Supporting Information

for

Hydrogen Production from Hydrolytic Oxidation of Organosilanes Using a Cationic Oxorhenium Catalyst

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Materials and Methods. Reactions were performed in a nitrogen-filled glove-box or open to the ambient atmosphere as stated. Solvents were degassed, and distilled over CaH₂ prior to use. Trityl tetra(pentafluorophenyl) borate was purchased from Strem Chemicals and used as received. Organosilanes, were purchased from Gelest and used as received. The oxorhenium chloride complex 2, was prepared according to published procedures.¹ NMR spectra were recorded on Varian Inova300 instruments. Mass spectrometry was performed by the Purdue University Campus Wide Mass Spectrometry Center on a FinniganMAT LCQ mass spectrometer system (ESI) or a Hewlett Packard Engine mass spectrometer (GC/MS). A commercial gas evolution apparatus (ChemGlass) was used to determine the yields of hydrogen gas evolved. Hydrogen gas analyses were performed on a Hiden Analytical HPR20 mass-spectrometer at 70 eV ionization energy, utilizing a Faraday detector. H₂/HD/D₂ ratios were obtained via an empirical deconvolution table based on authentic H₂, HD, and D₂ samples (Aldrich, 98+%).

Preparation of [Re(O)(hoz)₂(Solv)]B(C₆F₅)₄, 1 (Isolated). Trityl tetra(pentafluorophenyl) borate, (2.05 g, 2.22 mmol) was dissolved in 25 mL of CH₃CN
in a nitrogen-filled glove-box and treated with PhMe₂SiH (0.35 mL, 2.22 mmol) to form the silylium cation [Et₃Si(CD₃CN)][B(C₆F₅)₄] as a brown solution. Treatment of this solution with Re(O)(hoz)₂Cl, 2, (1.25 g, 2.22 mmol) yields a green solution that contains 1, triphenyl methane, and PhMe₂SiCl. The solvent was removed *in vacuo* and the resulting green oil was washed repeatedly with pentane, to yield 1, as a green powder in 90% yield (2.5 g). \(^1\)H NMR (300MHz, CD₃CN), 7.93 (d, 1H, 6.8 Hz), 7.59 (t, 1H, 7.1 Hz), 7.10 (t, 1H, 7.1Hz), 7.03(d, 1H, 6.8 Hz). MS(ESI\(^+\)) m/z Calc. For C\(_{18}\)H\(_{16}\)N\(_2\)O\(_5\)Re: 525.06/527.06. Found 524.90/526.88. MS(ESI\(^-\)) m/z Calc. For C\(_{24}\)BF\(_{20}\): 678.98. Found 679.14

**Preparation of [Re(O)(hoz)₂(Solv)]B(C\(_6\)F\(_5\))₄, 1 (In Situ).** Trityl tetra(pentafluorophenyl) borate, (0.050 g, 0.053 mmol) was dissolved in 1 mL of CD₃CN in a nitrogen-filled glove-box and treated with Et₃SiH (8.7 \[ml\], 0.053 mmol) to form the silylium cation [Et₃Si(CD₃CN)][B(C₆F₅)₄] as a brown solution. Treatment of this solution with Re(O)(hoz)₂Cl, 2, (0.030 g, 0.053 mmol) yields a green solution that contains 1, triphenyl methane, and Et₃SiCl.

**Oxygen exchange between \(^{18}\)OH\(_2\) and 1.** In a nitrogen-filled glove box trityl tetra(pentafluorophenyl) borate, (0.050 g, 0.053 mmol) was dissolved in 1 mL of CD₃CN and treated with Et₃SiH (8.7 \[ml\], 0.053 mmol) to form the silylium cation. The brown solution was then treated with 2 (0.030 g, 0.053 mmol) and the green solution removed from the glove box. \(^{18}\)OH\(_2\) (95% \(^{18}\)O, 30.0 \[ml\], 1.66 mmol) was added to this solution and the solution stirred for 1 h. Analysis by mass spectrometry (ESI) revealed 1, as 84% \(^{18}\)O enriched (Figure S3).
Stoichiometric reaction between $^{18}$OH$_2$, 1, and Ph$_2$MeSiH (Table 2).  

**Entry 1:** Catalyst added last. In a nitrogen-filled glove box trityl tetra(pentafluorophenyl) borate (0.050 g, 0.053 mmol) was dissolved in 1 mL of CD$_3$CN and treated with Ph$_2$MeSiH (10.6 μL, 0.053 mmol) to form the silylium cation. The brown solution was then treated with 2 (0.030 g, 0.053 mmol) and the green solution removed from the glove box. Diphenylmethyl silane (10.6 μL, 0.053 mmol) was combined with $^{18}$OH$_2$ (1.1 μL, 0.053 mmol), and added to the catalyst solution. The resulting homogeneous reaction mixture was allowed to stand for 30 minutes, passed through a plug of silica (benzene/hexanes), and collected fractions analyzed by GC/MS and ESI/MS.

**Entry 2:** Ph$_2$MeSiH added last. In a nitrogen-filled glove box trityl tetra(pentafluorophenyl) borate (0.050 g, 0.053 mmol) was dissolved in 1 mL of CD$_3$CN and treated with Ph$_2$MeSiH (10.6 μL, 0.053 mmol) to form the silylium cation. The brown solution was then treated with 2 (0.030 g, 0.053 mmol) and the green solution removed from the glove box and treated with $^{18}$OH$_2$ (1.1 μL, 0.053 mmol) and allowed to stand for 30 minutes. Diphenylmethyl silane (10.6 μL, 0.053 mmol) was added to this solution. The resulting reaction mixture was allowed to stand for 15 minutes, passed through a plug of silica (benzene/hexanes), and collected fractions analyzed by GC/MS and ESI/MS.

**Entry 3:** $^{18}$OH$_2$ added last. In a nitrogen-filled glove box, trityl tetra(pentafluorophenyl) borate (0.050 g, 0.053 mmol) was dissolved in 1 mL of CD$_3$CN and treated with Ph$_2$MeSiH (10.6 μL, 0.053 mmol) to form the silylium cation. The brown solution was then treated with 2 (0.030 g, 0.053 mmol), the resulting green solution was treated with diphenylmethyl silane (10.6 μL, 0.053 mmol), and allowed to stand for 30 minutes during which the solution became red in color. The solution was removed from
the glove box and treated with $^{18}\text{OH}_2$ (1.1 mL, 0.053 mmol), allowed to stand for 15 minutes, passed through a silica plug (benzene/hexanes), and recovered fractions analyzed by GC/MS and ESI/MS.

**Catalytic Hydrolytic Oxidation of Et$_3$SiH and H$_2$ production (Typical procedure with catalyst generated in situ).** Et$_3$SiH (0.87 mL, 0.053 mmol) was added to a CD$_3$CN solution of trityl tetra(pentafluorophenyl) (0.050 g, 0.053 mmol) in a Schlenk tube. Re(O)(hoz)$_2$Cl (0.030 g, 0.053 mmol) was added, and the schlenk tube was sealed and removed from the glove box. Water (28.6 mL, 1.59 mmol) was first added to the catalyst solution followed by Et$_3$SiH (1.25 mmol). Hydrogen evolution ensued upon the addition of organosilane and the solution remained green throughout the reaction. Hydrogen yields were quantified with a gas evolution apparatus obtained commercially from ChemGlass®. After hydrogen evolution ceased, an aliquot was analyzed by $^{29}$Si NMR.

**Catalytic Hydrolytic Oxidation of PhMe$_2$SiH and H$_2$ production (Typical procedure with isolated catalyst).** An acetonitrile solution of [Re(O)(hoz)$_2$][B(C$_6$F$_5$)$_3$], 1, (0.050 g, 0.040 mmol) was treated water (3 mL, 166 mmol) in a Schlenk tube. Phenyltrimethyl silane (1 mL, 6.53 mmol) was then added and the evolution of hydrogen was monitored using a glass evolution apparatus. Upon cessation of hydrogen evolution the reaction mixture was poured onto ice and treated with pentane to precipitate the catalyst. The mixture was filtered and the organic layer was extracted with diethyl ether and pentane. The solution was dried with anhydrous MgSO$_4$ and filtered. Pentane and ether were removed in vacuo to afford 88% isolated yield of PhMe$_2$Si(OH) (95%) and (PhMe$_2$Si)$_2$O (5%).
Analysis of HD, D\textsubscript{2}, and H\textsubscript{2} gases by mass spectrometry. M/Z measurements were performed on Hiden Analytical HPR20 mass-spectrometer at 70 eV ionization energy, utilizing a Faraday detector. H\textsubscript{2}/HD/D\textsubscript{2} ratios were obtained via an empirical deconvolution table based on authentic H\textsubscript{2}, HD and D\textsubscript{2} samples (Aldrich, 98+%).
Equations

Contrasting H$_2$ yield per mass of organosilane for tertiary, secondary, primary, and polysilyl$^3$ silane (eqs S1-S4), respectively. The calculations were done for 3.0 kg H$_2$, a benchmark requirement for storage in automotive applications.$^4$

\[
\text{Et}_3\text{SiH} + \text{H}_2\text{O} \rightarrow \text{Et}_3\text{Si(OH)} + \text{H}_2 \\
173 \text{ kg} \quad 27 \text{ kg} \quad 3.0 \text{ kg} \quad (238 \text{ L}) \quad (27 \text{ L}) \quad V_{\text{total}} = 265 \text{ L (70 gal.)} \quad (S1)
\]

\[
\text{Et}_2\text{SiH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Et}_2\text{Si(OH)}_2 + 2\text{H}_2 \\
66 \text{ kg} \quad 27 \text{ kg} \quad 3.0 \text{ kg} \quad (96 \text{ L}) \quad (27 \text{ L}) \quad V_{\text{total}} = 123 \text{ L (32 gal.)} \quad (S2)
\]

\[
\text{PhSiH}_3 + 3\text{H}_2\text{O} \rightarrow \text{PhSi(OH)}_3 + 3\text{H}_2 \\
54 \text{ kg} \quad 27 \text{ kg} \quad 3.0 \text{ kg} \quad (62 \text{ L}) \quad (27 \text{ L}) \quad V_{\text{total}} = 89 \text{ L (23 gal.)} \quad (S3)
\]

\[
\text{HC(SiH}_3)_3 + 9\text{H}_2\text{O} \rightarrow \text{HC(Si(OH))}_3 + 9\text{H}_2 \\
18 \text{ kg} \quad 27 \text{ kg} \quad 3.0 \text{ kg} \quad (21 \text{ L}) \quad (27 \text{ L}) \quad V_{\text{total}} = 48 \text{ L (12 gal.)} \quad (S4)
\]

Isotope labeling experiment showing H$_2$O as the source of oxygen in the silicon product.

\[
\text{Et}_3\text{Si} - \text{H} + \text{H}_2^{18}\text{O} \rightarrow \text{Et}_3\text{Si}^{18}\text{O} \quad \text{Re Cat. (1)} \\
^{18}\text{O} : \sim 95% \quad \text{92%} \quad (S5)
\]

Oxo exchange between water (H$_2^{18}$O) and complex 1

\[
\text{(S6)}
\]
**Figure S1.** A typical kinetic profile obtained by $^1$H NMR spectroscopy for oxorhenium catalyzed hydrolytic oxidation of organosilanes. Conditions: $\text{Ph}_2\text{MeSiH} = 1.00 \text{ M}, \text{H}_2\text{O} = 2.0 \text{ M}, \text{and}[\text{I}] = 0.0090 \text{ M}$ in $\text{CH}_3\text{CN}$ at 25.0 ± 0.2 °C. Ph$_2$MeSiH (open circles) is fitted to a mixed second-order equation, Ph$_2$MeSiOH (closed squares) and (Ph$_2$MeSi)$_2$O (open diamonds) are fitted to a consecutive reactions model

$$\text{(Ph}_2\text{MeSiH} \xrightleftharpoons{k_1} \text{Ph}_2\text{MeSi(OH)} \xrightleftharpoons{k_2} \frac{1}{2}(\text{Ph}_2\text{MeSi})_2\text{O}).^5$$
Figure S2. Picture depicting the dehydrogenative oxidation of organosilanes with water as catalyzed by complex 1. Cell A: 1 and H₂O in CH₃CN. Cell B: 1 and Et₃SiH in CH₃CN in the absence of water. Cell C: Catalytic mixture, 1, Et₃SiH, and H₂O in CH₃CN.
Figure S3. MS-ESI$^+$ spectra of (a) [Re(O)(hoz)$_2$]$^+$, and (b) [Re$^{^{18}}$O(hoz)$_2$]$^+$ (84% $^{18}$O-enriched).
Figure S4. MS-ESI$^+$ spectrum of the reaction from entry 3 in Table 2 shows both [Re(O)(hoz)$_2$]$^+$ and reduced [Re(hoz)$_2$]$^+$ (m/z = 509 and 511).
Figure S5. $^{29}$Si NMR spectrum (in CDCl$_3$) for the reaction products of diphenylsilane (Ph$_2$SiH$_2$) shows the diol Ph$_2$Si(OH)$_2$ (δ –31.3) and silanol Ph$_2$SiH(OH) (δ –38.4). TMS was used as an internal reference (δ 0.00).

References and Notes


