

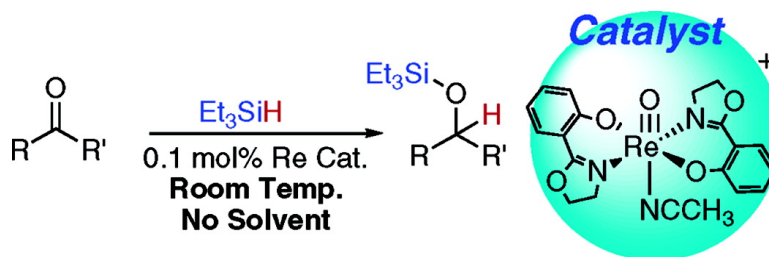
Communication

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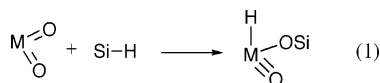
Mechanism for Reduction Catalysis by Metal Oxo: Hydrosilation of Organic Carbonyl Groups Catalyzed by a Rhenium(V) Oxo Complex

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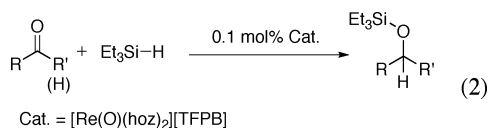
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High oxidation state oxo complexes are widely used in catalytic oxidations and oxygen atom transfer reactions.¹ However, the use of such complexes in catalytic reductions is extremely rare.² Few reports have appeared recently describing rhenium(V), rhenium(VII), and molybdenum(VI) oxo catalysts for the hydrosilation of aldehydes and ketones.³ In their mechanistic interpretation of the rhenium dioxo system, Toste and co-workers proposed Si-H addition across the Re=O multiple bond to give a hydrido-oxorhenium(V) complex.^{3a} The additional oxo ligand was hypothesized to stabilize the resulting oxo-hydrido, compensating for the loss of π donation from one of the oxo ligands (eq 1). However, several mechanistic questions remain, including the role of the additional oxo ligand and if indeed a dioxo complex is needed.⁴

















Herein, we report a new system for the hydrosilation of aldehydes and ketones using a monooxorhenium(V) catalyst. The highlights of our system are the following: (1) it offers mechanistic insight on activation of organosilanes by oxometalates; (2) the reaction proceeds efficiently under ambient temperature and atmosphere with low catalyst loading (0.1 mol %); and (3) the reaction may be performed without a solvent, wherein the catalyst precipitates at the end of reaction. This last feature is very attractive because it limits the amount of organic waste generated and facilitates catalyst separation.

We have reported recently on the hydrolytic oxidation of organosilanes using the catalyst [Re(O)(hoz)₂][TFPB] (hoz = 2-(2'-hydroxyphenyl)-2-oxazoline(-), TFPB = tetrakis(pentafluorophenyl)borate), **1**.⁵ In the presence of an aldehyde or ketone, reduction of the carbonyl group occurs, yielding the protected alcohol as silyl ether, eq 2.



Representative yields for the reduction of different substrates are shown in Table 1.⁶ The reaction may be performed with or without a solvent. Furthermore, for the solvent-free reaction, the catalyst precipitates out of solution as the polarity of the solvent changes from the reactants (aldehyde or ketone and Et₃SiH) to the silyl ether product. The catalyst retains activity after being recycled (entry 4). Even though preparative reactions were run with Et₃SiH, other organosilanes, such as PhMe₂SiH, work quite well. For example, NMR scale reaction of acetophenone with 1.5 equiv of PhMe₂SiH and 5 mol % of **1** in CD₃CN afforded PhC(H)(OSiMe₂-Ph)(CH₃) in quantitative yields.

Table 1. Hydrosilation of Organic Carbonyl Compounds Catalyzed by Oxorhenium **1**^a

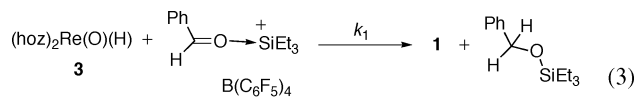
Entry	Substrate	Product	Solvent	% Yield ^b
1			CH ₂ Cl ₂	86
			Neat	86
2			CH ₂ Cl ₂	72
			Neat	76
3			CH ₂ Cl ₂	71
			Neat	71
4			Neat ^c	
			1 st cycle	80
			2 nd cycle	50
5			CH ₂ Cl ₂	67
			Neat	75
6			CH ₂ Cl ₂	57
			Neat	75
7			CH ₂ Cl ₂	59
			Neat	71

^a Reaction conditions: 0.1 mol % of **1**, substrate = 8–10 mmol, and 1.5 equiv of Et₃SiH. ^b Isolated yields. ^c NMR yields.

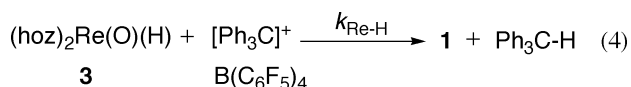
The accepted mechanism for metal-catalyzed hydrosilation of organic carbonyl compounds involves insertion of the carbonyl group into a metal hydride bond, which is formed by either oxidative addition (late metals) or σ -bond metathesis (early metals).⁷ Toste proposed a new mechanism in which silane adds across a Re=O bond (eq 1).^{3a} However, we have shown through ¹⁸O labeling studies that addition of Si-H across the Re=O bond is an unlikely pathway.⁵ Moreover, the resulting siloxyrhenium(V) hydride would not be sufficiently hydridic to reduce organic carbonyl groups, which is discussed next.⁸

Another mechanism that has been documented in recent years by Bullock is ionic hydrogenation. In this mechanism, the proposed metal hydride complex acts as a hydride donor to an activated carbonyl compound, bypassing the insertion step.⁹ To test the viability of an ionic hydrogenation mechanism, we prepared the rhenium hydride complex, Re(O)(hoz)₂H (**3**), from the reaction of Re(O)(hoz)₂Cl, **2**, with Bu₃SnH.⁶ Complex **3** did not react with benzaldehyde. However, **3** converted to **1** in the presence of the silylium adduct of benzaldehyde, which was prepared according to the methodology of Lambert et al.,¹⁰ affording the silyl ether (eq 3). Furthermore, under steady-state conditions, the experimental rate law for hydrosilation exhibits first-order dependencies on [1] and [Et₃SiH] and no dependence on [benzaldehyde]: $d[\text{PhC-}$

$(\text{OSiEt}_3)_2\text{H}_2/dt = k[\text{Et}_3\text{SiH}][\mathbf{1}]$.⁶ Therefore, the reaction described by eq 3 would involve two steady-state intermediates, and their reaction must be facile enough to account for the observed rate law.

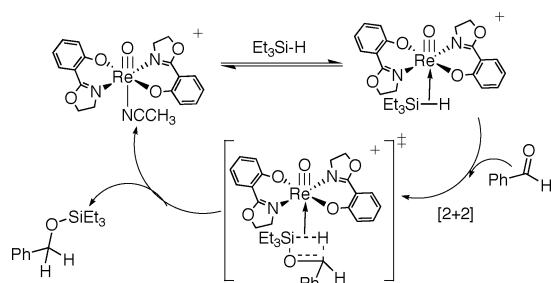


To probe the hydricity of **3**, we studied its reaction with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (eq 4). The kinetics of hydride abstraction was determined by stopped-flow following the disappearance of the trityl cation at 450 nm. Bullock and co-workers have used the reaction of metal hydrides with trityl cation to establish a hydricity scale for a series of transition metal carbonyl hydrides.¹¹ To check the reliability of our stopped-flow kinetics, we reproduced the kinetics for the reaction of Et_3SiH and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($k_{\text{Et}_3\text{SiH}} = 170 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$), which is in excellent agreement with that observed previously ($150 \text{ M}^{-1} \text{ s}^{-1}$).¹¹ In comparison, the rate constant observed for complex **3** is approximately 70 times less than that for Et_3SiH ($k_{\text{Re-H}} = 2.40 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$).¹² This positions **3** among the least hydric of all the transition metal carbonyl hydrides studied by Bullock.¹¹ The kinetic data suggest that the ionic hydrosilylation mechanism cannot account for the observed catalysis. Under steady-state conditions, any silylium benzaldehyde adduct generated is more likely to react with Et_3SiH than complex **3** because (1) Et_3SiH is present in higher concentration, and (2) Et_3SiH is significantly more hydric than **3**. Thus, if silane and **1** produce silylium and complex **3**, rhenium would act as a mere initiator and $[\text{Et}_3\text{Si}^+]$ would be the true catalyst. This mechanism, however, is refuted as it has been shown that the product distribution for $[\text{Et}_3\text{Si}^+]$ -catalyzed hydrosilylation reactions is significantly different from what we observed for our system.¹³ The rhenium hydride **3** can be reactivated for catalysis by reaction with $[\text{Et}_3\text{Si}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ to afford Et_3SiH and **1**. Additionally, a siloxy-rhenium(V) hydride, produced as a steady-state intermediate from the addition of silane across the $\text{Re}=\text{O}$ bond, would be less hydric than complex **3** due to the absence of π -bonding from a terminal oxo, providing further evidence against such a mechanism.⁸



By process of elimination, the most viable mechanism would involve organosilane activation through formation of $\eta^2\text{-Et}_3\text{SiH}$ complex (Scheme 1), with the rate-determining step (RDS) being formation of the organosilane Re adduct.^{14,15} The observed kinetic isotope effects from NMR kinetics ($\text{Et}_3\text{SiH}/\text{Et}_3\text{SiD} = 1.3$ and benzaldehyde-H/benzaldehyde-D = 1.0) are also consistent with the proposed mechanism.¹⁴

Scheme 1



We have presented herein a new mechanism for metal-oxo-catalyzed hydrosilylation of organic carbonyl compounds. Like Bullock's ionic hydrogenation mechanism, prior coordination of the aldehyde/ketone and insertion are not required. However, formation of a metal hydride is not necessary either as the resulting oxorhenium hydride is not sufficiently hydric. The featured catalyst exhibits high activity in comparison to that of other metal oxo hydrosilylation catalysts.^{3c} Further studies on the synthetic scope of this system and its utility in asymmetric hydrogenation are ongoing in our laboratory.

Acknowledgment. Acknowledgment is made to Purdue University and NSF for financial support.

Supporting Information Available: Experimental details and kinetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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