Catalytic Hydrosilylation of Carbonyl Compounds with Cationic Oxorhenium(V) Salen

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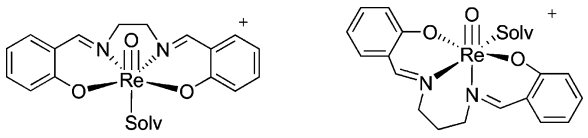
Summary: High-valent cationic oxorhenium(V) salen complexes efficiently catalyze the reduction of carbonyl compounds by organosilanes under mild, open-flask conditions. Good to excellent yields of silyl-protected alcohols are obtained in one step, and a variety of functional groups are compatible.

1. Introduction

Catalytic hydrosilylation of ketones and aldehydes is a valuable transformation because it generates protected alcohols in one step. Thus, hydrosilylation is more attractive than the conventional two-step methodology of reduction by a metal hydride followed by silyl protection. Many transition metal complexes, especially those based on ruthenium, rhodium, iridium, and titanium, as well as zinc and copper, are known to catalyze hydrosilylation.[1,2] More recently even an organocatalytic version of the reaction has been realized.[3]

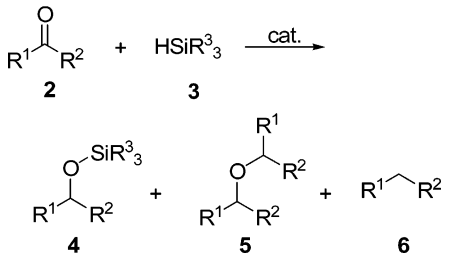
High-valent transition metal oxo complexes are ubiquitous in oxidations and oxygen atom transfer (OAT) reactions.[4] Recently, a few reports have appeared in the literature on the use of rhenium(V/VII) and molybdenum(VI) oxo catalysts for the reduction of ketones, aldehydes, and imines.[5−8] We have developed convenient syntheses for cationic monooxo-rhenium(V) salen complexes [Re(O)(salen)(Solv)] $[B(C_6F_5)_4]$ (**1a**) and [Re(O)(salpn)(Solv)][$B(C_6F_5)_4$] (**1b**) (Figure 1)[9] via oxygen abstraction from the readily available μ-oxo dinuclear compounds.[10] Complexes **1a** and **1b** activate organosilanes under mild conditions. These as well as the aforementioned systems are of considerable interest because they are practical catalysts, being air and moisture tolerant, and they also represent a new mechanistic paradigm for the use of high oxidation state transition element complexes in reductions.[11] In this paper we present the application of **1a** and **1b** as catalysts for the hydrosilylation of ketones and aldehydes and propose a viable reaction mechanism.



1a **1b**

Figure 1. Cationic monooxo-rhenium(V) salen catalysts (Solv = H_2O or CH_3CN, anion = $B(C_6F_5)_4^-$).

Scheme 1. Reduction of Carbonyl Compounds by Organosilanes



2. Results and Discussion

Reduction of ketones and aldehydes (**2**) by organosilanes (**3**) usually produces silyl ether (**4**) as the major product (Scheme 1). Ether **5** and the deoxygenated species **6** are often among the observed byproducts. The hydrosilylation reactions with **1a** and **1b** were conveniently carried out under ambient temperature and open to air because the oxorhenium catalysts are air and moisture stable. It is worth noting that the trimethylene-bridged **1b** is considerably more reactive than the ethylene-bridged **1a**, requiring less reaction time (Table 1, entries 1 and 2). This

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(9) Abbreviations: salen: dianion of 1,2-bis(salicylidene)ethylenediamine; salpn: dianion of 1,3-bis(salicylidene)propyldiamine.

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Table 1. Hydrosilylation of Acetophenone (2a) and Butanone (2b)[a]

entry	substrate (**2**)	cat. (mol %)	silane (**3**)[b]	time	% yield products **4**[c]	% yield products **5/6 (%)**
1	**2a**	**1a** (1%)	Et_3SiH	7 d	68	nd[d]
2	**2a**	**1b** (1%)	Et_3SiH	2.5 h	97 (88)	**6** (3)
3[e]	**2a**	**1b** (1%)	Et_3SiH	24 h	98 (88)	nd
4[f]	**2a**	**1b** (0.1%)	Et_3SiH	48 h	95 (71)	nd
5	**2a**	**1b** (5%)	Et_3SiH	2 h	48	**5** (23)[g]
6	**2a**	**1b** (1%)	$^tBuMe_2SiH$	7 d	84 (73)	nd
7	**2a**	**1b** (1%)	$PhMe_2SiH$	4 d	75 (57)	nd
8	**2a**	**1b** (1%)	Ph_2MeSiH	7 d	87 (87)	nd
9	**2b**	**1b** (5%)	Et_3SiH	0.5 h	100 (91)	nd
10	**2b**	**1b** (5%)	Ph_2MeSiH	5.5 h	70	**5** (30)

[a] Reaction conditions: 0.7 mmol of ketone substrate (**2**) (~1 M) and Re-oxo catalyst (**1**) in CD_2Cl_2unless noted otherwise, 1.5 equiv of silane (**3**) added last. See Supporting Information for details. [b] **3a**: Et_3SiH; **3b**: $^tBuMe_2SiH$; **3c**: $PhMe_2SiH$; **3d**: Ph_2MeSiH. [c] NMR yield on reaction mixtures. Isolated yields in parentheses. [d] nd: not detected. [e] In benzene. [f] Neat. [g] As a ~1:1 mixture of *meso* and *dl* diastereomers.

enhancement in **1b** originates from structural differences between **1a** and **1b** (Figure 1). The salen ligand occupies the equatorial plane of a distorted octahedron in **1a**, leaving the solvent ligand *trans* to the rhenium oxo multiple bond, whereas **1b** adopts a *cis* geometry in solution.[10]

As for solvent effect, the reaction displays a preference for polar solvents because of the charge on the catalyst. Methylene chloride is the solvent of choice, and it dissolves the cationic rhenium catalysts reasonably well. The reaction can also be carried out in acetonitrile, but with reduced kinetic efficiency due to its coordinating ability. Oxorhenium salen complexes catalyze the hydrolysis and alcoholysis of organosilanes.[12] Therefore, protic solvents are not suitable for the hydrosilylation reaction. Use of predried solvents with 4 Å molecular sieves is beneficial but not necessary. The reaction can also be carried out in nonpolar solvents such as benzene (Table 1, entry 3) because the polarity of carbonyl compounds allows the dissolution of the cationic rhenium catalyst. Furthermore, the hydrosilylation can be performed neat (without a solvent) (Table 1, entry 4). As the reaction proceeds and the less polar silyl ether product builds up, the rhenium catalyst precipitates out of solution. Such systems are promising as self-separating homogeneous catalysts, allowing easy catalyst recovery and recycling.[13,14]

Catalyst concentrations were generally employed at 1 mol % (relative to substrate), although loadings as low as 0.05 mol % could be used, albeit requiring longer reaction time. However, higher catalyst loading of 5 mol % works well with aliphatic ketones (Table 1, entry 9) but not for aryl ketones. For instance, reduction of acetophenone yielded the desired silyl ether product **4** in low yield along with a significant amount of ether **5** (Table 1, entry 5). Benzophenone affords diphenylmethane (**6**) (>60% yield) as the major reduction product. These observations demonstrate a possible approach for complete deoxygenation of carbonyl compounds under mild conditions.[15]

For most systems, the reactivity trend with respect to organosilane is generally primary ($-SiH_3$) > secondary ($-SiH_2$) > tertiary ($-SiH$).[1a] However, in our system monohydrosilanes are sufficiently reactive. Triethylsilane (**3a**) is the reductant of choice, giving fast reaction times and high selectivity. With bulkier or aryl silanes (**3b**−**d**), although the conversion and selectivity remain excellent, the reactions are slower (Table 1, entries 6−8).

With these conditions in hand, we examined a number of representative carbonyl compounds, mainly ketones,[16] for hydrosilylation, using 1 mol % **1b** and 1.5 equiv of Et_3SiH in CH_2Cl_2 under ambient temperature and atmosphere. The results are summarized in Table 2. Both ketones, aromatic or aliphatic, and aromatic aldehydes can be effectively reduced by triethylsilane (**3a**) with good to excellent yields. A variety of functional groups, C=C, C≡C, halogens, nitro, and esters, are tolerated under these conditions. Notably dialkyl ketones, which are often less reactive in reduction reactions, are the more successful substrates in the present system, being fast and most selective. On the other hand, substrates such as ethyl benzoylacetate (a β-keto ester) and *p*-(dimethylamino)benzaldehyde gave no reaction, and 2-cyclohexen-1-one led to a complex mixture of products, which included *dl*- and *meso*-3,3′-dicyclohexanones[17] from β-reductive dimerization as the major species, cyclohexanone, and 2-cyclohexen-1-ol.

Hydrosilylation of aliphatic aldehydes with Et_3SiH is less satisfactory. For ^{i}PrCHO, ether **5** is obtained as the major product. Fortunately, replacement of Et_3SiH with Ph_2MeSiH results in nearly quantitative conversion to the corresponding silyl ether (Table 2, entries 10 and 11). Both catalysts **1a** and **1b** work well in this regard. It is worth noting that the situation for ketones is quite different; Ph_2MeSiH gives more of the ether product **5** (compare with Table 1, entry 10). The ether product **5** probably results from the reductive condensation of carbonyl compounds with alkoxysilanes,[18] but the reason for this selectivity difference is not clear at this point. For the purpose of generating silyl-protected alcohols, however, one can simply choose the appropriate organosilane for a given carbonyl substrate.

To demonstrate the practical utility of these catalysts in hydrosilylation reaction, several representative carbonyl substrates are examined at 0.1 mol scale, using 1.1 equiv of Et_3SiH and 0.05 mol % catalyst **1b** under solvent-free conditions (Table 2, entries 14−16). Good yields of silyl ethers are obtained after purification. These results compare favorably with many transition metal-based hydrosilylation catalysts, considering the inexpensive rhenium, low catalyst loading, and mild, open-flask conditions.

Preliminary experiments were carried out to probe the hydrosilylation mechanism in the present system. In the solid state, catalyst **1a** has water as the sixth ligand, while in solution, the sixth ligand is CH_3CN.[10] Upon addition of 2-butanone, the CH_3CN signal in the ^1H spectrum shifts upfield toward the position of free CH_3CN as the concentration of butanone is increased. This indicates that an equilibrium exists between butanone and the rhenium catalyst. Furthermore, a transient species with *m*/*z* equal to the sum of $ReO(salen)^+$ and organosilane (Et_3SiH or $PhMe_2SiH$) was observed by ESI-MS in

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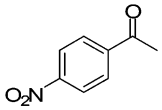
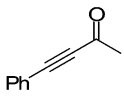
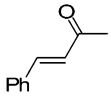
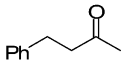
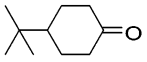
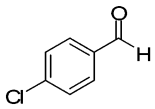
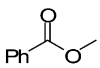
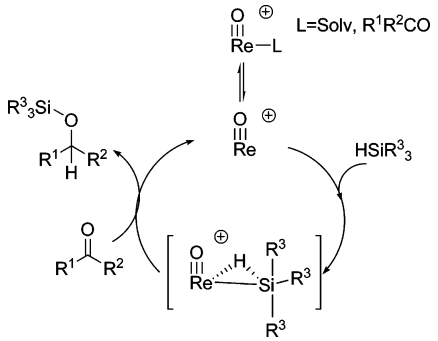
Table 2. Hydrosilylation of Various Carbonyl Compounds Catalyzed by 1b[a]

entry	Substrate (**2**)	Silane (**3**)[b]	time	% Yield Products	
				4[c]	**5/6 (%)**
1		**3a**	2.5 h	97 (88)	**6** (3)
2		**3a**	20 h	50 (47)	nd[d]
3		**3a**	47 h	(67)	nd
4		**3a**	2 h	(77)	nd
5		**3a**	3 h	99 (98)	nd
6		**3a**	24 h	95 (92)	nd
7		**3a**	2 h	99 (93)[e]	nd
8		**3a**	2 h	88 (70)	**5** (12)
9		**3a**	0.5 h	88 (88)	**5** (12)
10		**3a**	0.5 h	36	**5** (64)
11		**3d**	0.5 h	98(93)	nd
12[f]		**3d**	6 h	95(92)	nd
13		**3a**	67 h	0	0
14[g]		**3a**	5 h	(71)	
15[g]		**3a**	84 h	(81)	
16[g]		**3a**	69 h	(64)	

[a] Reaction conditions: 0.7 mmol of ketone or aldehyde (**2**) (~1 M) and **1b** (1 mol %) in CD_2Cl_2, 1.5 equiv of silanes added last. See Supporting Information for details. [b] **3a**: Et_3SiH; **3d**: Ph_2MeSiH. [c] NMR yield on reaction mixtures. Isolated yields in parentheses. [d] nd: not detected. [e] As a 1:1 *tran/cis* mixture. [f] **1a** as catalyst. [g] These reactions were run at 0.1 mol scale under neat conditions: **1b** (0.05 mol %) dissolved in carbonyl substrates, 1.1 equiv of Et_3SiH added at ambient temperature.

Scheme 2. Consensus Mechanism for Re-oxo-Catalyzed Hydrosilylation ($Re(O)^+$ represents 1a or 1b)



the early stages of the reaction.[19] However, this presumed silane adduct was not detected by ^1H NMR, even at low temperature (−80 °C). Instead, a new, diamagnetic species, with two more mass unit (*m*/*z* 469/491), was obtained. The exact identity of this species awaits further elucidation. Kinetics of reduction of benzaldehyde with $PhMe_2SiH$ was followed by ^1H NMR. In addition to first-order dependence on catalyst, the analysis revealed an important feature of the reaction, namely, inhibition by the substrate PhCHO (Figure S1 in Supporting Information). On the basis of these observations, we propose the viable mechanism depicted in Scheme 2. The presence of an open coordination site or a labile ligand on rhenium seems to be essential for catalytic activity. The substrate inhibition is significant, as it effectively excludes mechanisms where the reaction is initiated by carbonyl coordination to rhenium. More likely, the organosilane is activated by forming a σ-complex, followed by nucleophilic attack of the carbonyl substrate at silicon. This mechanism is analogous to Crabtree's mechanism for Ir-catalyzed organosilane alcoholysis.[20] In this consensus mechanism, the organosilane acts as a σ-donor and π-acceptor toward rhenium(V). We suggest the latter interaction (π-donation from the metal nonbonding d_{xy} orbital to the σ^* of Si−H) to be key in activating the organosilane substrate. Nevertheless, catalytic hydrosilylation is often complicated, as has been cautioned previously;[21] thus, it is prudent to not generalize the hydrosilylation mechanism.

In conclusion, we have demonstrated an air-stable, high-valent monooxo-rhenium(V) catalyst containing a salen ancillary ligand for the hydrosilylation of a variety of carbonyl compounds under mild, open-flask conditions. The reaction proceeds through silane activation most likely through a η^2-silane σ-adduct.

3. Experimental Section

General Procedure for Re-oxo-Catalyzed Hydrosilylation of Carbonyl Compounds. The following procedure for the hydrosilylation of PhC≡CCOMe is representative. A NMR tube was charged with **1b** (8.5 mg, 1 mol %), PhC≡CCOMe (100 μL, 0.69 mmol, ~1 M), and CD_2Cl_2 (0.5 mL) and a magnetic stir bar. After the complex was dissolved, Et_3SiH (164 μL, 1.03 mmol, 1.5 equiv) was added. The resulting solution was stirred under ambient temperature and monitored by ^1H NMR. After 47 h, the reaction mixture was subjected to flash chromatography on a silica gel column, eluted with 2% Et_3N in hexanes. Yield: 120 mg (67%).

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General Procedure for Catalytic Hydrosilylation of Carbonyl Compounds on a Preparative Scale. In a typical procedure, to a 250 mL round-bottom flask with a magnetic stir bar were added $[ReO(salpn)(solv)^+][B(C_6F_5)_4^-]$ (**1b**) (67.8 mg, 0.0556 mmol) and butanone (9.96 mL, 0.111 mol). Et_3SiH (19.5 mL, 0.122 mol) was added to the solution while stirring. The solution warmed and changed to a reddish-brown color within 5 min. The progress of the reaction was monitored by ^1H NMR. After a period of time, as indicated in Table 2, the resulting mixture was distilled under reduced pressure to obtain a pure, colorless silyl ether product. Yield: 13.39 g, 64%.

Triethyl((1-methyl-3-phenyl-2-propynyl)oxy)silane, (PhC≡CCH(CH_3)OSiEt_3). ^1H NMR (300 MHz, $CDCl_3$): δ 7.34 (m, 2H, Ph), 7.24 (m, 3H), 4.70 (q, J = 6.6 Hz, 1H), 1.49 (d, J = 6.6 Hz, 3H), 0.98 (t, J = 7.8 Hz, 9H), 0.66 (q, J = 7.8 Hz, 6H). ^{13}C NMR (75.438 MHz, $CDCl_3$): δ 131.6, 128.3, 128.2, 123.2, 91.9, 83.2, 59.2, 25.6, 6.9, 4.9. GC-MS: *m*/*z* 260 (1), 245 (2), 231 (100), 203 (63), 187 (90), 159 (82), 131 (37). HRMS: calcd for $C_{16}H_{24}OSi$ 260.1596, found 260.1599.

Triethyl(1-(4-nitro-phenyl)ethoxy)silane, (4-NO_2-C_6H_4CH(CH_3)OSiEt_3). ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, 2H, J = 8.7 Hz, Ar), 7.51 (d, 2H, J = 8.7 Hz, Ar), 4.95 (q, 1H, J = 6.6 Hz), 1.44 (d, J = 6.6 Hz, 3H), 0.92 (t, J = 8.1 Hz, 9H), 0.58 (q, J = 8.1 Hz, 6H). ^{13}C NMR (75.438 MHz, $CDCl_3$): δ 154.4, 147.0, 126.0, 123.6, 69.9, 27.1, 6.8, 4.8. GC-MS: *m*/*z* 281 (1), 252 (100), 103 (47), 75 (24). HRMS: calcd for $C_{14}H_{23}NO_3Si$ 281.1447, found 281.1448.

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Supporting Information Available: Detailed experimental procedures and characterization of silyl ether products. This material is available free of charge via the Internet at http://pubs.acs.org.

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