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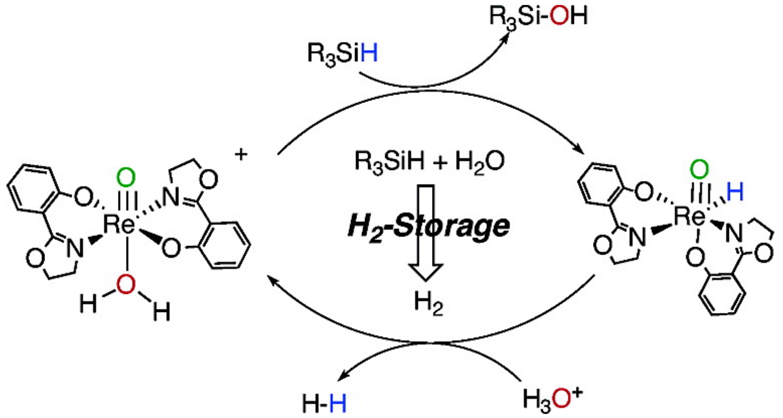

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Hydrogen Production from Hydrolytic Oxidation of Organosilanes Using a Cationic Oxorhenium Catalyst

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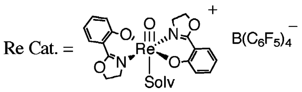
Interest in hydrogen utilization as a fuel has intensified recently because its use in fuel cells affords water and heat as the only byproducts, and the prospects of a future hydrogen economy.[1] The two key areas in need of research development are related to hydrogen sources and storage.[1] While the source of hydrogen constitutes a significant scientific challenge, addressing issues of hydrogen storage, transport, and delivery is equally important. None of the current hydrogen storage options, liquefied or high-pressure H_2 gas, metal hydrides, etc., satisfy criteria of size, cost, kinetics, and safety for use in transportation.[2]

Herein we report on the production of hydrogen under ambient conditions from catalytic hydrolytic oxidation of organosilanes using an oxorhenium(V) oxazoline coordination complex (eq 1).[3] The presented reaction is novel because (1) it offers a new methodology for the production of hydrogen on demand and under kinetic control from organic liquid and only water as co-reagent, (2) the yield of hydrogen is proportional to the water stoichiometry, and (3) it presents a new paradigm for the use of high-valent oxometalate catalysts in dehydrogenative oxidations with water. A drawback of the described reaction is the cost of organosilanes.[4] This concern, however, would be addressed if the organic silicon byproduct is recycled efficiently.

$$R_{4-x}Si - H_{x(l)} + xH_2O_{(l)} \xrightarrow{\text{1 mol\% Re Cat.}} xH_{2(g)} + R_{4-x}Si(OH)_{x(l)} \tag{1}$$

R = alkyl or aryl
x = 1, 2, or 3
Solv = CH_3CN or H_2O



1

The cationic rhenium catalyst is readily prepared from the chloride precursor ($Re(O)(hoz)_2Cl$, **2**) via halide abstraction by the silylium cation [Et_3Si^+] generated in situ from the reaction of silane (Et_3SiH) and [Ph_3C][$B(C_6F_5)_4$].[5] This synthetic strategy is convenient because it offers an easy method for generating the active catalyst (**1**) in situ from **2**, which is synthesized on a mutligram scale and stable for years on the benchtop.[6]

Conceptually, the described catalytic reaction (eq 1) could be regarded as “splitting” of water from the stoichiometric sense with organosilane providing the needed energy by forming a Si−O bond: $H_2O \rightarrow [O] + H_2$. The oxygen atom in brackets, [O], denotes its transfer to silicon, which circumvents the uphill oxygen evolution problem. In this context, the yields of dihydrogen per mass of organosilane can be enhanced significantly by utilizing secondary and primary silanes. This impressive improvement in hydrogen yields is illustrated by contrasting H_2 production from tertiary, secondary, versus primary silane (eqs S1−S3). A quantity of 173 kg of Et_3SiH (in addition to 27 kg of H_2O) produces 3.0 kg of hydrogen, but only 54 kg of $PhSiH_3$ is needed to produce the same amount of H_2. However, polysilyl organics such as polysilylmethanes and polysilylarenes are even more attractive because their hydrogen content per eq 1 is ≥6 wt % (eq S4).

Table 1. Rhenium-Catalyzed Production of Hydrogen from Organosilane

			% yield[b]		
entry	substrate	method[a]	H_2	-SiOH	–SiOSi–
1	Ph_2MeSiH	A	94	100	0
		B	98	100	0
2	$PhMe_2SiH$	B[c]	78	(88)[d]	−
		C	95	−	(70)
3	Et_3SiH	A	97	92	8
4	Et_2SiH_2	A	72	n.d.[e]	n.d.
5	Ph_2SiH_2	A	82	100[f]	0
		B	88	100[f]	0
6	$PhSiH_3$	A	66	*g*	*g*

[a] Method A: 1 mol % **2**/[Ph_3C][$B(C_6F_5)_4$], 1.0 M silane substrate, 2.0−10.0 equiv of H_2O in CH_3CN at 20 °C. Method B: 1 mol % **1** (isolated catalyst), 1.0 M silane substrate, 2.0−10.0 equiv of H_2O in CH_3CN at 20 °C. Method C: Neat as a biphasic reaction without solvent; same conditions as method B. [b] Isolated yields for silicon products are reported in parentheses; otherwise, silanol and silyl ether product yields were determined by ^{29}Si NMR. [c] 0.1 mol % catalyst **1**. [d] 95:5 $PhMe_2Si(OH)/(PhMe_2Si)_2O$. [e] n.d. = not determined. [f] 26% $Ph_2SiH(OH)$ and 74% $Ph_2Si(OH)_2$. [g] Multiple silicon containing products result.

Representative yields of hydrogen for different organosilanes are shown in Table 1. The catalytic reactions are carried out at ambient temperature with 1 mol % catalyst loading or less. Reactions reach completion (100% conversion) in less than 1 h and give silanol selectively. Even though acetonitrile is used as solvent to maintain homogeneous conditions, the reaction proceeds smoothly in the absence of a solvent (entry 2). Once hydrogen evolution ceases, the initial silicon product is silanol (Figure S1), which condenses over time to the silyl ether. However, when the reaction is run neat, the silicon product is silyl ether (entry 2). Since water inhibits silanol condensation to silyl ether (vide infra), biphasic conditions reduce the effective concentration of water in the organic phase, resulting in silyl ether. In the case of primary silanes, the initially formed silanol condenses to oligomeric/polymeric siloxanes.[7] These were not characterized fully. It is worth noting that while secondary silanes afford nearly 2 equiv of H_2 per silane, primary silanes do not afford the expected 3 equiv of H_2 (entry 5 versus 6). Once silanediol is generated, the reactivity of the remaining Si−H bond is markedly reduced.

Under steady-state conditions, the major catalyst species is complex **1** (per UV−vis and ESI-MS). When **1** is reacted with organosilane in the absence of water, the solution turns red with production of stoichiometric (relative to Re) amounts of hydrogen and silyl ether (eq 2 and Figure S2). The reduced red rhenium(III) complex is not catalytically relevant.[8] Addition of water and/or air in the presence of excess organosilane does not ensure catalysis. Furthermore, the rate of reduction of catalyst **1** is slower than the rate of the catalytic reaction. It is worth noting that other simple oxorhenium complexes such as $Re(O)Cl_3(PPh_3)_2$, CH_3ReO_3 (MTO), [NH_4]ReO_4, and $Re(O)_2I(PPh_3)_2$ do not catalyze the hydrolytic oxidation of organosilanes. The latter complex is of particular interest because it has been shown to effect hydrosilation of organic carbonyl compounds.[9]

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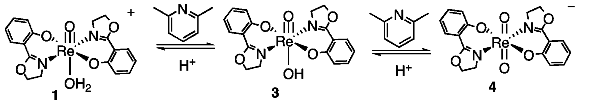
$$[\mathrm{Re(O)(hoz)_2}]^+ + 2\mathrm{Et_3SiH} \xrightarrow{\mathrm{Ar}} \mathrm{H_2} + (\mathrm{Et_3Si})_2\mathrm{O} + [\mathrm{Re(hoz)_2(CH_3CN)}_x]^+$$
$$\mathrm{hoz} = 2-(2'\text{-hydroxyphenyl})-2-\text{oxazoline}(-) \quad (2)$$

To ascertain the source of oxygen in the silicon product, we conducted the catalytic reaction in open air with $^{18}OH_2$ (eq S5). Quantitative ^{18}O-enrichment was observed in the product, confirming water as the oxidant. To investigate whether silane adds across a Re═O multiple bond, we conducted two experiments.[9,10] The first was an isotope labeling experiment under stoichiometric conditions ($Re/Ph_2MeSiH/H_2{}^{18}O$ = 1:1:1) using a different order of substrate addition (Table 2). The slightly reduced ^{18}O-enrichment in the silyl ether product is due to oxo exchange between $H_2{}^{18}O$ and **1** (eq S6 and Figure S3) and the minor side reduction of **1** by Ph_2MeSiH. It is notable that adding the silane last after incubation of **1** and $H_2{}^{18}O$ afforded less enrichment (entry 1 versus 2). Addition of water last (entry 3) gave the least enrichment because incubation of **1** and Ph_2MeSiH prior to water addition resulted in reduction of some of the rhenium catalyst (vide supra and Figure S4).

In the second experiment, we tested base catalysis by employing a hindered noncoordinating base, 2,6-lutidene, which shifts the acid/base equilibria in favor of dioxorhenium (eq 3). Thus, if **4** is the active form, 2,6-lutidene would promote catalysis. On the contrary, we found that addition of base shuts down the catalytic reaction completely. Therefore, we concluded that **4** is not the active catalyst, and a second multiply bonded ligand is not needed, contrary to a previous report.[9,11]



(3)

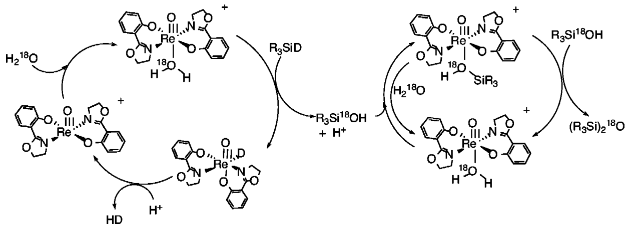
The source of each hydrogen atom in the dihydrogen product was discerned by employing Et_3Si-D with H_2O, and Et_3Si-H with D_2O (eqs 4 and 5). The produced hydrogen gas was analyzed by mass spectrometry and found to be exclusively HD.

$$\mathrm{Et_3Si{-}D}\ ({\sim}97\%) + \mathrm{H_2O} \xrightarrow{1\ \text{mol\% Re Cat. (1)}} \mathrm{HD} + \mathrm{Et_3SiOH}$$
$$\text{gas analysis: } \mathrm{H_2} = 5.6\%, \mathrm{HD} = 94.2\%, \text{ and } \mathrm{D_2} = 0.2\% \quad (4)$$

$$\mathrm{Et_3Si{-}H} + \mathrm{D_2O}\ (99\%\ ) \xrightarrow{1\ \text{mol\% Re Cat. (1)}} \mathrm{HD} + \mathrm{Et_3SiOH}$$
$$\text{gas analysis: } \mathrm{H_2} = 2.0\%, \mathrm{HD} = 97.6\%, \text{ and } \mathrm{D_2} = 0.4\% \quad (5)$$

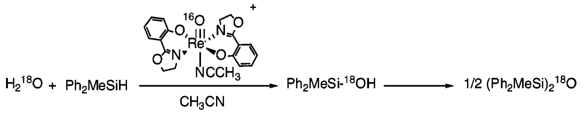
The progress of reaction was investigated by ^1H NMR for Ph_2MeSiH (Figure S1). The rate of formation of silanol is first-order in $[Ph_2MeSiH]$, $[Re]_T$, and $[H_2O]$. The rate of silyl ether formation is first-order in $[Ph_2MeSiOH]$ and [Re], but inhibited by water. A mechanism that is consistent with the observed isotope labeling and kinetic experiments is given in Scheme 1.[12,13]

Scheme 1



We have described a new methodology for storage and production of pure H_2 via catalytic hydrolytic oxidation of an organic liquid (organosilanes). This catalytic reaction is remarkable because the use of high-valent metal complexes in dehydrogenative oxidation with water has no precedence. The reaction proceeds via a novel mechanistic paradigm in which organosilane adds selectively to water, and the produced H_2 is composed of one hydrogen atom from organosilane and the other from H_2O. The mechanistic details for each of the steps in the proposed reaction of Scheme 1 are under investigation.

Table 2. Results from Isotope Labeling Experiments with $^{18}OH_2$[a]



entry	substrate added last	% ^{18}O[b]	
		$(Ph_2MeSi)_2O$	**1**
1	Re cat. **1**	86	∼2
2	Ph_2MeSiH	80	4
3	$H_2{}^{18}O$	69	5[c]

[a] Conditions: $[Ph_2MeSiH] = [\mathbf{1}] = [H_2{}^{18}O]$ (∼95% ^{18}O) = 0.053 M in CH_3CN at ambient temperature. Two substrates were incubated for 30 min prior to addition of the third. [b] ^{18}O-Incorporation into $(Ph_2MeSi)_2O$ was determined by GC−MS and into complex **1** by ESI-MS. [c] $[Re(hoz)_2]^+$ (*m*/*z* = 509, 511) was detected in addition to **1**.

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Supporting Information Available: Experimental details, eqs S1−S6, and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Oxidative addition to the five-coordinate cationic complex $[Re(O)(hoz)_2]^+$ to give initially a rhenium(VII) silyl hydride complex, $[Re(O)(SiR_3)(H)(hoz)_2]^+$, followed by nucleophilic attack of water onto the bound silicon is also possible.

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