New mechanism for reduction catalysis by metal oxo: Hydrosilation of organic carbonyl groups catalyzed by a rhenium(v) oxo complex

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Supporting Information

Materials and Methods. Reactions were performed in a nitrogen-filled glove-box or open to the environment as stated. Solvents were degassed, and purified with a solvent purification system developed by Anhydrous Engineering INC. prior to use. Trityl tetra(pentafluorophenyl) borate was purchased from Strem Chemicals and used as received. Organosilanes, were purchased from Gelest or Aldrich and used as received. The oxo-Re(V) catalyst, $[\text{Re}(\text{O})(\text{hoz})_2][\text{TFPB}]$ ($\text{hoz} = 2$ - (2'-hydroxyphenyl) - 2 - oxazoline(-), TFPB = tetrakis pentafluorophenyl borate), **1**, and the oxo-Re(V) chloride, $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$, were synthesized according to published procedures.^{1,2} NMR spectra were recorded on Varian Inova300 instruments. Mass spectrometry was performed by the Purdue University Campus Wide Mass Spectrometry Center using a Hewlett Packard Engine mass spectrometer (GC/MS).

General Procedure for Kinetic Studies (CD_2Cl_2). Stock solutions of **1** (16.4 mM) were prepared in CD_2Cl_2 in a nitrogen-filled glove box. A re-sealable NMR tube was filled with 1.0 mL of CD_2Cl_2 , 84 μL (0.64 M) of benzaldehyde, 75 μL (0.95 mM) of the catalyst stock solution and 10 mg of Ph_3CH (31.7 mM) (internal standard). The NMR tube was sealed and removed from the glove box. Prior to commencing the catalysis, Et_3SiH was added, the solution was vigorously shaken, and the tube placed in the NMR

probe. The progress of the reaction was monitored by integrating the methylene protons of the product $\text{PhCH}_2\text{OSiEt}_3$ relative to Ph_3CH with respect to time. The data was analyzed using the Kaleidograph[®] software package. The observed rate constants k_ψ were obtained from nonlinear least squares fitting of P_t to:

$$[P]_t = [A]_0 (1 - \exp(-k_\psi t)).$$

General Procedure for Kinetic Studies (CD_3CN). Reactions were performed similar to the CD_2Cl_2 reactions but with higher catalyst concentrations (1 mol%). Data was analyzed using the initial rate method and observed rate constants were obtained from the linear portion of the concentration time curve during the first half life.

Measurement of Deuterium Kinetic Isotope Effect. Benzaldehyde (16.8 μL , 0.17 mmol) was added to a dry NMR tube in a nitrogen filled glove-box. Complex **1**, (150 μL of a 16.4 mM stock solution) was added; the NMR tube was sealed and removed from the glove-box. Equimolar amounts of Et_3SiH and Et_3SiD (265 μL , 1.7 mmol) were then added and the NMR tube was shaken vigorously and the ^1H NMR spectrum obtained after 15 minutes. A mixture of products $\text{PhCH}_2(\text{OSiPh}_3)$ and $\text{PhCHD}(\text{OSiPh}_3)$ was observed, and the relative ratio of the two species was found to be 1.3:1, respectively, by integration, corresponding to a kinetic isotope effect $k_H/k_D = 1.3$.

Stopped-Flow Experiments. The flow circuit was flushed with dry, oxygen-free CH_2Cl_2 before the reagent solutions were loaded. One reservoir syringe was filled with $[\text{Ph}_3\text{C}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ (0.025 mM) solution and the other with a solution of the Re hydride, **3**, or Et_3SiH . The temperature of the solutions was controlled by a thermostated temperature bath. The two drive syringes were flushed with the solutions twice before collecting data. The rate of disappearance of the trityl signal at 450 nm with respect to

time was recorded. The observed rate constants (k_{ψ}) were obtained from nonlinear least squares fitting of A_t to:

$$[A_t] = \Delta A \exp(-k_{\psi}t) + A_{\infty} \text{ where } \Delta A = A_0 - A_{\infty}.$$

Despite using dried CH_2Cl_2 , plots of **[3]** versus time are linear with an intercept $k_2 = 10 \times 10^{-3} \text{ s}^{-1}$ (**3**) (Fig. S4). This is attributed to negligible side decomposition of the trityl cation in the stopped-flow analyzer due to small adventitious moisture. Activation parameters for the reaction of $[\text{Ph}_3^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ and **3** were evaluated from rate measurements over the temperature range 290 – 305 K (Fig. S6).

Synthesis of $\text{ReO}(\text{hoz})_2\text{H}$, **3.** To a green suspension of **2** (1.00 g, 1.77 mmol) in acetonitrile was added Bu_3SnH (1.0 mL, 3.79 mmol, 2.1 equivs). The suspension was allowed to stir overnight and then the green powder was filtered and washed several times with pentane to yield **3** (0.78 g, 84% yield). ^1H NMR (300MHz, CD_2Cl_2): δ 7.93 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.69 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.46 (td, $J = 7.0, 1.8$ Hz, 1H), 7.24 (td, $J = 8.8, 1.7$ Hz, 1H), 6.99-6.74 (overlapping, 4H), 5.32- 4.01 (overlapping, 8H), 1.53 (s, 1H); ^{13}C NMR (300MHz, CD_2Cl_2): δ 175.5, 172.1, 179.7, 168.5, 137.0, 135.5, 130.0, 128.1, 122.5, 120.0, 117.1, 116.9, 111.6, 75.3, 71.1, 70.5, 69.1, 59.5. Elemental analysis, Calc. For: $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_5\text{Re}$, C, 40.98, H, 3.25, N, 5.31; Found C, 40.83, H, 3.22, N, 5.38.

Hydrosilation of acetophenone in CH_2Cl_2 . To a 25 mL round-bottom flask with a magnetic stir bar was added $\text{Re}(\text{O})(\text{hoz})_2(\text{TFPB})$ (catalyst) (0.0103 g, 0.009 mmol, 0.1 mol%) in CH_2Cl_2 (2.0 mL). Addition of acetophenone (1 mL, 8.57 mmol, 1 equiv.) was followed by the addition of triethylsilane (2.05 mL, 12.8 mmol, 1.5 equivs). The resulting solution was stirred for three hours. Solvent was removed *in vacuo* and the

reaction mixture was subsequently extracted into pentane, removing the catalyst. Pentane was removed *in vacuo* and the resulting oil was vacuum distilled to obtain triethyl(1-phenylethoxy)silane (1.736 g, 86% yield).

Hydrosilation of 2-butanone without solvent. To a 25 mL round-bottom flask with a magnetic stir bar was added $\text{Re}(\text{O})(\text{hoz})_2(\text{TFPB})$ (0.0135g, 0.0111mmol, 0.1 mol%) and 2-butanone (1.0 mL, 11.2 mmol, 1 equiv.). To this solution was added triethylsilane (2.67 mL, 16.7 mmol, 1.5 equiv), and the resulting brown oil was stirred for 12 h. Over the course of the reaction a dark precipitate slowly formed. The reaction mixture was subsequently extracted into pentane, removing the catalyst as a green precipitate. Solvent was removed *in vacuo* and the resulting oil was vacuum distilled to obtain triethyl(*sec*-butoxy)silane (1.493 g, 71% yield).

Triethyl(1-phenylethoxy)silane. ^1H NMR (300 MHz, CDCl_3): δ 7.45 (t, J = 6.9 Hz, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.0 Hz, 1H), 4.99 (q, J = 6.3 Hz, 1H), 1.56 (d, J = 6.4 Hz, 3H), 1.05 (t, J = 7.8 Hz, 9H), 0.70 (q, J = 7.6 Hz, 6H); GCMS: m/z 236

Triethyl(*sec*-butoxy)silane. ^1H NMR (300 MHz, CDCl_3): δ 3.70 (m, J = 6.2 Hz, 1H), 1.43 (m, J = 7.3 Hz, 2H), 1.11 (d, J = 6.0 Hz, 3H), 0.95 (t, J = 7.9 Hz, 9H), 0.86 (t, J = 7.5 Hz, 3H), 0.58 (q, J = 8.1 Hz, 6H); GCMS: m/z 188

Triethyl(isopropoxy)silane. ^1H NMR (300 MHz, CDCl_3): δ 3.98 (m, J = 6.0 Hz, 1H), 1.14 (d, J = 6.2 Hz, 6H), 0.95 (t, J = 8.1 Hz, 9H), 0.58 (q, J = 8.1 Hz, 6H); GCMS: m/z 174

Triethyl(1,2-dimethyl *n*-propoxy)silane. ^1H NMR (300 MHz, CDCl_3): δ 3.57 (m, J = 5.9 Hz, 1H), 1.59 (m, J = 5.6 Hz, 1H), 1.08 (d, J = 6.2 Hz, 3H), 0.97 (t, J = 8.1 Hz, 9H),

0.88 (d, J = 2.5 Hz, 3H), 0.86 (d, J = 2.63 Hz, 3H), 0.60 (q, J = 7.9 Hz, 6H); GCMS: m/z 202

Triethyl(1-ethyl *n*-propoxy)silane. ^1H NMR (300 MHz, CDCl_3): δ 3.53 (m, J = 5.9 Hz, 1H), 1.46 (m, J = 7.3 Hz, 4H), 0.98 (t, J = 7.9 Hz, 9H), 0.88 (t, J = 7.6 Hz, 6H), 0.61 (q, J = 7.9 Hz, 6H); GCMS: m/z 202

Triethyl(benzyloxy)silane. ^1H NMR (300 MHz, CDCl_3): δ 7.34-7.48 (m, Ar, 5H), 4.86 (s, 2H), 1.12 (t, J = 7.9 Hz, 9H), 0.79 (q, J = 7.9 Hz, 6H); GCMS: m/z 222

References

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2. Mcpherson, L. D.; Drees, M.; Khan, S. I.; Strassner, T.; Abu-Omar, M. M. *Inorg. Chem.* **2004**, 43(13), 4036-4050.

Figure S1. Concentration versus time profile for the hydrosilylation of benzaldehyde(0.642 M) with Et₃SiH (0.642 M) and **1** (0.952 mM) in CD₂Cl₂ at 298 K. In addition to the product PhCH₂OSiEt₃ (circles) some of the dimeric ether (< 3%), (Ph CH₂)₂O was detected (squares).

Figure S2. Plot of the initial rate, V_i , versus the concentration of catalyst **1**. Rate measurements were carried out in CD_3CN at 298 K.

Figure S3. Plot of the initial rate, V_i , versus the concentration of benzaldehyde. Rate measurements were performed in CD_3CN at 298 K.

Figure S4. Plot of k_ψ versus $[\text{Re}(\text{O})(\text{hoz})_2(\text{H})]$ in CH_2Cl_2 at 295 K. Data was acquired in CH_2Cl_2 at 295 K following the disappearance of $[\text{Ph}_3\text{C}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ at 450 nm. $k_{\text{Re-H}} = 2.40 \pm .05 \text{ M}^{-1}\text{s}^{-1}$ and an intercept $k_2 = (1.10 \pm .02) \times 10^{-2} \text{ s}^{-1}$.

Figure S5. Plot of k_{ψ} versus $[\text{Et}_3\text{SiH}]$. Data was acquired in CH_2Cl_2 at 295 K following the disappearance of $[\text{Ph}_3\text{C}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ at 450 nm.

Figure S6. Eyring plot for the reaction of $[\text{Ph}_3\text{C}^+][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.081 mM) with $\text{Re}(\text{O})(\text{hoz})_2(\text{H})$ (7.81 mM). Data was acquired at 450 nm and was fitted to the Eyring equation:

$$k = \frac{k_b T}{h} \exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right).$$

Reported errors are from the non-linear fitting of the kinetic data to the Eyring equation shown above.