Catalysis by cationic oxorhenium(V): hydrolysis and alcoholysis of organic silanes†

Rex A. Corbin, Elon A. Ison‡ and Mahdi M. Abu-Omar*

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The cationic [2-(2′-hydroxyphenyl)-2-oxazolinato(−2)]oxorhenium(V) complex **1** promotes oxidative dehydrogenation of organosilanes with water and alcohols in a catalytic manner to give excellent yields of silanols and silyl ethers, respectively. The reactions proceed conveniently under ambient and open-flask conditions with low catalyst loading (≤1 mol%). The scope of the reaction with water is quite broad and includes aliphatic, aromatic, tertiary, secondary and primary silanes. The rate of reaction depends on the catalyst and silane concentrations and kinetic isotope effect measurements demonstrate involvement of the Si–H bond in the activated complex. The most influential factor on the silane affecting reactivity is steric hindrance and a quantitative correlation with the Taft steric parameter (E) is presented. A combination of kinetic data and isotope labelling results are used to discuss plausible mechanisms for the oxidative dehydrogenation reaction pathway.

Introduction

An efficient and versatile method for the preparation of organic silanols is highly valuable because silanols are widely employed in the production of silicon-based polymers as well as intermediates in organic synthesis.[1,2] The conventional method of preparation is hydrolysis of silyl halides under strictly buffered conditions to avoid condensation of the silanol to give the less desirable siloxane product.[3] The latter reaction is catalyzed by acid or base and especially difficult to control for unhindered silanols. An alternative approach is oxidation of the Si–H bond in organosilanes. Most available oxidation methods require stoichiometric oxidant and present the problem of wasteful byproducts.[4] Some transition-metal catalysts have been reported for the oxidation of silanes with varying range of substrates and levels of siloxane byproduct formation.[5] Noteworthy of special mention are the systems based on the precious metals ruthenium and iridium that utilize water and air,[6] and the MTO/H_2O_2 system.[7] Adam and co-workers have optimized the latter to favour silanol formation by employing urea hydrogen peroxide in organic media.[8] These systems are desirable because they utilize green oxidants, air and hydrogen peroxide. Another approach to inserting an oxygen atom into Si–H is hydrolytic oxidation, eqn (1), where the atom economy is excellent (98.5% for Et_3SiH to $Et_3Si{-}OH$) and the only byproduct is dihydrogen. $[(Ph_3P)Cu(H)]_6$ catalyzes hydrolysis of silanes in polar organic solvents such as THF with moderate yields of silanol when the organosilane is added slowly.[9] We have reported recently an air and water-stable oxorhenium(V) catalyst (Fig. 1) that exhibits high reactivity and selectivity under ambient conditions for silanol formation from the reaction of organosilane and water (eqn (1)).[10]

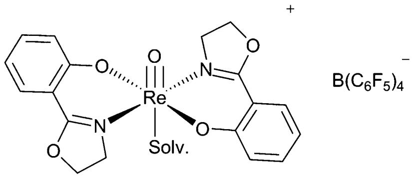


Fig. 1 Cationic oxorhenium(V) catalyst (**1**); solv. = H_2O or CH_3CN.

$$\begin{gathered} R_3SiH + H_2O \rightarrow R_3SiOH + H_2 \\ R = \text{alkyl, aryl, etc.} \end{gathered} \tag{1}$$

The analogous reaction with alcohols affords silyl ethers (eqn (2)) and constitutes a widely used protecting group reaction in organic synthesis.[11] The alcoholysis of organosilanes requires a catalyst because alcohols are not sufficiently nucleophilic to react with Si–H bonds under normal conditions. The standard method is to treat silyl chloride with alcohol in the presence of a base such as imidazole in polar organic solvents such as DMF.[12] Verkade and co-workers have shown that convenient organic solvents (such as CH_3CN and CH_2Cl_2) can be used with a super base.[13] However, base-sensitive functional groups cannot be tolerated and the production of ammonium hydrochloride salt byproduct makes this approach less appealing. Cationic iridium and iron catalysts have been employed for the alcoholysis of silanes.[14,15] The mechanism is believed to proceed through nucleophilic attack by the alcohol onto an η^2-silane adduct. Drawbacks of these catalysts include the need for rigorously anaerobic and water-free conditions, slow rates especially with bulky tertiary silanes, and poor functional group tolerance. The highly Lewis acidic borane $B(C_6F_5)_3$ has been shown to effect the dehydrogenative silylation of alcohols with various silanes albeit at very slow rates.[16] Reaction times at room temperature with 2 mol% catalyst loading range from 1–6 d.

Brown Laboratory, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana, 47907, USA. E-mail: mabuomar@purdue.edu; Fax: +1-765-494-0239; Tel: +1-765-494-5302

† Electronic supplementary information (ESI) available: Schematic figure of RGA-MS and description of general instrument design, figure of log k_1 *vs.* ν_{Si-H}, and log k_1 *vs.* the Taft constant $\Sigma\sigma^*$. See DOI: 10.1039/b822783g

‡ Current address: Department of Chemistry, North Carolina State University, Box 8204, 2620 Yarbrough Drive, Raleigh, NC 27695, USA.

$$\begin{gathered} R_3SiH + R'OH \rightarrow R_3SiOR' + H_2 \\ R = \text{alkyl, aryl, etc.} \\ R' = \text{alkyl} \end{gathered} \tag{2}$$

In this study, we report on the use of cationic oxorhenium(V) complex **1** (Fig. 1) as a highly effective and selective catalyst for the hydrolysis and alcoholysis of organosilanes including tertiary substrates under ambient open-flask conditions. The reactions at 1 mol% catalyst loading are complete in *ca.* 1–2 h. The scope of our system with different substrates is defined. The kinetics have been investigated following dihydrogen evolution using an in-house built mass spectrometer. We report the preparation, isolation, and characterization of a rhenium oxo hydride, and its potential involvement in catalysis. We discuss viable mechanistic pathways that are consistent with our collective experimental observations including kinetics, linear free energy relationships, kinetic isotope effects, and isotope labelling experiments.

Experimental

Materials and instrumentation

Organosilanes were purchased from Gelest or Aldrich and used as received. [Re(O)(hoz)$_2$Cl] (**2**) (where, hoz = 2-(2′-hydroxyphenyl)-2-oxazolinato(−2)) was prepared according to a published procedure.[17] HPLC grade acetonitrile was used for kinetic measurements. Trityl tetra(pentaflourophenyl) borate was purchased from Strem Chemicals and used as received. NMR spectra were recorded on a Varian Inova300 spectrometer. 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.

Dihydrogen gas analyses were performed using an in-house built residual gas analyzer (Stanford Research Systems RGA100) electron impact ionization quadrupole mass spectrometer. Typically, the reaction solution (1–2 mL) was stirred in a custom made glass RGA cell with a minimum (1–2 mL) head space. An inert carrier gas (Ar or N$_2$) was drawn over the reaction head space at 2 mL min^{-1} by a Varian model SH 100 vacuum pump and analyzed by a Stanford Research Systems RGA 100 mass spectrometer equipped with an Alcatel ATH31 Series turbopump. The RGA-MS was customized for real time gas evolution observation. The relative intensity of H$_2$ in terms of partial pressure as directly monitored at $m/z = 2$ with respect to time provided for rate determinations. Carrier gas regulated at 4 psi (over atmospheric pressure) was passed over the reaction flask atmosphere at a flow rate of ≈ 2 cm^2 min^{-1} through 0.007 inch internal diameter capillary tubing into a series of pressure reduction apertures for mass analyzer system introduction. A detailed schematic of the RGA instrument setup is provided in the ESI.†

Synthesis

[Re(O)(hoz)$_2$(Solv)]B(C$_6$F$_5$)$_4$, 1. Trityl tetra(pentaflourophenyl) borate, (2.05 g, 2.22 mmol) was dissolved in 25 mL of CH$_3$CN in a nitrogen-filled glove-box and treated with PhMe$_2$SiH (0.35 mL, 2.22 mmol) to form the silylium cation [Et$_3$Si(CD$_3$CN)][B(C$_6$F$_5$)$_4$] as a brown solution.[18] Treatment of this solution with Re(O)(hoz)$_2$Cl, **2**, (1.25 g, 2.22 mmol) yields a green solution that contains **1**, triphenyl methane, and PhMe$_2$SiCl. The solvent was removed under vacuum 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 δ (300 MHz, CD$_3$CN), 7.93 (d, 1H, 6.8 Hz), 7.59 (t, 1H, 7.1 Hz), 7.10 (t, 1H, 7.1 Hz), 7.03(d, 1H, 6.8 Hz). MS(ESI$^+$) m/z calcd For C$_{18}$H$_{16}$N$_2$O$_5$Re: 525.06/527.06. Found 524.90/526.88. MS(ESI$^-$) m/z calcd For C$_{24}$BF$_{20}$: 678.98. Found 679.14.

Alternatively, **1** can be prepared *in situ* as follows: trityl tetra(pentaflourophenyl) borate, (0.050 g, 0.053 mmol) was dissolved in 1 mL of CD$_3$CN in a nitrogen-filled glove-box and treated with Et$_3$SiH (8.7 µL, 0.053 mmol) to form the silylium cation [Et$_3$Si(CD$_3$CN)][B(C$_6$F$_5$)$_4$] as a brown solution. Treatment of this solution with Re(O)(hoz)$_2$Cl, **2**, (0.030 g, 0.053 mmol) yields a green solution that contains **1**, triphenyl methane and Et$_3$SiCl.

^{18}O-enriched complex 1 (Re=^{18}O). In a nitrogen-filled glove box trityl tetra(pentaflourophenyl) borate, (0.050 g, 0.053 mmol) was dissolved in 1 mL of CD$_3$CN and treated with Et$_3$SiH (8.7 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. ^{18}OH$_2$ (95% ^{18}O, 30.0 µL, 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.

Re(O)(hoz)$_2$(H), 3. To a green suspension of **2** (1.00 g, 1.77 mmol) in acetonitrile was added Bu$_3$SnH (1.0 mL, 3.79 mmol, 2.1 equiv.). 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). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): 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}CNMR (300 MHz, CD$_2$Cl$_2$): 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, calcd For: C$_{18}$H$_{17}$N$_2$O$_5$Re, C 40.98, H 3.25, N 5.31; Found C 40.83, H 3.22, N 5.38.

Typical catalytic procedure

Hydrolytic oxidation of PhMe$_2$SiH. An acetonitrile solution of [Re(O)(hoz)$_2$][B(C$_6$F$_5$)], **1**, (0.050 g, 0.040 mmol) was treated with water (3 mL, 166 mmol) in a Schlenk tube. Phenyldimethyl 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 (1.5 h) 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%).

Kinetics

Pseudo first-order conditions, with 10-fold excess water or alcohol concentration, were utilized. In a typical run the total sample volume was 1 mL in CH_3CN solvent and the temperature was maintained constant at 25.0 ± 0.2 °C. Reagent concentrations were as follows: [organosilane] = 0.10 M, [H_2O] or [ROH] = 2.0–5.0 M, and [**1**] = 0.0020-0.018 M. Catalyst stock solutions were prepared fresh and used within one day. A solution of the catalyst (**1**) and H_2O or ROH was incubated in the RGA-MS reaction vessel, equipped with magnetic stirring bar, and purged with solvent saturated Ar carrier gas until the solution and headspace were effectively degassed. Confirmation was provided by monitoring the decline of N_2, O_2 and H_2 gas intensity within the carrier gas as determined by the RGA-MS instrument. The reaction was initiated by addition of the organosilane substrate using a gas tight syringe. Gas evolution was followed by monitoring $m/z = 2$.

Results

Reaction scope

Typically the reactions reported here are carried out in CH_3CN or CH_2Cl_2 by adding 1 mol% of catalyst **1** to a solution containing the organosilane substrate and water or alcohol. Clean reactions occur with quantitative conversion of the organosilane as observed by ^1H and ^{29}Si NMR and quantitative evolution of H_2. Since catalyst **1** is air- and water-stable, no extra precaution is needed and the described reactions proceed smoothly under open-flask conditions. Furthermore, the catalyst can be prepared *in situ* starting with the rhenium chloride precursor complex **2** and adding to the reaction mixture 1 molar equivalent relative to **2** $[Ph_3C][B(C_6F_5)_4]$. Formation of the active cationic catalyst is rapid compared to the oxidative hydrolysis or alcoholysis of organosilane. The results for silanol and silyl ether formation from the reaction of organosilanes with water and alcohols as catalyzed by **1** are given in Table 1.

The conversion to the silanols is excellent for aryl, alkyl, and alkoxy silanes. Isolated yields of silanol are quite good (Table 1, entry 3) because the subsequent conversion of silanol to silyl ether is slow. Secondary and primary organosilanes are reactive and afford high conversions. In the case, of secondary silanes a mixture of mono- and di-silanol is obtained (Table 1, entries 5 and 6). However, primary silanes give multiple silicon containing products (Table 1, entry 7). This finding is not surprising because organosilanetriols tend to condense more readily than silanediols to give siloxane polymers and/or rings.[19]

Even though the catalytic reaction can be run neat (no solvent) as a biphasic reaction to high conversion (Table 1, entry 4), the isolated product is disiloxane, which arises most likely from the coupling of $PhMe_2SiH$ and $PhMe_2SiOH$ under neat conditions. It should be noted that while secondary silanes afford 2 equivalents of H_2, the primary silane $PhSiH_3$ does not afford 3 equivalents of H_2 (Table 1, entry 7). In fact, the H_2 yield from $PhSiH_3$ indicates that precisely 2 molar equivalents of H_2 are given. In other words, once the silandiol is formed the third Si–H bond is markedly less reactive.

The alcoholysis reaction proceeds to high conversions with aliphatic alcohols. The reaction need not be dry as silylation of primary and secondary alcohols are quite competitive with the water reaction. However, tertiary (*t*-BuOH) and aromatic (ArOH) alcohols are not effective and only trace amounts of H_2 evolution is detected.

Kinetics

We have chosen to evaluate the kinetics by following H_2 evolution in real time using RGA-MS. The employed conditions have water or alcohol in excess and the organosilane substrate limiting. This was selected because it provides for pseudo-first-order conditions and hence simplified rate equation. Additionally, reversal of the

Table 1 Rhenium-catalyzed hydrolysis and alcoholysis of organosilanes[a]

				% Yield[b]			
Entry	Silane	ROH	Catalyst	Silanol (SiOH)	Siloxane (SiOSi)	Silyl ether (SiOR)	H_2
1	Ph_2MeSiH	H_2O	**2**/Ph_3C^+ [c]	>95	<2	—	95
2	Ph_2MeSiH	H_2O	**1**	>95	<2	—	98
3	$PhMe_2SiH$	H_2O	**1**	88[d]	—	—	78
4[e]	$PhMe_2SiH$	H_2O	**1**	—	70[d]	—	95
5	Ph_2SiH_2	H_2O	**2**/Ph_3C^+ [c]	>95[f]	—	—	82
6	Ph_2SiH_2	H_2O	**1**	>95[f]	—	—	88
7	$PhSiH_3$	H_2O	**2**/Ph_3C^+ [c]	[g]	[g]	—	66
8	$EtMe_2SiH$	H_2O	**1**	>95	—	—	95
9	Et_2MeSiH	H_2O	**1**	>95	—	—	95
10	Et_3SiH	H_2O	**1**	92	8	—	97
11	$Et_2{}^iPrSiH$	H_2O	**1**	>95	—	—	95
12	$^nPr_3SiH$	H_2O	**1**	>95	—	—	95
13	$Me_2(OEt)SiH$	H_2O	**1**	—	—	—	95
14	$^tBuMe_2SiH$	H_2O	**1**	>95	—	—	95
15	Et_3SiH	MeOH	**1**	—	—	>98	98
16	Et_3SiH	EtOH	**1**	—	—	>98	98
17	Et_3SiH	^iPrOH	**1**	—	—	>98	98

[a] Conditions: 1 mol% **1** or **2**:$[Ph_3C][B(C_6F_5)_4]$ (1 : 1), 1.0 M silane substrates, 2–10 equivalents of H_2O or ROH in CH_3CN or CH_2Cl_2 under ambient temperature (*ca.* 20 °C), reaction time 2–4 h. [b] For silicon containing compounds, determined by NMR and/or GC unless otherwise indicated. H_2 yields determined by volumetric displacement apparatus. [c] Catalyst prepared *in situ* by addition of 1 equiv. $[Ph_3C][B(C_6F_5)_4]$ to precursor rhenium chloride **2**. [d] Isolated yields. [e] Neat in the absence of solvent. [f] 26% $Ph_2SiH(OH)$ mono-silanol and 74% $Ph_2Si(OH)_2$ silanediol determined by ^{29}Si NMR. [g] Multiple silicon containing products result.

Table 2 Rate constants for the oxorhenium-catalyzed dehydrogenative oxidation of organosilanes with water, ν_{Si-H} stretching frequencies, and Taft electronic (σ^*) and steric (E) parameters

Entry	Silane	$k_1{}^a$/L mol^{-1} s^{-1}	ν_{Si-H}/cm^{-1}	$\Sigma\sigma^{*b}$	$\Sigma E_{Si}{}^c$
1	$EtMe_2SiH$	1.27 ± 0.07	2120	−0.10	−0.15
2	Et_2MeSiH	0.71 ± 0.08	2113	−0.20	−0.30
3	Et_3SiH	0.30 ± 0.02	2107	−0.30	−0.45
4	$^nPr_3SiH$	0.18 ± 0.02	2109	−0.36	−0.65
5	$Et_2{}^iPrSiH$	0.023 ± 0.002		−0.39	−0.854
6	$^tBuMe_2SiH$	0.063 ± 0.005	2117	−0.30	−1.46
7	$(EtO)Me_2SiH$	0.85 ± 0.09		0.09	−0.15
8	$PhMe_2SiH$	1.2 ± 0.2	2129	+0.60	—
9	Ph_2MeSiH	0.11 ± 0.01	2132	+1.20	—
10	Ph_2SiH_2	0.10 ± 0.02	2139	—	—
11	$PhSiH_3$	0.19 ± 0.01	2160	—	—

[a] In CH_3CN at 25.0 °C. [b] Ref. 21. [c] Ref. 22.

excess reagent, that is silane in excess and water or alcohol limiting, is not feasible because it leads to reduction in oxorhenium(V) to an inactive form and thus catalyst degradation.[10] Indeed the time profiles follow first-order dependence on [silane]. A plot of the observed first-order rate constant k_ψ *vs.* catalyst concentration $[Re]_T$ for one of the substrates, Et_3SiH, defines a straight line that passes through the origin (Fig. 2). Variation in $[H_2O]$ has no effect on the observed rate constant. Therefore, under these conditions the experimental rate constant is given in eqn (3). The slope from the plot of k_ψ *vs.* $[Re]_T$ affords the second-order rate constant k_1. Other substrates behave similarly. The values of the second-order rate constants k_1 for all the silanes studied are presented in Table 2.

$$\frac{-d[silane]}{dt} = \frac{d[H_2]}{dt} = k_1[silane][Re]_T \qquad (3)$$

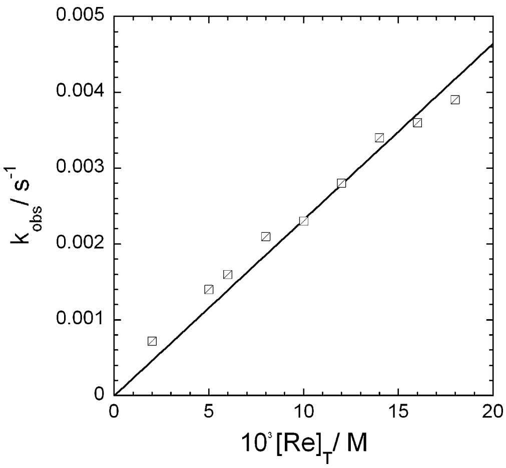


Fig. 2 Rhenium dependence on the pseudo-first-order rate constants for the hydrolysis of Et_3SiH catalyzed by **1** in CH_3CN at 25.0 °C (R = 0.982).

The choice to follow H_2 production also removes complications from the subsequent condensation reaction of silanol to give disiloxane. This point is pertinent only for the water reaction and not alcoholysis. To confirm the reliability of our kinetic measurements, we have followed the reaction progress for two substrates (Ph_2MeSiH and $PhMe_2SiH$) by ^1H NMR. Representative time profiles are shown in Fig. 3. These verified the kinetics from H_2 evolution and illustrated nicely that subsequent condensation of silanol is slower than its formation. Detailed kinetics of disiloxane formation was not investigated.

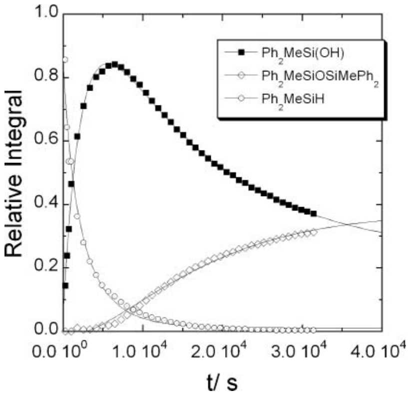


Fig. 3 A typical ^1H NMR kinetic profile for oxorhenium catalyzed hydrolysis of organosilanes. Conditions: Ph_2MeSiH = 1.00 M, H_2O = 2.0 M, and $[\mathbf{1}]_0$ = 0.0090 M in CH_3CN at 25.0 ± 0.2 °C. Ph_2MeSiH (open circles), $Ph_2MeSiOH$ (closed squares) and $(Ph_2MeSi)_2O$ (open diamonds) are fitted to a consecutive reactions model $Ph_2MeSiH \rightarrow Ph_2MeSi(OH) \rightarrow (Ph_2MeSi)_2O$.

Kinetics of the alcoholysis reaction was studied using Et_3SiH as the prototypical silane substrate and different alcohols. As mentioned above, tertiary alcohols (^tBuOH) and phenolic substrates (ArOH) were not reactive and only trace amount of dihydrogen was detected. Therefore, the kinetics of Et_3SiH alcoholysis was investigated with CH_3OH, CH_3CH_2OH, and ^iPrOH. All three follow an experimental rate law that is identical to that observed with water, first-order in $[Et_3SiH]$ and $[Re]_T$, and zero-order in [ROH], eqn (3). The second-order rate constants k_1 (in CH_3CN at 25 °C) for the three alcohols are as follows: 0.26 ± 0.04 (MeOH), 0.18 ± 0.01 (EtOH), and 0.11 ± 0.01 (^iPrOH) L mol^{-1} s^{-1}.

Activation parameters

The second-order rate constant k_1 was evaluated for the hydrolysis and alcoholysis with MeOH of Et_3SiH over the temperature range 15–45 °C. Kinetic data for both reactions was collected at 5° intervals and analyzed by the Arrhenius and transition-state theory equations, eqn (4) and (5), respectively. The results are summarized in Table 3 for hydrolysis and methanolysis of Et_3SiH.

$$k_1 = Ae^{-E_a/RT} \qquad (4)$$

$$k_1 = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \qquad (5)$$

Kinetic isotope effect

The variation of k_1 with deuterium substitution on silicon in triethylsilane and on oxygen in water and methanol was investigated.

Table 3 Activation parameters

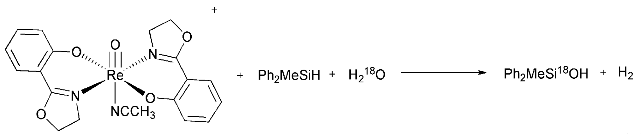
ROH	E_a/kJ mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J mol^{-1} K^{-1}
H_2O	34.9(3)	32.4(3)	−148(1)
MeOH	34.6(1)	31.9(2)	−151(1)

The use of deutero-water (D_2O, 95% enrichment) or deuteron-methanol (CH_3OD, 95% enrichment) has no effect on the rate of reaction with Et_3SiH. The collected values were as follows: $k_1(H_2O)/k_1(D_2O) = 1.03 \pm 0.03$ and $k_1(MeOH)/k_1(MeOD) = 1.1 \pm 0.1$. This finding is expected since the experimental rate laws do not exhibit dependence on the concentrations of water and alcohol. The value of k_1 for Et_3SiD (97% enrichment) in comparison with the same quantity for Et_3SiH gave a primary KIE for the reactions with water and methanol as follows: $k_1(Et_3SiH)/k_1(Et_3SiD) = 1.3 \pm 0.1$ (with H_2O), and 1.4 ± 0.2 (with MeOH).

Isotope labelling experiments

The source of hydrogen atoms in the H_2 product was established by employing Et_3SiD with H_2O and Et_3SiH with D_2O. The produced gas was exclusively HD (94 and 98%, respectively) as determined by mass spectrometry.

To ascertain the source of the oxygen in the silanol product is water and not air, we conducted the catalytic reaction in open air with $H_2{}^{18}O$. Quantitative ^{18}O-enrichment was observed in the Et_3SiOH product. To investigate the role of the multiply bonded oxo ligand on the elementary steps of the reaction with silane, we conducted ^{18}O isotope labelling experiments under single-turnover conditions. Equimolar amounts of **1**, Ph_2MeSiH, and $H_2{}^{18}O$ were reacted in CH_3CN and the silanol product analyzed by mass spectrometry gave high ^{18}O-enrichment (86%), eqn (6). The observed enrichment is less than the expected theoretical value starting with *ca.* 95% $H_2{}^{18}O$ because of some oxo exchange between $H_2{}^{18}O$ and Re=^{16}O, eqn (7).



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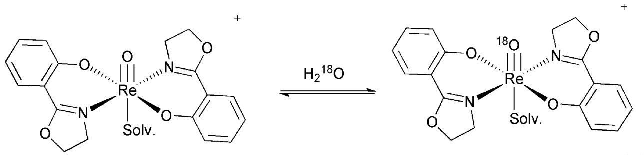


(7)

Reactivity of the rhenium hydride complex 3

The reaction of silane with complex **1** does not yield a rhenium hydride. Instead the rhenium is reduced slowly to an uncharacterized rhenium(III) species.[10] Nevertheless, the potential involvement of an oxorhenium(V) hydride in the catalytic reaction is worth consideration. We prepared the rhenium hydride **3** from the reaction of the rhenium chloride **2** and tin hydride. Complex **3** is not very hydridic.[20] It is stable towards water, alcohols, and even acetic acid. However, **3** reacts with strong acids such as HOTf (OTf = trifluoromethane sulfonate) in acetonitrile to give H_2 and $[Re(O)(hoz)_2(CH_3CN)][OTf]$ (complex **1**).

Discussion

Complex **1** is an effective catalyst for the preparation of silanol from the reaction of organosilanes and water under ambient open-flask conditions. The oxorhenium complex also catalyzes silylation of alcohols with high efficiency. The versatility of the reactions is quite good. Tertiary, secondary, and primary silanes are suitable substrates. While secondary silanes give mixtures of mono-silanol and silanediol, primary silanes give complex mixtures of silicon-containing products and are not selective for discrete silanetriols. Aliphatic and aromatic tertiary silanes are effective; however, triaryl silane such as Ph_3SiH is not reactive. Only trace amounts of H_2 was detected. As for aliphatic silanes, substrates bulkier than $^iPr_3SiH$ are not reactive either. For the alcohol silylation reaction, the only limitations are tertiary alcohols (^tBuOH) and phenolic substrates (ArOH). These are sluggish and afford only small yields of H_2.

Our kinetics results show that the substituents on the silicon have an effect on the rate of reaction. The trend for alkyl silanes follows this order of reactivity: $EtMe_2SiH > Et_2MeSiH > Et_3SiH > {}^nPr_3SiH > {}^tBuMe_2SiH \geq {}^iPrEt_2SiH$. We took the Si–H stretching vibration as measure for the electronic variation in the Si–H bond strength (Table 2). However, a plot of $\log(k_1)$ against ν_{Si-H} revealed no correlation. The expectation was that silane compounds with the smallest vibrational frequencies (that is the weakest Si–H bonds) would be most reactive since the experimental rate law depended on [silane]. Since the substituents we employed are aliphatic, aromatic, and one mesomeric substrate, we tested the Taft linear-free energy relationship. Adding the σ^* values for each of the substituents on silicon gives $\Sigma\sigma^*$, which reflects the total electronic environment at silicon.[21] However, the experimentally measured second-order rate constants (k_1) showed no correlation with the Taft $\Sigma\sigma^*$ values. The trend observed for the aliphatic silanes at least follows steric hinderance. For example, $^nPr_3SiH$ is more reactive than $Et_2{}^iPrSiH$. Therefore, we took an analogue to the Taft steric parameter (E) that has been developed for organosilicon compounds (E_{Si}).[22] The plot of $\log(k_1)$ against ΣE_{Si}, which is the sum of the steric E_{Si} value for each of the substituents, is given in Fig. 4. $^tBuMe_2SiH$ was excluded because it was the only outlier. The relationship is linear with a slope $\delta^* = 2.2 \pm 0.3$ with a correlation factor $R = 0.97$. The positive value is consistent with a transition-state that is sensitive to steric congestion of the silane substrate and the value is larger than unity, which is observed for ester hydrolysis.

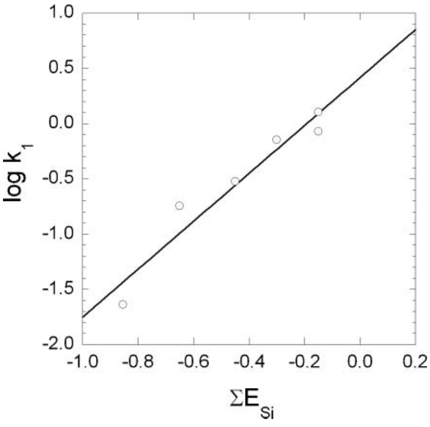
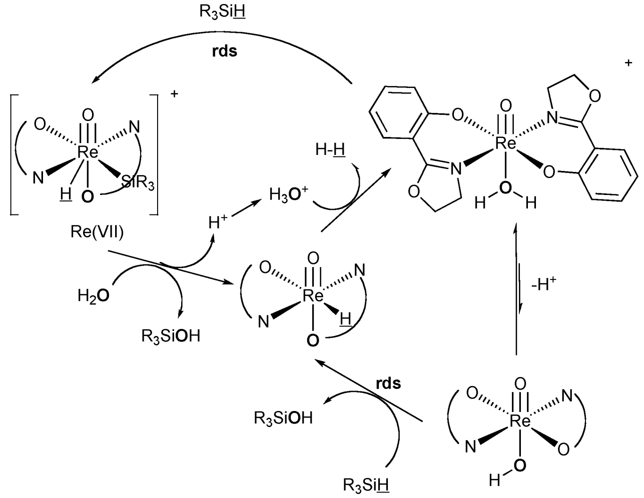


Fig. 4 Taft steric correlation plot, log k_{obs} *vs.* Taft steric substituent constants. The correlation coefficient (δ^*) value is 2.2 ($R = 0.97$).

The kinetic isotope effects (kie) of 1.3 and 1.4 for $Et_3Si–H/D$ reactions with H_2O and MeOH, respectively, are consistent with a primary isotope effect, and comparable to the kie of 1.23 observed for dichlorocarbene insertion into Bu_3SiH.[23] Therefore, we postulate insertion of the Si–H bond in the activated complex. The ^{18}O-labelling studies show that even under single turnover conditions the water oxygen is exclusively transferred to the silicon atom of silane. Thus, we suggest attack of Si, the electrophilic site of the Si–H bond, onto a hydroxo or alkoxo ligand (a nucleophilic site on rhenium) with concurrent hydride transfer to afford silanol or sily ether and oxorhenium(V) hydride. The latter reacts with solvated [H^+] to evolve H_2 and regenerate the cationic active catalyst. This mechanism is outlined in Scheme 1. The activation parameters support this mechanistic model. The negative values of $\Delta S^{\ddagger}$ are consistent with a bimolecular reaction and the modest $\Delta H^{\ddagger}$ values are indicative of compensating bond making and bond breaking processes that are involved in the insertion process. It is interesting to note that while other metal oxo systems such as OsO_4[24] and $Re(O)_2(I)(PPh_3)_2$[25] have been shown to undergo Si–H addition across dioxo ligands [3 + 2], we do not detect Si–H insertion into the oxo ligand for this monooxo rhenium(V) complex **1**, nor for other mono-oxo systems.[26]



Scheme 1 Postulated mechanism for rhenium-catalyzed hydrolysis and alcoholysis of organic silanes.

Another indistinguishable mechanism would involve a rate-determining oxidative addition of the organosilane to give a transient rhenium(VII) complex (Scheme 1). Water or alcohol would attack the electrophilic Si atom on rhenium to give silanol or silyl ether, respectively. The cycle is completed by H_2 formation from the reaction of the rhenium oxo hydride and H^+. Cationic rhenium(VII) has been characterized for this ligand system in the context of atom transfer reactions, and indeed the resulting rhenium(VII) species was shown to exhibit electrophilic reactivity.[27]

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