

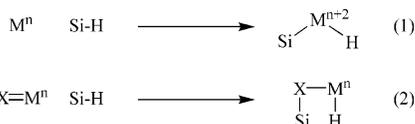
Reversing the Role of the Metal–Oxygen π -Bond. Chemoselective Catalytic Reductions with a Rhenium(V)-Dioxo Complex

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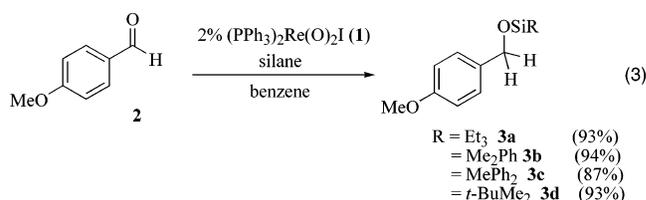
Transition metal complexes with metal–oxygen multiple bonds have found numerous applications in organic chemistry as catalysts for oxidation and oxygen atom transfer reactions.¹ Aside from oxidation reactions, applications of this class of metal complexes to other organic transformations are extremely rare.² We became interested in the possibility that these high oxidation metal complexes could be used as catalysts for other transformations. For example, hydride reduction of a carbonyl group followed by protection of the resulting alcohol as a silyl ether is one of the most prevalent sequences in organic chemistry. Hydrosilylation of carbonyl compounds represents a one-step alternative to these procedures, but it is rarely employed because traditional metal catalysts suffer from air and moisture sensitivity, functional group incompatibility, and the requirement to use reactive polyhydric silanes.³ Use of high oxidation state metal complexes could alleviate many of these drawbacks.



Generation of metal hydrides from silanes generally involves an oxidative addition of the silicon–hydrogen bond to the metal and therefore requires low-valent metal complexes (eq 1). On the basis of recent reports,⁴ we envisioned an alternative mechanism in which the metal hydride is produced by a [2 + 2]-type addition of the Si–H bond to a metal ligand π -bond (eq 2). The overall effect of this process is to convert the strongly oxidizing $\text{M}=\text{O}$ complex to a silyloxy-substituted metal hydride which could potentially be employed as a reductant. A variety of complexes containing metal–ligand multiple bonds were first considered; however, we chose to examine metal dioxo complexes in the hope that the reactivity of the metal–oxygen multiple bond would be enhanced by the presence of a second oxo ligand (spectator oxo effect⁵). As such, we chose to begin our study by investigating rhenium(V)dioxo complexes as catalysts. Herein we describe an air- and moisture-tolerant catalytic one-step reduction-protection of carbonyl groups employing rhenium-oxo complexes as catalysts. This novel reactivity represents a striking reversal of the redox properties typical of rhenium-oxo complexes (such as MTO^6).

We initiated our investigation by employing the readily available iododioxo(bistriphenylphosphine)rhenium(V) (**1**)⁷ as a catalyst. We were pleased to find that, at 60 °C in benzene, 5 mol % **1** rapidly (15 min) catalyzed the addition of triethylsilane to *p*-anisaldehyde (**2**) to afford the corresponding triethylsilyl ether (**3a**) in 91% yield. Lowering the catalyst loading to 2 mol % **1** required slightly increased reaction times (2 h), but had no detrimental effects on the yield of **3a** (eq 3). The reaction temperature could be lowered to 25 °C, but under these conditions the reaction required

significantly longer reaction times (18 h) to proceed to completion. A variety of other silanes, including dimethylphenylsilane (DMPS–H) and diphenylmethylsilane (DPMS–H), participate equally well in the rhenium(V)-dioxo catalyzed hydrosilylation.⁸ Notably, 2 mol % **1** catalyzes the addition of *tert*-butyldimethylsilane (TBDMS–H) to afford the TBDMS-protected alcohol (**3d**) in 93% yield. However, **1** showed no reactivity toward the sterically encumbered *tri-iso*-propylsilane (TIPS–H). Benzene proved to be the most general solvent, but in many cases the reactions could be performed in other common solvents such as THF, dioxane, dichloromethane, and acetonitrile.



With these conditions in hand, we examined the rhenium-dioxo catalyzed hydrosilylation of a variety of aldehydes (Table 1). The catalyst showed excellent reactivity toward a wide range of aromatic (entries 1–5), heteroaromatic (entry 6), and aliphatic aldehydes (entries 7 and 8), affording the corresponding DMPS ethers in good to excellent yields. This catalyst system tolerates a wide range of functional groups including a Lewis-basic tertiary amine (entry 5). Furthermore, functional groups that are prone to reduction, such as aryl nitro (entry 1), aryl halo (entry 2), ester (entry 3), and keto (entry 4) groups, are left untouched. This is further exemplified by the chemoselective reduction of aldehyde **4i**, in the presence of an aryl iodide and α,β -unsaturated ester, to afford silyl ether **5i** in 68% yield (entry 9).

The Re-dioxo catalyzed reaction was readily extended to the hydrosilylation of aromatic and aliphatic ketones (Table 2, entries 10–15). The reduction of ketones required slightly increased catalyst loadings and longer reaction times, but the corresponding silyl ethers were isolated in good to excellent yields. The reaction remains highly chemoselective, tolerating functional groups such as cyano (entry 4) and ester (entry 2). Notably, no products derived from cyclopropane ring-opening were detected (¹H NMR, GCMS) in the reduction of cyclopropylphenyl ketone (entry 14). This observation suggests that the reduction is not proceeding through a mechanism involving electron transfer.⁹

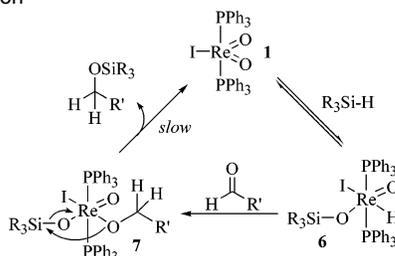
We propose the sequence outlined in Scheme 1 as the likely mechanism of this new type of reaction.¹⁰ The first step involves a formal [2 + 2]-addition^{4,11} of silane to the $\text{Re}=\text{O}$ bond in **1** to produce metal hydride **6**. In accord with this hypothesis, the reaction of excess triethylsilane with **1** produced a new rhenium complex, which we believe to be **6**. This complex shows new ¹H NMR signals at 6.60 (triplet, 1H, $\text{Re}-\text{H}$), 0.78 (triplet, 9H, $\text{OSi}(\text{CH}_2\text{CH}_3)_3$), and

Table 1. Re-Dioxo Catalyzed Hydrosilylation of Aldehydes and Ketones

entry	aldehyde	temp.(°C)/time	yield ^a
1	4-nitrobenzaldehyde (4a)	60 / 15 min.	94% (5a)
2	4-bromobenzaldehyde (4b)	60/ 30 min.	89% (5b)
3	4-acetoxybenzaldehyde (4c)	60 / 1h	95% (5c)
4	4-acetylbenzaldehyde (4d)	rt / 26h	86% (5d)
5	4-dimethylaminobenzaldehyde (4e)	60 / 30 min.	86% (5e)
6	3-thiophenecarboxaldehyde (4f)	60 / 45 min.	73% (5f)
7	2-phenylpropionaldehyde (4g)	60 / 15 min.	91% (5g)
8	2-benzoyloxyacetaldehyde (4h)	60 / 2h	69% ^b (5h)
9	 4i	60 / 2h	68% (5i)
10	4- <i>t</i> -butylcyclohexanone (4j)	75 / 7h	87% ^c (5j)
11	ethyl levulinate (4k)	75/ 16h	63% (5k)
12	5-methoxytetralone (4l)	75 / 20h	66% (5l)
13	4-acetylbenzoxonitrile (4m)	75 / 14h	82% (5m)
14	cyclopropylphenylketone (4n)	75 / 20h	69% (5n)
15	4-phenyl-2-butanone (4o)	60 / 14h	76% ^d (5p)

Reaction conditions: aldehydes 2 mol % **1**, ketones 5 mol % **1**, 1.2 equiv of DPMS-H, 1 M (substrate) in C₆H₆. ^a Isolated yield after chromatography. ^b Accompanied by 24% desilylated alcohol. ^c >25:1 trans:cis. ^d DPMS-H used as silane.

Scheme 1. Mechanistic Proposal for Re-Dioxo Catalyzed Hydrosilylation



−0.20 ppm (quartet, 6H, OSi(CH₂CH₃)₃) that were assigned to the Re-H and OSi(CH₂CH₃)₃ resonances.^{12,13} This assignment was confirmed by reaction with **1** with triethylsilyldeuteride (TES-D), which produced an identical complex lacking the signal at 6.60 ppm in the ¹H NMR. Addition of 4-nitrobenzaldehyde to **6** afforded the corresponding silyl ether (**5a**). However, under catalytic conditions, monitoring by ¹H NMR showed that a different complex is present until the end of the reaction. This complex also shows an upfield signal for the silyl group (−0.5 ppm), but it lacks the signal for the rhenium hydride. Instead, this complex shows a new signal at 4.10 ppm (2H, Re−OCH₂Ph), which we have assigned to alkoxy-metal intermediate **7** produced by addition of the rhenium hydride to the carbonyl group.¹⁴ Transfer of the silyl group to the alkoxy ligand, formally a *retro*-[2 + 2] reaction, produces the silyl ether product and regenerates dioxo catalyst **1**.¹⁵

In summary, we have developed an air- and moisture-tolerant hydrosilylation of aldehydes and ketones using a rhenium-dioxo complex as catalyst. The reaction is compatible with a wide range of functional groups such as amino, cyano, nitro, aryl halo, ester, and alkene. As such, this reaction provides an efficient and practical one-step reduction-protection method in which no byproducts are

produced. Furthermore, the use of a metal-dioxo complex as a catalyst for the reduction of organic functional groups represents a complete reversal from the traditional role of these complexes as oxidation catalysts. This novel reactivity suggests that metal–ligand π -bonds may catalyze other types of σ -bond activation reactions. Further studies on the mechanism and new applications, including the enantioselective version, of this reaction are ongoing in our laboratories.

Acknowledgment. We gratefully acknowledge the University of California, Berkeley, the Camille and Henry Dreyfus Foundation, Research Corporation (Research Innovation Award), and Merck Research Laboratories for financial support. We thank Professors R. H. Grubbs (Caltech) and R. G. Bergman for many helpful discussions.

Supporting Information Available: Experimental procedures and compound characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA029498Q