *J* = 5.8, 4.2 Hz, 2H, *H*_{Ar}), 6.88 (dd, *J* = 8.5, 1.8 Hz, 2H, *H*_{Ar}), 2.21 (s, 6H, CH₃), 2.18-2.03 (m, 4H, CH(CH₃)₂), 1.20 (dd, *J* = 16.3, 7.2 Hz, 12H, CH(CH₃)₂), 0.99 (dd, *J* = 14.6, 7.1 Hz, 12H, CH(CH₃)₂). ¹³C NMR (75 MHz, C₆D₆) δ 162.10 (s, C_{Ar}), 133.03 (s, C_{Ar}), 131.41 (s, C_{Ar}), 127.85 (t, *J* = 3.3 Hz, C_{Ar}), 127.48 (t, *J* = 19.5 Hz, C_{Ar}), 114.80 (t, *J* = 5.2 Hz, C_{Ar}), 25.05 (t, *J* = 15.4 Hz,

CH(CH₃)₂), 20.72 (s, CH(CH₃)₂) 19.85 (t, *J* = 3.3 Hz, CH(CH₃)₂), 18.25 (s, CH₃). ³¹P NMR (121 MHz, C₆D₆) δ 57.7 (s). ²H NMR (300 MHz, C₆H₆) δ -24.8 (t, *J* = 10.2 Hz).

Synthesis of (PNP)Ir(py)H₂. To a solution of (PNP)IrH₂ (**1**, 62 mg, 0.1 mmol in 5 mL pentanes), excess of pyridine (80 mg, 1 mmol in 5 mL pentanes) was added dropwise with stirring. The solution turned yellow and was stirred for an additional 30 min at room temperature. The volatiles were removed under reduced pressure to generate pure (PNP)Ir(py)H₂ as a yellow powder. Further recrystallization from pentanes yielded 65 mg of yellow, microcrystalline (PNP)Ir(py)H₂ (93%). For (PNP)Ir(py)H₂: ¹H NMR (300 MHz, C₆D₆) δ 8.81 (d, *J* = 4.1 Hz, 2H, *H*_{Ar}), 8.36-8.19 (m, 2H, *H*_{Ar}), 8.12 (dt, *J* = 8.9, 2.4 Hz, 1H, *H*_{Ar}), 6.48-6.19 (m, 6H, *H*_{Ar}), 2.23 (s, 6H, CH₃), 2.11 (m, 2H, CH(CH₃)₂), 1.98 (m, 2H, CH(CH₃)₂), 1.30 (dd, *J* = 15.9, 7.0 Hz, 6H, CH(CH₃)₂), 1.13 (dd, *J* = 14.7, 7.0 Hz, 6H, CH(CH₃)₂), 0.98 (dd, *J* = 14.5, 7.0 Hz, 6H, CH(CH₃)₂), 0.39 (dd, *J* = 14.1, 7.0 Hz, 6H, CH(CH₃)₂), -17.33 (td, *J* = 13.0, 7.2 Hz, 1H, IrH), -23.39 (td, *J* = 17.0, 6.8 Hz, 1H, IrH). ¹³C NMR (74.5 MHz, C₆D₆) δ 143.5 (s, C_{Ar}), 137.3 (s, C_{Ar}), 133.2 (s, C_{Ar}), 129.7 (s, C_{Ar}), 129.0 (s, C_{Ar}), 127.9 (s, C_{Ar}), 126.3 (s, C_{Ar}), 126.6 (s, C_{Ar}), 116.8 (s, C_{Ar}), 31.3 (t, *J* = 8.2 Hz, CH(CH₃)₂), 28.6 (t, *J* = 10.6 Hz, CH(CH₃)₂), 23.1 (t, *J* = 2.3 Hz, CH(CH₃)₂), 21.4 (t, *J* = 1.3 Hz, CH(CH₃)₂), 20.9 (t, *J* = 5.6 Hz, CH(CH₃)₂), 19.5 (t, *J* = 1.0 Hz, CH(CH₃)₂), 16.1 (s, CH₃). ³¹P NMR (121 MHz, C₆D₆) δ 42.81 (s). Anal. (%) Calcd. for C₃₁H₄₇IrN₂P₂: C, 53.05; H, 6.75; N, 3.99. Found: C, 53.21; H, 6.88; N, 3.82.

Control experiments

A mixture of **1** (5 mg, 0.008 mmol) and 1 mL cyclohexane-*d*₁₂ was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 °C. The reaction was monitored by ¹H NMR spectroscopy for 1 week. No hydrogen exchange between the solvent and **1** was observed by NMR.

A mixture of **1** (5 mg, 0.08 mmol), 0.1 mL H₂O and 0.9 mL cyclohexane-*d*₁₂ was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 °C. The reaction was monitored by ¹H NMR spectroscopy for 1 week. No hydrogen incorporation in C₆D₁₂ was observed by NMR or MS.

A mixture of **1** (5 mg, 0.08 mmol), 0.1 mL cyclohexane and 0.9 mL C₆D₆ was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 °C. The reaction was monitored by ¹H NMR spectroscopy for 1 week. No hydrogen incorporation in C₆H₁₂ was observed by NMR.

Typical deuteration experiment of aromatic substrates. A mixture of the substrate, catalyst **1** (3.1 mg, 1% mol) and C₆D₆ (1 mL) or D₂O/C₆D₁₂ (0.1 mL/0.9 mL) was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 °C. The reactions were monitored by ¹H NMR spectroscopy.

Typical deuteration experiment of tertiary silanes. A mixture of the substrate, catalyst **1** (see Table T1) and 0.8 ml C₆D₆ saturated with D₂O was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 °C. The reactions were monitored by ¹H NMR spectroscopy.

Table T1. Experimental deuteration results.

Substrate (mg/mmol)	Catalyst (mg/mmol)	Solvent (mL)	Time (h)	Product	D (%)
C ₆ H ₆ (39/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	C ₆ D ₆	>95
C ₆ H ₅ CH ₃ (46/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	C ₆ H ₂ D ₃ CH ₃	>95
<i>o</i> -C ₆ H ₄ (CH ₃) ₂ (53/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	<i>o</i> -C ₆ H ₂ D ₂ (CH ₃) ₂	>95
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ (53/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	<i>m</i> -C ₆ H ₃ D(CH ₃) ₂	>95
<i>p</i> -C ₆ H ₄ (CH ₃) ₂ (53/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	no exchange	n/a
C ₁₀ H ₈ (64/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	C ₁₀ H _{5.6} D _{2.4}	40(β); 20(α)
C ₄ H ₄ O (34/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	C ₄ D ₄ O	92
C ₄ H ₄ S (42/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1)	72	C ₄ D ₄ S	90
C ₄ H ₂ O(CH ₃) ₂ (48/0.5)	3.1/0.005	1 mL C ₆ D ₁₂ /D ₂ O (9:1) or 1 mL C ₆ D ₆	72	C ₄ H _{1.7} D _{0.3} O(CH ₃) ₂	15
Et ₃ SiH (58/0.5)	3.1/0.005	0.8 mL C ₆ D ₆ /D ₂ O (sat.)	65	Et ₃ SiD	>95
Et ₃ SiH (58/0.5)	3.1/0.005	0.8 mL C ₆ D ₆	65	Et ₃ SiD	51
Et ₃ SiH (23.2/0.2)	6.2/0.01	0.8 mL C ₆ D ₆ /D ₂ O (sat.)	20	Et ₃ SiD	>95
<i>i</i> -Pr ₃ SiH (32/0.2)	3.1/0.005	0.8 mL C ₆ D ₆ /D ₂ O (sat.)	24	<i>i</i> -Pr ₃ SiD	>95
(C ₆ H ₅ CH ₂) ₃ SiH (30/0.1)	3.1/0.005	0.8 mL C ₆ D ₆ /D ₂ O (sat.)	132	(C ₆ H _{4.7} D _{0.3} CH ₂) ₃ SiD	>95
(Me ₃ Si) ₃ SiH (25/0.1)	3.1/0.005	0.8 mL C ₆ D ₆ /D ₂ O (sat.)	90	(Me ₃ Si) ₃ SiD	>90
PhSiHMe ₂ (34/0.25)	3.1/0.005	0.8 mL C ₆ D ₆ /D ₂ O (sat.)	60	no exchange	N/A
<i>i</i> -Pr ₂ SiH(Cl) (38/0.25)	3.1/0.005	0.8 mL C ₆ D ₆ /D ₂ O (sat.)	60	no exchange	N/A

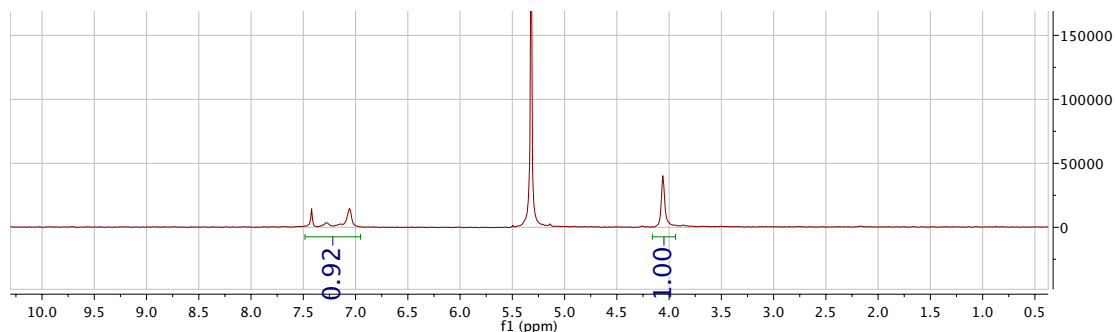


Figure S1. Deuterium NMR spectrum of $(\text{C}_6\text{H}_4\text{DCH}_2)_3\text{SiD}$ in CH_2Cl_2 showing competing SiH/D and CH/D exchanges.

Kinetic measurements. A mixture of the substrate, catalyst **1** (3.1 mg, 5% mol), internal standard and C_6D_6 (0.7 mL) was charged in a J. Young NMR tube under dinitrogen atmosphere and heated at 80 °C. The progress was monitored by ^1H NMR spectroscopy.

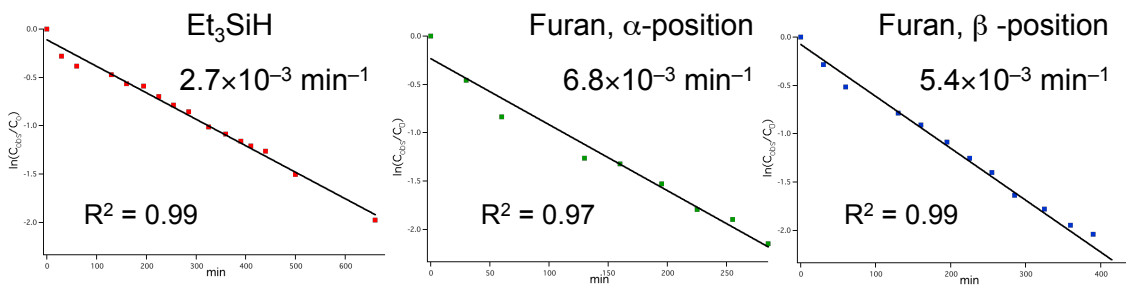


Figure S2. Observed first order plots for deuteration of triethylsilane and furan with 5 mol% of **1** in C_6D_6 .

2. References

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(2) Fan, L.; Parkin, S.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 16772.