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# An Efficient Method for the Preparation of Oxo Molybdenum Salalen Complexes and Their Unusual Use as Hydrosilylation Catalysts

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A number of molybdenum(VI) dioxo salalen complexes were prepared from the reaction of $Mo(CO)_6$ and salen ligands containing bulky substituents, providing a novel and facile entry to Mo−salalen compounds. Two of the complexes were characterized by single-crystal X-ray diffraction. Reduction with organic phosphines or silanes afforded the monooxo molybdenum(IV) complexes, along with dinuclear molybdenum(V) species featuring a bridged oxo ligand ($\mu$-O). One of the dinuclear complexes as well as a molybdenum(VI) dioxo salan complex was characterized structurally. All of the molybdenum compounds except the monooxo molybdenum(IV) were fully characterized by NMR, mass spectrometry, and elemental analyses. Investigations of acetophenone and 4-Ph-2-butanone reduction with $PhSiH_3$ showed that all of these molybdenum oxo complexes could serve as catalysts at reasonably low loading (1 mol % Mo) and ∼110 °C. The time profiles and efficacy of catalysis varied depending on the precursor form of the catalyst, $Mo^{VI}(O)_2$ vs $(O)Mo^{V}-O-Mo^{V}(O)$ vs $Mo^{IV}(O)$. Solvent effects, radical scavenger probes, and other mechanistic considerations reveal that the monooxo molybdenum(IV) is the most likely active form of the catalyst.

## Introduction

Use of the salen ligand framework in transition-metal chemistry is well-documented, especially in the area of asymmetric catalysis.[1] Less common is the related salan (reduced salen) complexes, which often display different structural conformation and thus lead to different reactivity and selectivity.[2] In recent years, partially reduced salen complexes (Figure 1), salalen for short, have emerged as a new platform in asymmetric catalysis.[3,4]

Application of high oxidation state transition metals, particularly rhenium and molybdenum, in catalytic reductions has been studied actively since the initial report by Toste and co-workers on the use of *cis*-$Re(O)_2(I)(PPh_3)_2$ as a catalyst for the hydrosilylation of aldehydes and ketones.[5] Several oxo and imido Re[6,7] and Mo[8,9] compounds have been evaluated for the catalytic hydrosilylation of organic carbonyl compounds. Several mechanistic schemes were put forth on the basis of experimental and computational investigations.[10] Among the catalysts screened so far, cationic monooxo rhenium(V) oxazoline and salen complexes exhibit the

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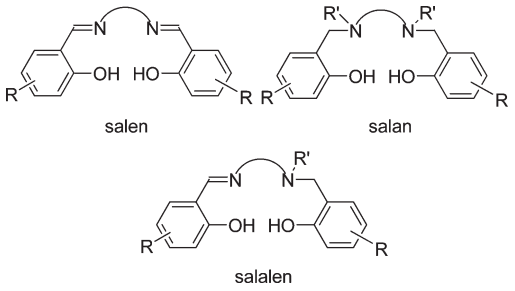


**Figure 1.** Salen, salan, and salalen ligands (R = alkyl, halide, etc.; R′ = Me or H).

highest activities. However, the chiral version gives low enantioselectivity,[6a] except for a mono-oxo oxazoline complex that has been shown to catalyze the hydrosilylation of imines with high enantioselectivity.[7d] In contrast, the Mo catalysts examined thus far have been primarily simple dioxo Mo(VI) such as $Mo(O)_2Cl_2$.

Our initial thought was to examine oxomolybdenum(IV) salen analogues on the basis of diagonal relationships of the periodic table and their isoelectronic configuration to oxorhenium(V). We were also interested in understanding the effect of charge on catalytic activity. Oxorhenium(V) oxazoline and salen are cationic while their molybdenum analogues would be neutral. In this report, we describe a novel and simple entry to molybdenum salalen complexes, attempts to obtain isolable Mo(IV) monooxo complexes, and their application in catalytic hydrosilylation.

## Results

**Synthesis and Characterization of Dioxomolybdenum(VI) Salalen Complexes.** In an effort to prepare $Mo^{IV}(O)$(salen) complexes and test their applicability in catalytic hydrosilylation of organic carbonyl compounds, we first followed a literature procedure[11] that calls for refluxing $Mo(CO)_6$ with $H_2$salen (the parent ligand—no substituents on the phenyl rings and an ethyl bridged diimine) under air. As reported, a dark brown powder was obtained, which is insoluble in common organic solvents. We reasoned that *t*-butyl substituents on the phenyl ring would facilitate dissolution of the Mo-containing product. Indeed, when $H_2$(3,5-$^t$Bu$_2$-salen) was employed instead of the parent salen in the reaction, the isolated orange product was soluble in common organic solvents, including THF, $CH_2Cl_2$, acetone, methanol, benzene, and hexanes. Unlike the presumed $Mo^{IV}$(O)(salen),[11] this compound is diamagnetic and gives a clean $^1$H NMR. However, the spectrum cannot be accounted for by either a symmetrically or asymmetrically coordinated salen-$^t$Bu$_2$ ligand. In the aromatic region, one singlet (8.09 ppm), assignable to one imine proton (HC=N), was accompanied by four doublets (at 7.61, 7.21, 7.18, and 6.19 ppm, with $J$ = 2.4 Hz), assignable to four ArH protons, suggesting one of the two imine C=N double bonds was hydrogenated during the course of the reaction (see eq 1). Accordingly, two doublets ($J$ = 12.9 Hz) were observed at 4.62 and 4.01 ppm. Furthermore, the FT-IR showed multiple strong bands in the Mo=O stretching region, 910−840 cm$^{-1}$, characteristic of *cis* dioxo

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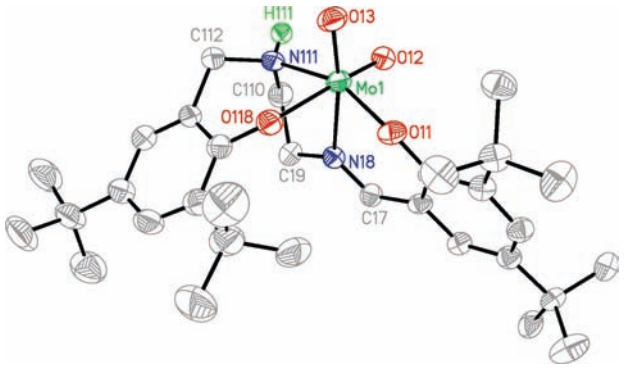
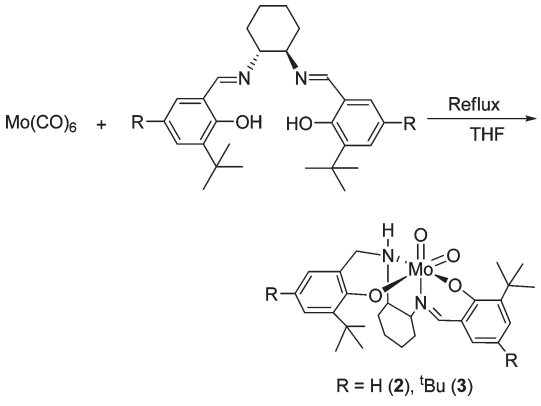



**Figure 2.** ORTEP diagram (drawn at 50% probability ellipsoids) of $Mo(O)_2$(salalen-$^t$Bu$_2$) compound **1**. The hydrogen atoms except the one on nitrogen are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Mo1−O13, 1.697(3); Mo1−O12, 1.734(3); Mo1−O11, 1.917(3); Mo1−O118, 2.012(3); Mo1−N111, 2.216(4); Mo1−N18, 2.281(4); N18−C17, 1.285(5); N111−C110, 1.492(6); N111−H111, 0.75(4); O13−Mo1−N18, 171.67(13); O12−Mo1−O118, 159.08(13); O11−Mo1−N111, 155.52(14); O13−Mo1−O12, 101.58(15); O13−Mo1−O11, 105.47(13).

stereochemistry. The presence of a medium strength broadband at 3120 cm$^{-1}$ is indicative of NH group. On the basis of these observations, the product was formulated as a salalen *cis*-dioxo complex, $Mo^{VI}(O)_2$(salalen-3,5-$^t$Bu$_2$) (**1**). X-ray diffraction analysis on single crystals confirmed this assignment (see below).

We extended this synthetic approach further to a number of substituted salen ligands incorporating a chiral backbone (eq 1). Two complexes were isolated and fully characterized. The $^1$H spectra show a pattern similar to that observed for **1** above, which is consistent with the reduction of one of the C=N linkages on the ligand to an amine HC—NH. It is noteworthy that two diastereomers with equal intensity were observed for **2** and **3** due to the chirality at the amine nitrogen.




(1)

**1** and **2** were characterized structurally by single crystal X-ray diffraction analysis. ORTEP drawings along with selected bond lengths and angles are shown in Figures 2 and 3 (where saladach refers, by analogy, to the half-reduced parent salalen ligand with a cyclohexane diamine (dach) bridge). The structures reveal that the metal center adopts a distorted octahedral geometry. The two oxo ligands are located mutually *cis* with bond angels of 101.58 (**1**) and 101.59° (**2**). *Trans* to the oxo ligands are an imine nitrogen and a phenoxy oxygen from the salan portion. Consistent with the stronger *trans* effect of oxo

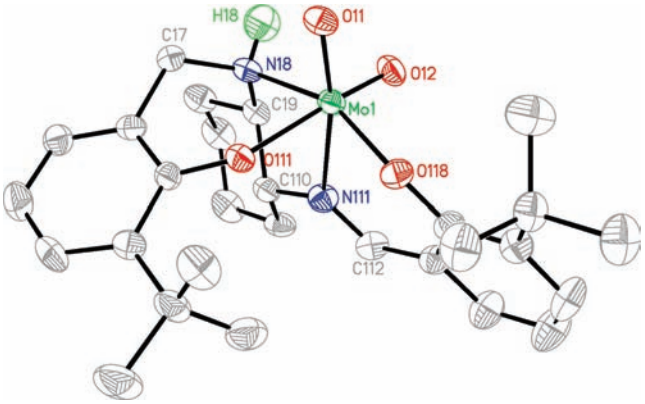



**Figure 3.** ORTEP diagram (drawn at 50% probability ellipsoids) of $Mo(O)_2$(saladach-$^t$Bu) compound **2**. The hydrogen atoms except the one on nitrogen are omitted for clarity. Selected bond distances (Å) and bond angels (deg): Mo1−O12, 1.702(3); Mo1−O11, 1.712(2); Mo1−O118, 1.924(3); Mo1−O111, 2.016(2); Mo1−N18, 2.200(3); Mo1−N111, 2.297(3); N111−C112, 1.277(5); N18−C17, 1.501(4); N18−H18, 0.99(4); N28−H28, 0.71(4); O12−Mo1−O111, 160.20(12); O118−Mo1−N18, 155.79(12); O11−Mo1−N111, 169.51(12); O12−Mo1−O11, 101.59(12); O12−Mo1−O118, 100.87(13).

groups, the Mo−O(phenoxy) bond (2.012 in **1**, 2.016 Å in **2**) trans to the oxo is longer than the Mo−O(phenoxy) bond (1.917 in **1**, 1.924 Å in **2**) *trans* to the amine nitrogen. The salalen ligands bind to the molybdenum center in a *fac-mer* fashion, with the salan portion *fac* and the salen portion *mer*, which are the typical binding modes for the parent salan and salen ligands, respectively.

**Synthesis and Structure of *cis*-Mo(O)$_2$(salan-$^t$Bu$_2$) (4).** In the context of asymmetric catalysis, we prepared *cis*-$Mo(O)_2$(salan-$^t$Bu$_2$) with a chiral backbone from $Mo(O)_2$-$(acac)_2$ and $H_2$salan. The simplicity of the product's $^1$H-NMR spectrum suggests *cis*-α conformation. This stereochemistry is confirmed by X-ray structural analysis, which revealed a symmetric arrangement of the salan ligand with two amine nitrogens trans to the two multiply bonded oxo ligands (Figure 4).

**Reduction of Dioxo Molybdenum with Phosphines and Silanes.** Because our initial targets are Mo(IV) complexes, we attempted to prepare oxo $Mo^{IV}$ salalen by reduction of dioxo $Mo^{VI}$ complexes with organic phosphines and silanes. The latter is relevant to hydrosilylation. Most reactions were carried out with $Mo(O)_2$(salalen-$^t$Bu$_2$) (**1**). Despite several attempts of varying concentrations and identity of the phosphine, **1** proved to be resistant to reduction with phosphine under ambient conditions. However, at elevated temperature (ca. 100 °C) a color change from orange to dark red was observed and accompanied by formation of $OPPh_3$. The Mo product was diamagnetic and displayed shifted $^1$H NMR signals in comparison to the starting dioxo complex. We conclude that the product is a five-coordinate monooxo molybdenum(IV) because the byproduct $OPPh_3$ and excess $PPh_3$ are not coordinated based on their $^{31}$P chemical shifts. The resulting $Mo^{IV}$ complex is air sensitive. It turns yellow upon exposure to air. Use of polymer-bound $PPh_3$ afforded the same product, based on $^1$H NMR, allowing for easy removal of the $OPPh_3$ byproduct via filtration.

Trimethyl phosphine ($PMe_3$), a stronger reducing agent, still required elevated temperature and gave similar

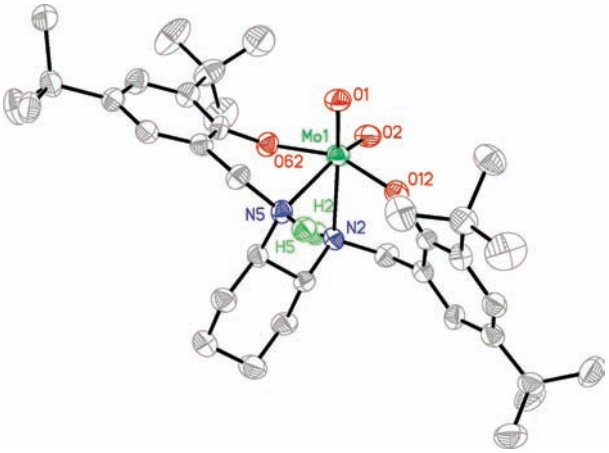
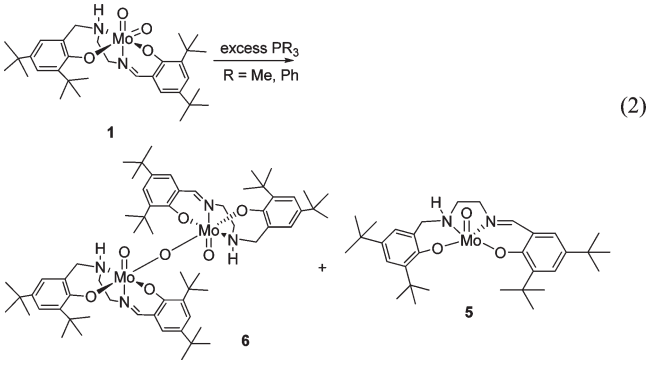



**Figure 4.** ORTEP diagram (drawn at 50% probability ellipsoids) of $Mo(O)_2$(salan-3,5-$^t$Bu$_2$) compound **4**. The hydrogen atoms except the one on nitrogen are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Mo1−O2, 1.688(4); Mo1−O1, 1.709(4); Mo1−O12, 1.924(4); Mo1−O62, 1.941(4); Mo1−N2, 2.347(5); Mo1−N5, 2.351(5); O2−Mo1−O1, 107.6(2); O2−Mo1−O12, 101.9(2); O1−Mo1−O12, 93.82(19); O2−Mo1−O62, 94.3(2); O1−Mo1−O62, 96.43(19); O12−Mo1−O62, 157.24(17); O2−Mo1−N2, 86.55(19); O1−Mo1−N2, 165.3(2); O12−Mo1−N2, 78.82(17); O62−Mo1−N2, 86.38(18); O2−Mo1−N5, 156.93(19); O1−Mo1−N5, 94.51(19); O12−Mo1−N5, 82.70(18); O62−Mo1−N5, 76.29(17); N2−Mo1−N5, 72.03(16).

results to $PPh_3$ (by UV−vis and $^1$H NMR). However, careful quantitative integration of the NMR signals showed that only about half of the starting material converted to $Mo^{IV}$(O)(salalen-$^t$Bu$_2$) (eq 2). Upon recrystallization, a yellow crystalline material was obtained, which was found to be NMR silent. X-ray crystal diffraction analysis revealed a $\mu$-oxo-bridged $Mo^V$ dinuclear complex (Figure 5), presumably resulting from a facile reaction between $Mo^{VI}$ and $Mo^{IV}$. The individual arrangement around the metal center is similar to the parent mononuclear $Mo(O)_2$(salalen-$^t$Bu$_2$) (**1**). Two terminal oxygens, trans to the imine nitrogens, adopt an anti configuration.




(2)

In the context of hydrosilylation, we also employed organic silanes as reductants. No reactions were observed with $Et_3SiH$ and $Ph_2SiH_2$ even at elevated temperature. When two equivalents of $PhSiH_3$ was employed, reduction was observed at ∼ 110 °C to afford $Mo^{IV}$(O)-(salalen-$^t$Bu$_2$) (**5**) as one of the major products based on $^1$H NMR. Prolonged heating, however, led to the disappearance of **5**. It is worth noting that during the course of reaction, there is another intermediate species observed by $^1$H NMR, alongside the starting $Mo^{VI}(O)_2$(salalen-$^t$Bu$_2$)

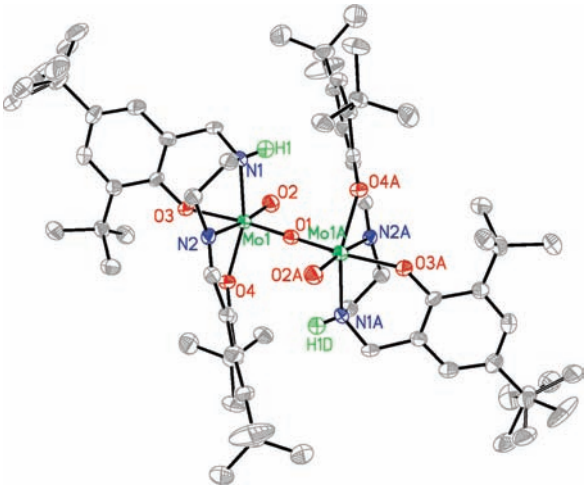



**Figure 5.** ORTEP diagram (drawn at 50% probability ellipsoids) of $\mu$-oxo-(Mo(O)(salalen-$^t$Bu$_2$))$_2$ compound **6**. The hydrogen atoms, except the ones on nitrogen, are omitted for clarity. Selected bond distances (Å) and bond angels (deg): Mo1−O2, 1.686(2); Mo1−O1, 1.8884(3); Mo1−O4, 1.992(2); Mo1−O3, 2.013(2); Mo1−N1, 2.204(3); Mo1−N2, 2.302(3); N1−H1, 0.83(4); O2−Mo1−O1, 98.74(9); O1−Mo1−O4, 93.38(7); O1−Mo1−O3, 162.10(7); O4−Mo1−N1, 153.42(11); O2−Mo1−N2, 169.10(11); Mo1−O1−Mo1, 180.000(12).

and the reduction product **5**. Due to the overlap, only signals in the 5.5−2.5 ppm region can be clearly identified. For example, peaks at 5.07 and 3.30 ppm can be assigned to the benzylic $CH_2$ adjacent to the amine nitrogen. This intermediate is tentatively formulated as Mo$^{IV}$(OH)(OSiPhH$_2$)(salalen-$^t$Bu$_2$), resulting from a 3 + 2 addition of the Si−H bond across the Mo(O)$_2$ core.[12] For cis-dioxo molybdenum or rhenium compounds such as Mo(O)$_2$Cl$_2$ and ReI(O)$_2$(PPh$_3$)$_2$, 2 + 2 cycloaddition of Si−H has been reported.[5,7] In our case, a 2 + 2 pathway would result in a seven-coordinate molybdenum, and thus appears less likely. Supposedly, further elimination of PhH$_2$SiOH from Mo$^{IV}$(OH)(OSiPhH$_2$)(salalen-$^t$Bu$_2$) would lead to the Mo$^{IV}$O(salalen-$^t$Bu$_2$) product. However, we were unable to confirm the identity of this intermediate species by ESI-MS.

**Catalytic Hydrosilylation of Acetophenone and 4-Phenylbutanone.** Mo(O)$_2$(salalen-$^t$Bu$_2$), **1**, was investigated initially as a typical representative of the obtained, soluble, and pure molybdenum dioxo complexes. Consistent with the observed reactivity with organic silanes, no catalysis was detected with acetophenone (a standard ketone) at room temperature. As for tertiary silanes such as Et$_3$SiH, no hydrosilylation product was detected even when the reaction mixture was heated in a sealed NMR tube to 110 °C. With a more active dihydrosilane, Ph$_2$SiH$_2$, a small amount of hydrosilylation product could be detected. When a primary silane, PhSiH$_3$, was employed at 110 °C in a sealed NMR tube, quantitative conversion of acetophenone was observed (Table 1). A control reaction under identical conditions (acetophenone and PhSiH$_3$ at 110 °C in a sealed NMR tube) in the absence of catalyst resulted in no conversion and the starting compounds were stable under these conditions. A number of solvents were examined to discern

(12) For [3 + 2] addition of tertiary silane to OsO$_4$ :Valliant-Saunders, K.; Gunn, E.; Shelton, G. R.; Hrovat, D. A.; Borden, W. T.; Mayer, J. M. *Inorg. Chem.* **2007**, *46*, 5212–19.

**Table 1.** Hydrosilylation of Acetophenone Catalyzed by Mo(O)$_2$(salalen-$^t$Bu$_2$) (**1**)[a]

| entry | silane | solvent | time/ h | % conversion |
|---|---|---|---|---|
| 1 | Et$_3$SiH | benzene | 24 | N.R. |
| 2 | Cl$_3$SiH | benzene | 24 | N.R. |
| 3 | Ph$_2$SiH$_2$ | benzene | 24 | 20 |
| 4[b] | PhSiH$_3$ | benzene | 24 | N.R. |
| 5 | PhSiH$_3$ | benzene | 7 | >98 |
| 6 | PhSiH$_3$ | toluene | 4 | >98 |
| 7 | PhSiH$_3$ | 1,2-dichlorobenzene | 23 | >98 |
| 8 | PhSiH$_3$ | chloroform | 28 | 42 |
| 9 | PhSiH$_3$ | dichloromethane | 24 | 8 |
| 10 | PhSiH$_3$ | acetonitrile | 28 | 38 |

[a] Reaction conditions: 1.0 mmol acetophenone, 1.2 mmol silane, and 5 mol % **1** in a sealed NMR tube heated to ca. 110 °C. [b] Room temperature.

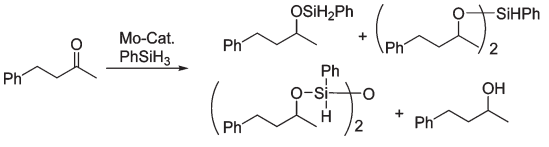
**Table 2.** Molybdenum-Catalyzed Hydrosilylation of Acetophenone (**A**) and 4-Phenylbutanone (**B**) with PhSiH$_3$[a]

| entry | substrate | catalyst | time/ h | % conv. | % yield[b] |
|---|---|---|---|---|---|
| 1 | **A** | **1** | 7 | >98 | 80 |
| 2 | **B** | **1**[c] | 19 | >98 | 76 |
| 3 | **A** | **3**[c] | 16 | >98 | 80 |
| 4 | **B** | **3**[c] | 19 | >98 | 83 |
| 5 | **A** | **2** | 7 | 97 | — |
| 6 | **A** | **4**[c] | 7 | >98 | 58 |
| 7 | **A** | **5** | 3 | 93 | — |
| 8[d] | **A** | **6** | 8 | >98 | — |

[a] Reaction conditions: 1.0 mmol ketone, 1.2 mmol PhSiH$_3$, 5 mol % catalyst in benzene, sealed NMR tube at ~110 °C. [b] Isolated alcohol yield after acid aqueous workup. [c] 1 mol % catalyst. [d] In 1,2-dichlorobenzene.

medium effects on the efficiency of the reaction. Benzene, toluene, and 1,2-dichlorobenzene performed best. There seems to be no discernible dependencies on solvent polarity or coordinating ability. Hence, benzene or toluene was the solvent of choice from this point forward.

In addition to acetophenone, we investigated 4-phenylbutanone as a representative aliphatic ketone. It was found to be comparable in reactivity to the aryl ketone acetophenone (Table 2). In the case of 4-phenylbutanone, a mixture of hydrosilylation products were observed (eq 3). These products were characterized by $^1$H NMR and GC-MS. Interestingly, in 1,2-dichlorobenzene only one product was observed, which is the expected initial hydrosilylation product (H−C−OSiH$_2$Ph; see eq 3). Despite the complication of several silylated products, acid workup afforded the alcohol in high to modest isolated yields (Table 2). Different catalysts were studied to probe the dependence on the oxidation state and ligand identity of the catalyst precursor. The dioxomolybdenum(VI) catalyst containing a chiral ligand (**2**) behaved comparably to **1**. So did the fully reduced salan complex **4**.




(3)

Reaction progress for all of the catalysts was followed by $^1$H NMR. All dioxomolybdenum(VI) complexes (**1**−**4**) as well as the dinuclear $\mu$-oxo molybdenum(V) (**6**) showed an induction period. In comparison, the monooxo

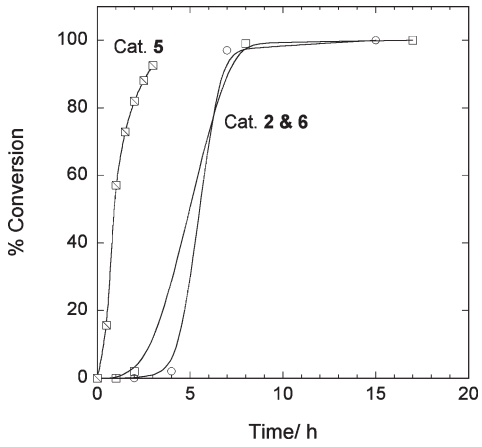



**Figure 6.** Reaction progress for the hydrosilylation of acetophenone with $PhSiH_3$ at 110 °C catalyzed by dioxomolybdenum(VI) **2** (open circles), dinuclear molybdenum(V) **6** (open squares), and oxomolybdenum(IV) **5** (hatched squares). % Conversion was determined by $^1H$ NMR. The lines are a smoothing function and not a kinetic fit.

molybdenum(IV) (**5**) did not exhibit an induction period (Figure 6). After the induction period, precursors **1**−**4** and **6** appear to follow comparable conversion rates to the oxomolybdenum(IV) catalyst **5**. Even though **5** did not show an induction period, it should be noted that **5** did not catalyze hydrosilylation under ambient temperature. Temperatures of around 110 °C were still necessary in the case of oxomolybdenum(IV) catalyst. The use of a chiral ligand in catalysts **2**, **3**, and **4** deserves a comment. Although these catalysts gave high conversions and excellent yields of the alcohol after aqueous workup, none of them showed significant asymmetric induction (<8 ee%) with either substrate, acetophenone or 4-phenylbutanone. This could be attributed to the high reaction temperature, which was necessary.

## Discussion

**Synthesis of Oxo Molybdenum Salalen Complexes.** There are several approaches available in the literature for the generation of salalen complexes. The most common approach is coordination of metal precursors with salalen ligands.[13] This method offers opportunities for easy tuning of steric and electronic properties and has been utilized in the synthesis of a number of catalysts. The drawback is that the ligand synthesis has to involve the stepwise construction of imine and amine linkages. The salalen complexes can also be generated by two other less generally applicable routes. One is the oxidative dehydrogenation of the C−N bonds in metal−salan complexes;[14] the other is from in situ reduction of salen upon coordination with titanium(IV), presumably via an intramolecular Meerwein−Ponndorf−Verley (MPV) reaction.[15] Remarkably the reaction stops at half way without going all the way to the salan complex. Although the preparation is usually simple and straightforward, these two routes are often metal and ligand specific.

Our study herein represents the first examples for preparation of Mo(VI) salalen complexes from the salen ligands. Despite the resemblance with the above-mentioned intramolecular MPV reduction, the reaction is more complex since it also involves the oxidation of Mo(0) to Mo(VI). Notably the reaction is quite general, as a number of Mo complexes are obtained in a similar fashion, as long as *t*-butyl groups are present in the 3,3′-positions. In retrospect, the partially reduced dioxo Mo(VI) species was probably present in the original preparation intended for $Mo^{IV}(O)$(salen);[11] ESI-MS of the sample using the parent salen ligand without substituents in our hands showed a pattern consistent with $Mo(O)_2$(salalen). However, multinuclear species can also be seen. We attribute these complications to the lack of steric bulk in unsubstituted salen. Furthermore, the poor solubility of the product with the parent salen ligand and apparent paramagnetism prevented further characterization. By comparison to Mo, reaction of $W(CO)_6$ with salen ligands only led to recovery of the free ligand under the same conditions.

Attempts to prepare $Mo^{VI}(O)_2$(3,5-$^t$Bu$_2$-salen) from $Mo(O)_2(acac)_2$ and $H_2$(3,5-$^t$Bu$_2$-salen) were unsuccessful despite the successful synthesis of $Mo^{VI}(O)_2$(3,5-$(OMe)_2$-salen) by this methodology;[16] multiple products formed and were not further identified. This is not surprising because the success of Mo- and Re-salen preparations is quite sensitive to substituents on the phenyl rings as well as the diamine bridge, and hard to predict.[17] Consequently, a systematic variation of substituents in these systems is often difficult to achieve. In contrast, *cis*-dioxo Mo−salan compounds with sterically bulky substituents have been prepared easily, though higher nucleation could pose some problems for ligands with less bulky substituents.[18] This suggests that the steric bulk is one of the driving forces for the partial reduction of the salen ligands, so that the unfavorable steric interaction could be relieved when one of the C=N double bonds is replaced by a saturated C−N single bond.

**Mechanistic Considerations of Mo-Catalyzed Hydrosilylation.** The dioxo functionality was suggested to be a critical feature for *cis*-$Re(O)_2I(PPh_3)_2$.[19] This idea has been supported by the reactivity of $Mo(O)_2Cl_2$ and by computational studies of these systems.[20] We and others, however, have shown that the dioxo functionality is not a prerequisite for catalysis, but the presence of an open coordination site or a labile ligand is. In contrast, the

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dioxo $Mo^{VI}$ and dinuclear oxo $Mo^{V}$ compounds investigated in this study are coordinatively saturated and do not contain a labile ligand. This premise is in agreement with the observation of an induction period for both dioxo $Mo^{VI}$ and $\mu$-oxo dinuclear $Mo^{V}$ catalysts. We hypothesize on the basis of experimental observations that during this induction period dioxo $Mo^{VI}$ and $\mu$-oxo $Mo^{V}$ are reduced by the organic silane. This proposal is also consistent with a $Re^{VII}$ system in which the $Re^{VII}$ precursor was first reduced to $Re^{V}$ by dihydrogen prior to catalysis.[7c] We observe an intermediate species during the reduction of $Mo(O)_2$(salalen-$^tBu_2$) (**1**), tentatively formulated as $Mo^{IV}(OH)(OSiPhH_2)$(salalen-$^tBu_2$). However, this intermediate is not likely to be the active catalyst because it is detected mostly during the induction period when comparing the reaction profile with and without a ketone substrate. In the presence of excess $PhSiH_3$, monooxo $Mo^{IV}$ can be reduced further to an unidentified paramagnetic species. However, when this over-reduced species was applied as a catalyst by adding ketone to the reaction mixture, no hydrosilylation product was observed at 110 °C. These observations collectively point to $Mo^{IV}$(O)-salalen as the active species, and indeed, $Mo^{IV}$(O)(salalen-$^tBu_2$) compound **5** exhibits the highest activity (Table 2, entry 7) and lacks an induction period (Figure 6).

We also considered a radical mechanism because it has been shown in several systems that organic silanes can undergo radical reactions with transition metals.[8g,20c] In the presence of the radical scavenger $CBr_4$, the conversion of acetophenone occurred with a much shorter induction period and reactions were complete within 1 h, regardless of the catalyst (**1**, **5**, or **6**). However, GC−MS analysis of the reaction products showed a small amount of the hydrosilylation product, and instead the major species was $PhCHBrCH_3$, which is the result of deoxygenative halogenation.[21] This finding may suggest that there is at least some radical character/involvement in the hydrosilylation reaction. In the presence of $CBr_4$, the hydrosilylation pathway is totally inhibited and another reaction prevails, yielding a totally different product.

In conclusion, a facile synthetic pathway to oxo molybdenum salalen complexes has been described. These compounds serve as catalysts for the reduction of ketones to alcohols with $PhSiH_3$ at 110 °C. Dioxo molybdenum(VI) and dinuclear $\mu$−oxo molybdenum(V) complexes display a long induction period. In contrast, monooxo molybdenum(IV) is the most reactive catalyst and lacks an induction period. At elevated temperatures (ca. 110 °C) dioxo molybdenum(VI) salalen complexes are reduced by organic phosphines ($PPh_3$ or $PMe_3$) and silanes ($Ph_2SiH_2$ or $PhSiH_3$) to mononuclear molybdenum(IV) and dinuclear $\mu$-oxo molybdenum(V). Mo catalysts containing chiral salalen ligands do not give a significant asymmetric induction (less than 8% ee). The results in hand are most consistent with the proposal that monooxo molybdenum(IV) is the active form of the catalyst; and involvement of radical pathways cannot be excluded.

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## Experimental Section

**General.** Solvents were purified with a solvent purification system (Anhydrous Engineering Inc.) prior to use. Organosilanes and ketones were obtained from commercial sources and used as received without further purification. The saldach ligand and its derivatives were prepared by refluxing an ethanol solution of (*R*, *R*)-1,2-diaminocyclohexane (dach) with two equivalents of appropriate salicyaldehydes. $Mo(CO)_6$ and $Mo(O)_2(acac)_2$ were obtained from commercial sources.

NMR spectra were recorded on Varian Inova 300 instruments at 20 °C. Proton resonances were referenced internally to residual solvent peaks ($CHCl_3$, 7.26; $CHDCl_2$, 5.32; $CD_2HCN$, 1.94). Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 2000 FT-IR spectrometer. UV−vis data were recorded on a Shimadzu 2501 spectrophotometer and reported as $\lambda_{max}$ in nm (log $\varepsilon$). Optical rotation was measured on a Rudolph Research Autopol III polarimeter. Mass spectrometry was performed by the Purdue University Campus-Wide Mass Spectrometry Center on a Hewlett-Packard Engine mass spectrometer (GC/MS) or a FinniganMAT LCQ mass spectrometer system (ESI). Enantiomeric excesses of the resulting silylethers were determined using an Agilent 6890 gas chromatograph equipped with a chiral CyclodexB column (30 m × 0.25 mm ID, 0.25 $\mu$m thick) on the corresponding alcohols after desilylation. Elemental microanalyses were done by the Purdue University Microanalytical Laboratory.

**$Mo(O)_2$(Salalen-$^tBu_2$) (1).** A mixture of *N,N′*-ethylene-bis-(3,5-di$^t$butyl-salicylideneimine), $H_2$(3,5-$^tBu_2$-salen), (241 mg, 0.489 mmol), $Mo(CO)_6$ (125 mg, 0.473 mmol) in THF (35 mL) was refluxed under air for 22 h. After cooling to ambient temperature, the resulting reddish solution was filtered and the filtrate was dried in vacuo. The residue was taken up by $CH_2Cl_2$ and layered with hexanes and stored at −20 °C. After several days the product was collected by filtration. Yield: 137 mg, 47%. X-ray quality crystals were obtained by slow evaporation of a concentrated $CH_2Cl_2$ solution of the product. $^1$HNMR ($CD_2Cl_2$, 300 MHz): $\delta$ 8.09 (s, 1H, C*H*=N), 7.61 (d, *J* = 2.4 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 5.61 (br s, 1H, N*H*, varies depending on the condition), 4.62 (d, *J* = 12.9 Hz, 1H, benzylic), 4.01 (d, *J* = 12.9 Hz, 1H, benzylic), 3.72 (m, 1H, ethylene), 3.44 (m, 1H, ethylene), 3.21 (m, 2H, ethylene), 1.49 (s, 9H, $^t$butyl), 1.32 (s, 9H, $^t$butyl), 1.26 (s, 9H, $^t$butyl), 1.11 (s, 9H, $^t$butyl). FT-IR (KBr): 3120 (NH), 1645 (C=N), 907, 875, 842 (Mo=O) cm$^{-1}$. MS (ESI$^+$): *m*/*z* 623 ($^{98}MoO_2L + H^+$), with correct isotopic pattern for Mo. Anal. Calcd (found) for $C_{32}H_{48}N_2O_4Mo$: C, 61.92 (61.68); H, 7.79 (7.71); N, 4.51 (4.59).

**$Mo(O)_2$(3-$^t$Bu-Saladach) (2).** A mixture of (*R,R*)-1,2-cyclohexanediamino-*N,N′*-bis(3-*t*-butyl-salicylidene), $H_2$(3-$^t$Bu-saldach), (333.5 mg, 0.767 mmol), $Mo(CO)_6$ (186.7 mg, 0.707 mmol) in THF (50 mL) was refluxed under air for 19 h in which time the color changed from yellow to green−brown and then red−brown. After cooling to ambient temperature, the mixture was filtered and the filtrate was dried in vacuo. The residue was treated with a small amount of hexanes and filtered again. The dark yellow solid obtained was dissolved in benzene and layered with hexanes. The resulting yellow crystals, suitable for X-ray diffraction crystallography, and powders were collected by filtration. Yield: 134 mg, 34%.

$^1$HNMR ($CD_2Cl_2$, 300 MHz): $\delta$ 8.08 (s, 1H, C*H* = N), 8.04 (s, 1H, C*H* = N), 7.57 (m, 2H), 7.30 (m, 3H), 7.14 (d, 1H), 7.00 (m, 3H), 6.79 (m, 1H), 6.59 (m, 2H), 6.02 (br s, 1H, N*H*), 5.51 (br, 1H, N*H*), 4.61 (d, *J* = 12.3 Hz, 1H, benzylic), 4.20−4.40 (m, 3H, benzylic), 3.16 (m, 1H, $C_6H_{10}$), 2.84 (m, 1H, $C_6H_{10}$), 2.65(m, 1H, $C_6H_{10}$), 2.32 (m, 3H, $C_6H_{10}$), 1.88 (m, 2H, $C_6H_{10}$), 1.50 (s, 9H, $^t$butyl), 1.43 (s, 9H, $^t$butyl), 1.11 (s, 9H, $^t$butyl), 0.96 (s, 9H, $^t$butyl) and other parts of $C_6H_{10}$. MS (ESI$^+$): *m*/*z* 564 ($^{98}MoO_2L + H^+$), with correct isotopic pattern for Mo. Anal. Calcd (found) for $C_{28}H_{38}N_2O_4Mo$: C, 59.78 (59.55); H, 6.81 (6.91); N, 4.98 (4.91).

**$Mo(O)_2$(3,5-$^t$$Bu_2$-Saladach) (3).** A mixture of (*R,R*)-1,2-cyclohexanediamino-*N,N′*-bis(3,5-di-*t*-butyl-salicylidene), $H_2$-(3,5-$^t$$Bu_2$-saldach), (553 mg, 1.01 mmol), $Mo(CO)_6$ (238 mg, 0.902 mmol) in THF (70 mL) was refluxed under air for 19 h in which time the color changed from yellow to green−brown and then dark purple. After cooling to ambient temperature, the resulting dark brown solution was filtered and the filtrate was dried in vacuo. The residue was treated with a small amount of hexanes, filtered, and washed with cold hexanes. The product was obtained as an orange powder. Yield: 232 mg, 38%.

$^1$HNMR ($CD_2Cl_2$, 300 MHz): $\delta$ 8.06 (s, 1H, C*H* = N), 8.02 (s, 1H, C*H*=N), 7.61 (d, $J$=2.1 Hz, 1H), 7.59 (d, $J$=2.4 Hz, 1H), 7.28 (d, $J$ = 2.4 Hz, 1H), 7.24 (d, $J$ = 2.4 Hz, 1H), 7.16 (d, $J$ = 2.4 Hz, 1H), 7.09 (d, $J$=2.4 Hz, 1H), 7.01 (d, $J$=2.4 Hz, 1H), 6.74 (d, $J$=2.4 Hz, 1H), 6.15 (br s, 1H, N*H*), 5.62 (br, 1H, N*H*), 4.60 (d, $J$=12.9 Hz, 1H, benzylic), 4.18−4.40 (m, 3H, benzylic), 3.15 (m, 1H, $C_6H_{10}$), 2.75 (m, 1H, $C_6H_{10}$), 2.62 (m, 1H, $C_6H_{10}$), 2.40 (m, 2H, $C_6H_{10}$), 2.23 (m, 2H, $C_6H_{10}$), 1.60−1.95 (m, 6H, $C_6H_{10}$), 1.51 (s, 9H, $^t$Bu), 1.43 (s, 9H, $^t$Bu), 1.35 (s, 9H, $^t$Bu), 1.33 (s, 9H, $^t$Bu), 1.28 (s, 9H, $^t$Bu), 1.22 (s, 9H, $^t$Bu), 1.13 (s, 9H, $^t$Bu), 0.94 (s, 9H, $^t$Bu). MS ($ESI^+$): $m/z$ 675 ($^{98}MoO_2L + H^+$), with correct isotopic pattern for Mo. Anal. Calcd (found) for $C_{36}H_{54}N_2O_4$-Mo: C, 64.08 (64.25); H, 8.07 (7.99); N, 4.15 (3.96).

**$Mo(O)_2$(3,5-$^t$$Bu_2$-Salan) (4).** The salan ligand was prepared in 86% yield by reduction of the corresponding salen ligand with $NaBH_4$ in THF-$H_2O$, following a literature protocol.[22] The dioxo Mo complex was synthesized by refluxing a mixture of $Mo(O)_2(acac)_2$ and $H_2$Salan (slight excess) in MeOH, according to a previous report.[23] Yield: 80%. $^1$H NMR ($C_6D_6$, 300 MHz): $\delta$ 7.49 (d, $J$ = 2.4 Hz, 2H), 6.86 (d, $J$ = 2.4 Hz, 2H), 5.23 (d, $J$ = 14.7 Hz, 2H, benzylic), 3.64 (d, $J$ = 14.7 Hz, 2H, benzylic), 2.08 (m, 4H), 1.66 (s, 18H, $^t$butyl), 1.32 (s, 18H, $^t$butyl), 0.90 (m, 2H), 0.099 (m, 4H). NH signals were not located.

**$Mo^{IV}(O)$($^t$$Bu_2$-Salalen) (5).** In a nitrogen-filled glovebox a three-neck round-bottom flask with a magnetic stir bar was charged with $Mo(O)_2$(Salalen-$^t$$Bu_2$), **1**, (0.200 g, 0.322 mmol) dissolved in toluene. The reaction flask was capped and taken out of the glovebox. Under nitrogen atmosphere a condenser was attached to the round-bottom flask. To this solution was added $PMe_3$ 1.0 M solution in toluene (1.61 mL, 1.61 mmol) through one of the side arms. The resulting solution was heated in a sand bath at ~120 °C for 24 h. The reaction mixture was filtered under inert atmosphere and the filtrate was dried in vacuo. Yield 0.049 g, 25%.

$^1$HNMR ($CD_2Cl_2$, 300 MHz): $\delta$ 8.15 (s, 1H, C*H*=N), 7.65 (m, 1H, aromatic), 7.35 (m, 1H, aromatic), 7.17 (s, 1H, aromatic), 6.76 (s, 1H, aromatic), 4.19 (d, $J$ = 8.6 Hz, 1H, benzylic), 3.52 (m, 2H, NH + benzylic), 3.33 (m, 1H, ethyl), 2.90 (m, 2H, ethyl), 2.59 (m, 1H, ethyl), 1.48 (s, 9H, $^t$butyl), 1.35 (s, 9H, $^t$butyl), 1.23 (s, 9H, $^t$butyl), 1.13 (s, 9H, $^t$butyl). MS ($ESI^+$): $m/z$ 606 ($^{98}$MoOL) with the correct isotope pattern for Mo.

**$\mu$-Oxo-(Mo(O)(salalen-$^t$$Bu_2$))$_2$ (6).** In a nitrogen-filled glovebox a three-neck round-bottom flask with a magnetic stir bar was charged with $Mo(O)_2$(Salalen-$^t$$Bu_2$), **1**, (0.200 g, 0.322 mmol dissolved in toluene. The reaction flask was capped, taken out of the glovebox, and under nitrogen atmosphere a condenser was attached to the flask. To this solution was added $PMe_3$ 1.0 M solution in toluene (644 $\mu$L, 0.644 mmol) through one of the side arms. The resulting solution was heated in a sand bath at ~120 °C for 24 h. The mixture was filtered and the remaining dark red solid was rinsed with toluene and dried in vacuo. Yield 0.0912 g, 46%. Anal. Calcd (found) for $C_{67}H_{96}Mo_2N_4O_7$: C, 62.73 (62.73); H, 7.90 (7.94); N, 4.57 (4.70).

**X-ray Data Collection and Structure Solution.** A summary of structure determination is provided here and further details can be found in the Supporting Information. Crystallographic data for **1**: $C_{32}H_{47}MoN_2O_4$, 0.465($CH_2Cl_2$), F.W. = 659.18, 0.44 × 0.40 × 0.13 mm crystal dimension, triclinic, space group $P\bar{1}$(#2), $a$ = 14.569(3), $b$ = 15.011(6), $c$ = 18.323(5) Å; $\alpha$ = 72.878(13), $\beta$ = 88.824(7), $\gamma$ = 72.504(11)°, $V$ = 3642.3(19) Å$^3$. $Z$ = 4, $\rho_{calcd}$ = 1.202 g/cm$^3$, $u$ = 0.451 mm$^{-1}$, 44292 reflections collected, 12726 unique ($R_{int}$ = 0.064), R1 = 0.057, R2 = 0.144, for 8629 reflections with $F_o^2 > 2\sigma(F_o^2)$.

Crystallographic data for **2**: $C_{28}H_{38}MoN_2O_4$, F.W. = 562.57, 0.38 × 0.31 × 0.25 mm crystal dimension, monoclinic, space group P 1 21 1(#4). $a$ = 8.50330(10), $b$ = 22.8862(4), $c$ = 14.9349(3) Å; $\beta$ = 106.2526(6)°, $V$ = 2790.30(8) Å$^3$. $Z$ = 4, $\rho_{calcd}$ = 1.339 g/cm$^3$, $u$ = 0.490 mm$^{-1}$, 30847 reflections collected, 12688 unique ($R_{int}$ = 0.039), R1 = 0.037, R2 = 0.075, for 9942 reflections with $F_o^2 > 2\sigma(F_o^2)$.

Crystallographic data for **4**: $C_{36}H_{56}MoN_2O_4$,$H_2O$,0.65-($CH_4O$), F.W. = 715.64, 0.38 × 0.15 × 0.13 mm crystal dimensions. Hexagonal, space group $P3_1$ (#144), $a$ = 17.0026(13), $c$ = 13.6160(12) Å, $V$ = 3408.9(5) Å$^3$. $Z$ = 3, $\rho_{calcd}$ = 1.046 g/cm$^3$, $u$ = 0.315 mm$^{-1}$, 9437 reflections collected, 6931 unique ($R_{int}$ = 0.079), R1 = 0.055, R2 = 0.136, for 5432 reflections with $F_o^2 > 2\sigma(F_o^2)$.

Crystallographic data for **6**: $C_{64}H_{96}Mo_2N_4O_7$,2($C_7H_8$), F.W. = 1409.66, 0.35 × 0.20 × 0.06 mm crystal dimension, monoclinic, C12/c1(#15), $a$ = 30.4913(17), $b$ = 13.6081(8) $c$ = 17.9982(6) Å; $\beta$ = 93.323(3)°, $V$ = 7455.4(7) Å$^3$. $Z$ = 4, $\rho_{calcd}$ = 1.256 g/cm$^3$, $u$ = 0.379 mm$^{-1}$, 42133 reflections collected, 6562 unique ($R_{int}$ = 0.094), R1 = 0.045, R2 = 0.111, for 4763 reflections with $F_o^2 > 2\sigma(F_o^2)$.

**Catalytic Hydrosilylation of Ketones: General Procedure.** To a J. Young NMR tube was added ketone (1.0 mmol), silane (1.2 mmol), Mo catalyst (1 or 5 mol %), and solvent (0.6 mL). The resulting solution was capped and heated in a sand bath at ~110 °C. The reaction progress was monitored by $^1$H NMR. After the reaction was complete, as indicated by the complete disappearance of ketone, the reaction mixture was hydrolyzed in acidic ether for a few hours. After extraction with diethylether, the organic phase was dried, concentrated, and subjected to flash chromatography on a silica gel column, and eluted with hexanes−EtOAc. The isolated alcohols were identified by comparing the $^1$H NMR spectra with literature reports.

**Reaction of $Mo^{VI}(O)_2$(Salalen-$^t$$Bu_2$) with $PhSiH_3$.** A mixture of $Mo(O)_2$(salalen-$^t$$Bu_2$) (22 mg, 0.035 mmol), $PhSiH_3$ (8.6 $\mu$L, 0.070 mmol) in $C_6D_6$ (0.62 mL) was heated in a sand bath to ~100 °C and the reaction progress was monitored by $^1$H NMR spectroscopy. New peaks in the 5.5−1.9 ppm region were observed alongside the starting complex $Mo^{VI}(O)_2$-(salalen-$^t$$Bu_2$). Further heating to 110 °C for several hours resulted in increasing the intensity of these peaks (~60% of total detectable Mo), accompanied by nearly complete disappearance of starting $Mo^{VI}(O)_2$(salalen-$^t$$Bu_2$) and the appearance of $Mo^{IV}(O)$(salalen-$^t$$Bu_2$), **5**. This intermediate species was tentatively assigned as $Mo^{IV}(OH)(OSiPhH_2)$(salalen-$^t$$Bu_2$). $^1$HNMR ($C_6D_6$, 300 MHz): $\delta$ 5.07 (d, $J$ = 14.1 Hz, 1H, benzylic), 3.30 (d, $J$ = 13.8 Hz, 1H, benzylic), 2.42 (br, 2H, OH and NH). Other peaks were difficult to assign because of their close proximity and overlap to peaks from compounds **1** and **5**.

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**Supporting Information Available:** Crystallographic tables for atomic coordinates and equivalent isotropic parameters, bond lengths, and angles for complexes **1**, **2**, **4**, and **6** (CIF). Experimental details for X-ray studies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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