Variable Pathways for Oxygen Atom Insertion into Metal–Carbon Bonds: The Case of Cp*W(O)₂(CH₂SiMe₃)

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**ABSTRACT:** Cp*W(O)₂(CH₂SiMe₃) (1) (Cp* = η^5-pentamethylcyclopentadienyl) reacts with oxygen atom donors (e.g., H₂O₂, PhIO, IO₄⁻) in THF/water to produce TMSCH₂OH (TMS = trimethylsilyl). For the reaction of 1 with IO₄⁻, the proposed pathway for alcohol formation involves coordination of IO₄⁻ to 1 followed by concerted migration of the -CH₂TMS ligand to the coordinated oxygen of IO₄⁻ with concomitant dissociation of IO₄⁻ to produce Cp*W(O)₂(OCH₂SiMe₃) (3), which undergoes protonolysis to yield free alcohol. In contrast to the reaction with IO₄⁻, the reaction of 1 with H₂O₂ results in the formation of the η²-peroxo complex Cp*W(O)(η²-O₂)(CH₂SiMe₃) (2). In the presence of acid (HCl) or base (NaOH), complex 2 produces TMSCH₂OH. The conversion of 2 to TMSCH₂OH catalyzed by Brønsted acid is proposed to occur through protonation of the η²-peroxo ligand, which facilitates the transfer of the -CH₂TMS ligand to a coordinated oxygen of the η²-hydroperoxo ligand. In contrast, the hydroxide-promoted conversion of 2 to TMSCH₂OH is proposed to involve hydroxide coordination, followed by proton transfer from the hydroxide ligand to the peroxide ligand to yield a η²-hydroperoxide intermediate. The migration of the -CH₂TMS ligand to the coordinated oxygen of the η²-hydroperoxide produces an alkoxide complex, which undergoes protonolysis to yield free alcohol.

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**INTRODUCTION**

Hydrocarbon oxidation is a fundamentally important process for the petrochemical industry. The development of new catalysts for the selective oxidation of hydrocarbons, especially alkanes, has the potential to enhance the efficiency of production of chemicals and fuels. However, the selective functionalization (e.g., direct partial oxidation) of alkanes is among the most demanding catalytic processes.

Transition-metal catalysts for the partial oxidation of alkanes to form alcohols must be able to perform two key steps: C–H bond activation and C–O bond formation. The Pt-based Shilov system, developed in the 1960s, was among the rst homogeneous catalysts to successfully activate alkanes to form alcohols or alcohol precursors. It has been proposed that C–H bond activation occurs at Pt⁰ followed by C–X (X = OH or CI) bond formation at Pt⁴–alkyl by reductive (i.e., reduction of Pt⁴ to Pt⁰) nucleophilic addition to an electrophilic Pt⁴–alkyl ligand. The use of expensive Pt⁰ as a stoichiometric oxidant to convert Pt⁰–alkyl to Pt⁴–alkyl limits the utility of this catalyst.

While C–X (X = OH or CI) bond formation in the Shilov-type catalysts has been proposed to involve nucleophilic addition of water or halide to an electrophilic Pt⁴–alkyl ligand, an alternative strategy for metal-mediated C–O bond formation involves net oxygen atom insertion into metal–alkyl bonds. For example, one possible catalytic cycle incorporates oxygen atom insertion into a M–R bond followed by C–H activation via net 1,2-addition across a M–OR bond to convert an alkane to an alcohol. Scheme 1 shows two distinct pathways for oxygen atom insertion into M–R bonds from the...
reaction of a M–R moiety with an oxygen atom delivery reagent (YO). One pathway involves a migration of the ligand R to a metal-oxo intermediate. The second pathway incorporates direct oxo-insertion from M(O)Y(R) without the formation of a metal-oxo intermediate. To be generally useful for selective oxidations at high conversion, ideally, the C–O bond forming step should proceed without the formation of radical intermediates and can be facilitated by catalysts including organocatalysts, as recently reported with vanadiums, and by metal-oxo complexes as reported by Goldberg and co-workers.

The 1,2-addition of C–H bonds across M–NHR and M–OR bonds is known. In 2003, our group studied and reported intramolecular C–H activation by a PCP-RuIII amido complex and commented on the potential utility of this transformation in catalytic transformations. Then, in 2005, we reported intermolecular benzene C–H activation by RuII hydroxide and anilide complexes. Related chemistry includes an IrIII complex and RuII complexes by Periana, Goddard, and co-workers, a RhII complex reported by Heinzeley, Goldberg, and co-workers, and a RhII complex reported by Bercaw, Labinger, and co-workers.

While insertions of oxygen atoms into M–C bonds are known, examples that occur by non-radical routes are rare. In a 1988 publication that focused on oxygen atom insertion into TaV hydrocarbonyl bonds, Bercaw and co-workers stated, "The details of the actual transfer under these controlled metal-mediated oxidations are still poorly understood...examples of clean carbon–oxygen bond formation for well-characterized compounds are rather rare."

Despite a few recent examples, we believe that this statement remains accurate.

Some early transition-metal complexes, such as group IV complexes, initiate oxygen atom insertion into M–R bonds; however, these reactions commonly proceed by radical pathways. Brown and Mayer reported oxo-insertion into M–Ar (Ar = aryl) bonds with ReVII via the migration of the Ar group to an oxo ligand. Similar mechanisms that involve the formation of metal–oxo have also been proposed for the oxygen atom insertion of Pd complexes, but mechanistic studies have not been disclosed. Hillhouse and co-workers have reported net oxygen insertion into a series of Ni–R bonds and a Hf–H bond upon reaction with N2O. Espenson and co-workers reported that methylalkoxyreium (MTO) reacts with oxidants to release methanol. Later, Periana, Goddard, and co-workers investigated the mechanism of this reaction. A pathway that involves migration of the methyl ligand to the oxygen of the coordinated oxidant was proposed, and an analogy between this reaction and the Baeyer–Villiger reaction (conversion of ketones to esters) was made.

Given the importance of metal-mediated C–O bond formation, we have been interested in understanding mechanisms and strategies to facilitate these transformations. To our knowledge, detailed studies of reactions that give clean oxygen atom insertion into metal–hydrocarbonyl bonds are limited to the studies of ReVII complexes. Herein, we present studies of oxygen atom insertion into the W–CH3SiMe3 bond of Cp2W(O)2(CH2SiMe3) (1) and Cp2W(O)(η2-O2)(CH2SiMe3) (2). Complexes 1 and 2 have been previously prepared and studied by Legzdins and co-workers.

### RESULTS AND DISCUSSION

**Reaction of Cp*W(O)2(CH2SiMe3) (1) with NaIO4**

The reaction of Cp*W(O)2(CH2SiMe3) (1) with H2O2 has been reported to yield the η2-peroxo complex Cp*W(O)(η2-O2)(CH2SiMe3) (2). However, the reaction of 1 with 1 equiv of NaIO4 in 1:1 THF-d8/D2O or 1:1 1,4-dioxane-d8/D2O (v/v) does not produce complex 2. Rather, TMSCH2OH (TMS = SiMe3, trimethylsilyl) is formed without observation of 2 as an intermediate. The reaction is complete within two hours at room temperature and produces TMSCH2OH in almost 100% yield by 1H NMR spectroscopy (eq 1).

![Equation 1](image)

**Pathway for the Conversion of 1 and NaIO4 to TMSCH2OH**

We considered the possibility that the η2-peroxo complex Cp*W(O)(η2-O2)(CH2SiMe3) (2) is formed as an intermediate, followed by oxo-insertion into the W–C bond and subsequent protonolysis to give free TMSCH2OH. Complex 2 was reacted with NaIO4 under the same conditions as the alcohol release from 1 and NaIO4, and no alcohol was observed by 1H NMR spectroscopy after 24 hours. Furthermore, 2 does not react with NaIO4 or D2O to produce TMSCH2OH under the same conditions. Thus, the evidence suggests that the formation of TMSCH2OH from 1 and NaIO4 does not likely proceed via complex 2.

The reaction of 1 and NaIO4 (5 equiv) in 1:1 THF-d8/D2O (v/v) was monitored at −1.3°C by 1H NMR spectroscopy. During the conversion, the disappearance of 1, the emergence of an intermediate, and the appearance of TMSCH2OH were observed. The formation of TMSCH2OH occurs with t1/2 = 40 min in approximately 100% yield. On the basis of 1H NMR spectroscopy, the intermediate is proposed to be the tungsten alkoxide complex Cp*W(O)(OCH2SiMe3) (3); however, we were not able to isolate 3. The 1H NMR resonances of the intermediate 3 are assigned as 4.17 (CH2), 2.04 (CH3), and −0.05 (SiMe3) ppm. Mo(O)2(OTf)2 exhibits a resonance due to the OCH2Me at 4.65 ppm, and the similar complex (ppy)Mo(O)2(OTf)2 (ppy = 2,2′-bipyrindine) exhibits a methane resonance at 3.86 ppm. In contrast, the CH2 groups of 1 and 2 resonate at 0.43 and 3.16 ppm, respectively. In addition to NaIO4, complex 1 reacts with iodosobenzene (PhIO) in 1,4-dioxane at room temperature to produce 3 in 20% yield in 20 min by 1H NMR spectroscopy (eq 2).

![Equation 2](image)

**Figure 1** depicts the concentration versus time plot for all species observed in the conversion of 1 and NaIO4 to TMSCH2OH, based on the integrations of the methylene resonances of 1, the TMSCH2OH product, and complex 3. The sum of concentrations of these three species (black X's, Figure 1) remains constant over the course of the reaction.

**Scheme 2** depicts a proposed organometallic Baeyer–Villiger (OMVB) pathway for the formation of TMSCH2OH from the reaction of 1 with NaIO4. Periodate coordinates to complex 1, followed by concerted migration of the alkyl ligand to
The formation of the adduct $1^-\text{OIO}_3^-$ is computed to be endergonic by $-25$ kcal mol$^{-1}$ in both solvents relative to separated $1$ and periodate. Presumably, the inclusion of counterion effects would reduce the endergonicity of the reaction to form an anionic adduct and thus also the corresponding overall activation barrier of the formation of complex 3. Periodate has been implicated in electron transfer reactions as well as two-electron oxygen atom transfer (OAT) chemistry. To model the possibility of one-electron chemistry, we investigated the thermodynamics of the following electron transfer reaction: $1 + [\text{IO}_4^-] \rightarrow 1^- + [\text{IO}_3^-]$. This reaction is clearly endergonic in 1,4-dioxane ($\Delta G_{\text{obs}} = +120$ kcal mol$^{-1}$) and water ($\Delta G_{\text{obs}} = +122$ kcal mol$^{-1}$). In the absence of corroborating experimental data, quantitative signs cannot be ascribed to the computed electron transfer thermodynamics. However, the sign cannot be computed endergonically suggests that, for these Cp*W$^0$ complexes, the periodate anion is not likely acting as a single electron transfer reagent.

The DFT calculations support the hypothesis that oxygen atom insertion into the $\text{W=CH}_2$TMS bond upon reacting with $\text{IO}_3^-$ occurs by an OMBV pathway. The calculated energy barrier for oxygen-insertion from $1^-\text{OIO}_3^-$ is 28 kcal mol$^{-1}$ (PCM water). Part of the difference between the computed and experimental barriers is, as delineated below, due to the neglect of explicit solvation of the periodate oxidant and particularly its isolate leaving group. Multiple attempts (see the Supporting Information) to isolate alternative transition states (TSs) (e.g., a TS for formation of a peroxo leading to 2, a $[3 + 2]$ addition of periodate, etc.) either led to already found stationary points or the OMBV TS depicted in Figure 4 (the TS is modulated based on studies of the impact of water; see below). The formation of 3 is calculated to be favorable, which is consistent with the observation of putative 3 as an intermediate in the overall reaction. The calculated $1^-\text{O}$ bond distance in the TS for oxygen atom insertion is 2.16 Å, which is much shorter than the 2.399 Å reported for the corresponding TS for MTO, implying an earlier TS for the Cp*W complex. The latter assertion is also supported by the calculated C–O distances for the carbon–oxygen bond being formed in the Baye–Villiger TS: 2.23 Å (for Cp*W complex) compared to 2.067 Å (MTO) TS. The reaction of complex 1 with $[\text{Bu}_n\text{N}]^+\text{IO}_4^-$ ($\text{Bu} = n$-butyl) (3 equiv) in rigorously dried THF for results in no reaction even upon heating at 80 °C for 24 h, while the same starting material produced the intermediate 3 and ultimately $\text{TMSCH}_2\text{OH}$ in 1:1 THF-d$_8$/H$_2$O (v/v) at room temperature in hours. The failure of 1 and IO$_3^-$ to produce free alcohol in the absence of water is perhaps not surprising, since the conversion of 3 to free alcohol requires a proton source. However, the lack of formation of 3 for the reaction of 1 and IO$_3^-$ in the absence of water is less readily rationalized, especially since calculations show that the formation of 3 is favorable from 1 and IO$_3^-$.

Water apparently facilitates the oxygen-insertion reaction. Possible routes for water in the conversion of 1 and IO$_3^-$ to 3 include the following: (1) as a solvent, water helps the ionization of the IO$_3^-$ anion for metal coordination, (2) as an electron donor, water can coordinate the metal center resulting in a more electron-rich metal center and more nucleophilic $\text{CH}_3\text{TMS}$ ligand, which is analogous to the role of pyridine in the conversion of MTO and pyridine-N-oxide to the oxygen-insertion product, and (3) water interacts with coordinated IO$_3^-$ to facilitate the dissociation of IO$_3^-$. Under pseudo-first-order conditions, the reaction of 1 and excess $[\text{Bu}_n\text{N}]^+\text{IO}_4^-$ (15 equiv) with various amounts of D$_2$O in THF-d$_8$ was monitored at 50 °C by $^1$H NMR spectroscopy. Kinetic plots reveal a pseudo-first-order decay of 1, and a plot of $k_{\text{obs}}$ (divided by the [IO$_4^-$]) as a function of [D$_2$O] shows that the decay of 1 with $[\text{Bu}_n\text{N}]^+\text{IO}_4^-$ has a second-order dependence on [D$_2$O] (Figure 5). Thus, the overall rate law for the conversion of 1 and IO$_3^-$ to $\text{TMSCH}_2\text{OH}$ is rate $= k[1][\text{IO}_3^-][\text{D}_2\text{O}]^2$. A plot of the plot in Figure 5 gives $k = 5.8(2) \times 10^{-5}$ M$^{-3}$ s$^{-1}$ after dividing by [IO$_3^-$] that corresponds to a $G = 25.2(1)$ kcal mol$^{-1}$ at 50 °C. The participation of water in the reaction is consistent with the relatively large $\Delta S$. The role of water in the reaction of 1 and periodate was investigated computationally. Attempts to model a four-legged piano stool complex with inner-coordination sphere water, Cp*W(OH)$_2$(H$_2$O)$_2$Re$_2$ led instead to an outer-coordination sphere aqua complex in which water is hydrogen bonded to an oxo ligand. The possibility that water enhances the oxidizing potential of IO$_3^-$ was probed computationally in several ways. The calculation of the OAT-free energy for IO$_3^-$ $\rightarrow$ IO$_3^-$ + $\frac{1}{2}$O$_2$ is exergonic by $\Delta G = -17$ kcal mol$^{-1}$ in the gas phase.
Inclusion of continuum solvent effects (CP/nm, water solvent) increases the exergonicity of this reaction to $-26$ kcal mol$^{-1}$. The calculations indicate that the increased driving force results from more favorable solvation of the smaller iodate ion in relation to periodate. Thus, the calculations predict that water should enhance the thermodynamics of oxygen atom transfer from IO$_3^-$, but the extent to which this would enhance the oxygen-insertion kinetics is uncertain without calculation of the corresponding hydrated OMBBV transition state.

Explicit solvation effects on periodate-mediated OMBBV reactions were modeled. Hydrogen bonding a water molecule to each oxo of the iodate leaving group in the OMBBV TS results in a reduction of the calculated energy barrier from 28 kcal mol$^{-1}$ (Scheme 3) to 24 kcal mol$^{-1}$ (Figure 6), which is closer to the experimental value of 18 kcal mol$^{-1}$ (see above). Bond lengths within the active site of the OMBBV TS (Figure 4) are little changed upon hydrogen bonding with three water molecules. What is more noticeable is the shortening of the O–H–O hydrogen bonds by 0.05 Å from 2.00 Å ([IO$_3^-$](CH$_2$)$_3$)$_2$) to 1.95 Å in the oxygen-insertion TS. In conjunction with the implicit solvation results above, these data lend credence to the proposal that preferential solvation of the iodate leaving group enhances oxygen-insertion of periodate into the W–C bond of I both kinetically and thermodynamically, effectively making the iodate a better leaving group and the periodate a more potent oxidant.

**Conclusion**

**Reaction of Cp$^*$W(O)$_2$(CH$_2$SiMe$_3$)$_2$ with NaOH.** Complex 2 reacts with NaOH to produce TMSCH$_2$OH in 1:1 THF-$d_8$/D$_2$O or 1,4-dioxane-$d_8$/D$_2$O (v/v). The reaction produces TMSCH$_2$OH in quantitative yield ($^1$H NMR) after 3 h at room temperature (eq 3).

![Diagram](image)

Under pseudo 1st-order conditions, the reaction of 2 with NaOH in 1:1 THF-$d_8$/D$_2$O (v/v) was monitored at 10.7 °C by $^1$H NMR spectroscopy. Kinetic plots reveal a 1st-order decay of 2, and a plot of $k_{obs}$ as a function of [OH$^-$] shows that the reaction of 2 with NaOH has a 1st-order dependence on [OH$^-$] (Figure 7). The slope of the plot in Figure 7 gives $k = 1.30(6) \times 10^{-2}$ M$^{-1}$ s$^{-1}$, which corresponds to $G = 19.1(1)$ kcal mol$^{-1}$ at 10.7 °C.

![Diagram](image)

**Figure 7.** Plot of $k_{obs}$ vs [OH$^-$] for the reaction of Cp$^*$W(O)$_2$(CH$_2$SiMe$_3$)$_2$ with NaOH showing a 1st-order dependence on [OH$^-$] ($R^2 = 0.99$).

The rate of the reaction between 2 and NaOH was monitored by $^1$H NMR spectroscopy at -1.3, 10.7, 22.7, and 34.7 °C. An Eyring plot (using $k$ values that were corrected for [HO$_2^-$]) was used to calculate $H = 13.6(4)$ kcal mol$^{-1}$ and $S = -20(1)$ cal mol$^{-1}$ K$^{-1}$.

![Diagram](image)

**Figure 8.** Plot of $\ln(k/T)$ vs $1/T$ for the reaction of Cp$^*$W(O)$_2$(CH$_2$SiMe$_3$)$_2$ with NaOH (5 equiv) ($R^2 = 0.99$).

Three possible pathways for the reaction of complex 2 with NaOH are shown in Scheme 4. In pathway A, the hydroxide undergoes direct nucleophilic addition to the TMSCH$_2$ ligand. For this pathway, the oxygen atom in the alcohol would...
Scheme 5. Calculated Free Energy for the Reaction of Cp₆WO(²-O)₂(CH₂SiMe₃) (2) with OH⁻

-originates from hydroxide. Pathway B involves hydroxide coordination to W followed by C–O reductive elimination. In pathway B, the oxygen atom of the alcohol would also originate from hydroxide. Pathway C involves hydroxide coordination to W, which would facilitate transfer of the –CH₂TMS ligand to an Mn-peroxo oxygen atom. Protonation with water generates alcohol. The oxygen atom of the alcohol in pathway C originates from complex 2. MeLi was reacted with ¹⁸O-labeled water to generate the ¹⁸O-labeled Li⁺OH in H₂¹⁸O. The alcohol product from the reaction of 2 with Li⁺OH was then analyzed by GC/MS. Only R¹⁸OH was observed in the MS spectrum, which is consistent with pathway C and inconsistent with pathways A and B in Scheme 4.

The role of hydroxide for the conversion of 2 to TMSCH₂OH was probed computationally. Several mechanisms were investigated (Scheme 5). The very large calculated free energy barriers (ΔG = 67 kcal mol⁻¹) led us to discount nucleophilic substitution (pathway A) and reductive elimination (pathway B). The calculations suggest that the hydroxide coordination-assisted allyl migration to an oxygen atom of the Mn-peroxo ligand (ΔG = 34 and 35 kcal mol⁻¹ in 1,4-dioxane and water) has almost the same energy barrier as the non-assisted allyl migration (35 and 32 kcal mol⁻¹ in 1,4-dioxane and water) (see Scheme 7 below). What emerged as the most reasonable pathway was a H atom transfer pathway in which hydroxide coordinates to W, followed by proton transfer (ΔG = 25 and 24 kcal mol⁻¹ in 1,4-dioxane and water, respectively) to yield a hydroperoxide intermediate, [(²-O)₃W(O)₂(R)(OOH)]⁺ (Scheme 5). The OMBV TS from the latter is calculated to be 24 and 23 kcal mol⁻¹ in 1,4-dioxane and water above the starting complex 1, in reasonable agreement with the experimental measurement. After oxy-insertion, hydroxide loss (to yield 3 + OH⁻) or proton transfer (to yield [Cp₆W(O)₃]⁺ + ROH) was determined to be facile (ΔG = 11 kcal mol⁻¹ in 1,4-dioxane and water, respectively).

The calculated transition state for oxy-insertion from [(²-O)₃W(O)₂(R)(OOH)]⁺ (Figure 9) is structurally similar to the corresponding TS for the transition state involving oxygen atom insertion from periodate (Figure 4). The C–O bond being formed is longer (2.23 vs 2.10 Å) and the W–C bond

Scheme 6. Two Possible Pathways for the Alcohol Release Reaction of Cp₆WO(²-O)₂(CH₂SiMe₃) (2) with HCl

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Scheme 7. Calculated Free Energy for the Reaction of Cp^8WO(\(\text{O}_2\))\((\text{CH}_2\text{SiMe}_3)\) (2) with \(\text{H}^+\)

"The cation (\(\text{H}^+\)(\(\text{H}_{2}\text{O}\))\(_2\))\(\text{O}^+\) (diox = 1,4-dioxane) was used to model the proton. Numbers are free energies (kcal mol\(^{-1}\)) for 1,4-dioxane (top, bold) and water (bottom, italics) and are relative to complex 2.

Figure 9. DFT calculated organometallic Baeyer-Villiger (OMBV) transition state for oxy-insertion of hydroperoxide into W-C bond of Cp^8W(O)(\(\text{O}_2\))(\(\text{CH}_2\text{SiMe}_3\)) (1). Bond lengths are given in Å and bond angles in degrees.

being broken is shorter (2.44 vs 2.61 Å) for the periodate TS, implying an earlier TS for the OMBV oxy-insertion with periodate in relation to the hydroperoxide congener. The tremendous kinetic and thermodynamic free energy preference for the OMBV pathway in relation to the pathways that lead to reduced W^V intermediates (nucleophilic substitution and reductive elimination, Scheme 5) is interesting in connection with the highly endergonic single-electron transfer reaction modeled above, and supports the notion of the important role of metal d orbital occupation in oxy-insertion, and further that movement away from \(\delta^\text{op}\) motifs will favor the OMBV pathway. Thus, while functionalization of alkyl ligands through processes that formally reduce the metal center can be facile for late transition metal complexes, similar reactions with middle transition metals may have inherently and prohibitively high activation barriers.

Reaction of Cp^8W(O)(\(\text{O}_2\))(\(\text{CH}_2\text{SiMe}_3\)) (2) with Bronsted Acid. The formation of alcohol is also observed when complex 2 is treated with HCl in 1,4-dioxane. The reaction is complete in 40 h at room temperature and produces Cp^8W(O)(\(\text{O}_2\))(\(\text{CH}_2\text{SiMe}_3\)) in 90% yield by \(^1\text{H}\) NMR spectroscopy (eq 4). The acid-promoted reaction of 2 is slower than the hydroxide-promoted conversion. For example, complex 2 with 3 equiv of NaOH quantitatively forms TMSCH\(_2\)OH in less than 1 h at room temperature.

Table 1 shows the conditions and results for the reactions of complex 2 with various proton sources. Without a proton source, when 2 is heated in benzene at 80°C for 24 h, no alcohol is observed, and the starting material decomposes to form complex 1 (entry 1). Heating increases the rate of conversion but decreases the yield (entries 3 and 4). The use of strong acid in 1,4-dioxane results in decomposition of the starting material with no alcohol production (entries 7 and 9). Adding \([\text{Bu}_4\text{N}]+\)(\(\text{Cl}^-\)) does not accelerate the reaction, which is consistent with the acceleration by HCl resulting from the addition of protons rather than chloride. Also, weaker acids, such as lutidine, do not facilitate this reaction at room temperature.

We have considered two roles for the acid in the conversion of 2 and HCl to Cp^8W(O)(\(\text{O}_2\))(\(\text{CH}_2\text{SiMe}_3\)) (Scheme 6): (1) the proton serves as a catalyst by protonating the \(\text{H}^3\)-peroxo ligand, which would increase oxygen electrophilicity and facilitate oxy-insertion. A similar mechanism was proposed for the acid-catalyzed rearrangement of an \(\text{H}^3\)-peroxo Ta alkyl to form oxo-alkoxide derivatives.\(^{26}\) (2) The proton is not a catalyst, but rather, the acid serves to generate free alcohol from Cp^8W(O)(\(\text{O}_2\))(\(\text{OCH}_2\text{SiMe}_3\)).

To investigate rate dependence of the reaction of 2 and HCl, we attempted to use excess HCl to achieve pseudo-first-order
conditions. However, when more than 5 equiv of HCl are used, complex 2 decomposed with little production of TMSCH$_2$OH.

Reaction coordinates for conversion of 1 to 3 in the absence and presence of a proton were evaluated computationally to help assess the impact of Bronsted acids upon the proposed mechanisms of oxy-insertion. Various basic sites were evaluated in the starting materials, products, intermediates, and transition states (e.g., protonation of oxo versus peroxo ligands). The discussion focuses on the most stable tautomers (Scheme 7). In the absence of a proton, the migration of R to the peroxide moiety has a calculated activation barrier of 35 or 32 kcal mol$^{-1}$ in 1,4-dioxane or water, respectively. Upon protonation (the protonated bis-dioxane cation, [dioxane]$^+$, was used to model HCl in dioxane), the corresponding barriers were reduced to 17 kcal mol$^{-1}$ (1,4-dioxane) or 22 kcal mol$^{-1}$ (water). The results thus support the observation of acceleration of the oxy-insertion reaction upon the introduction of Bronsted acids.

Analysis of the calculated oxy-insertion TS geometries from 2 with and without an added proton is revealing (Figure 10). The various bond distances in the active site point to an earlier TS upon the introduction of a proton, which is consistent with a lower barrier according to the Hammond postulate. Additionally, one may hypothesize that the protonation of the incipient oxide group in the peroxo TS yields a better leaving group (hydroxide). The greater exergonicity for neutral Cp$^*$W(O)($\eta^2$-O)$_2$(CH$_2$SiMe$_3$) versus the protonated variant (−69 kcal mol$^{-1}$ in 1,4-dioxane (Scheme 5) versus −80 kcal mol$^{-1}$ (Scheme 7)) provides additional support for these proposals and the role of Bronsted acids in catalyzing oxy-insertion from 2.

Reaction of Cp$^*$W(O)$_2$(CH$_2$SiMe$_3$) (1) with Hydrogen Peroxide in the Presence of Hydroxide. The reaction of complex 1 with H$_2$O$_2$ (3 equiv) in benzene generates complex 2 at room temperature after 24 h without production of alcohol. However, alcohol production is observed at room temperature when complex 1 is treated with a mixture of H$_2$O$_2$ (3 equiv) with NaOH (3 equiv) in 1:1 THF-$d_4$/D$_2$O (v/v). The reaction is complete in 4 h and produces TMSCH$_2$OH in >95% yield by $^1$H NMR spectroscopy (eq 5).

Espenson and co-workers observed faster decomposition and methanol release from MTO with H$_2$O$_2$ in a basic environment; Periana, Goddard, and co-workers studied the mechanism for the reaction of MTO with H$_2$O$_2$ in the presence of hydroxide. Calculations show that the OMBV pathway in which OOH$^-$ coordinates to rhenium followed by the migration of the methyl to the coordinated oxygen atom of Re--OOH has the lowest energy barrier. To determine whether the reaction of 1 with H$_2$O$_2$ in the presence of OH$^-$ proceeds via an OMBV pathway to form the alkoxy complex 3, as the reaction of 1 and IO$_4^-$ does (see above), the reaction of complex 1 with a mixture of 5 equiv of H$_2$O$_2$ and 5 equiv of NaOH in 1:1 THF-$d_4$/D$_2$O (v/v) was monitored at $-$1.5 C by $^1$H NMR spectroscopy. Under these conditions, the starting material 1 converts to complex 2 in 10 min. Complex 2 then undergoes slow transformation to TMSCH$_2$OH over a period of 8 h. Consequently, alcohol release from complex 1 and H$_2$O$_2$ in the presence of hydroxide proceeds by an $\eta^2$-peroxo pathway that involves two steps: the formation of the $\eta^2$-peroxo complex 2 and the conversion of 2 to TMSCH$_2$OH. Compared to the reaction with H$_2$O$_2$ under acidic conditions, the reaction rates of both steps (i.e., formation of 2 and release of TMSCH$_2$OH) are faster with hydroxide. For example, the reaction of complex 1 with a mixture of H$_2$O$_2$ (3 equiv) and HCl (3 equiv) produces complex 2 in hours at room temperature, which then converts to TMSCH$_2$OH in 48 h (Scheme 8).

Scheme 8. Comparison of Alcohol Release from Cp$^*$W(O)$_2$(CH$_2$SiMe$_3$) (1) with H$_2$O$_2$ in the Presence of H$^+$ and OH$^-$.

DFT was used to probe the conversion of dioxo complex 1 and hydrogen peroxide to the $\eta^2$-peroxo complex 2 (Scheme 9). A $[2 + 2]$ addition of the OH bond of hydrogen peroxide across the W--O bond of 1 (red line in Scheme 9) has a calculated barrier of 28 and 30 kcal mol$^{-1}$ for 1,4-dioxane and water, respectively. This $[2 + 2]$ TS leads to the hydroxy/hydroperoxy intermediate Cp$^*$W(R)(O)(OH)(OHOH, which is 10 kcal mol$^{-1}$ above complex 1. From this intermediate, a modest barrier of 12 kcal mol$^{-1}$ (1,4-dioxane) or 14 kcal mol$^{-1}$ (water) must be surmounted to transfer hydrogen from the hydroperoxide to hydroxide ligand to dissociate water and yield complex 2. Overall, with HOO$^-$/OH$^-$ as the oxygen atom transfer couple, the transformation of 1 to 2 is calculated to be mildly endergonic by 3 kcal mol$^{-1}$ in both 1,4-dioxane and water. Deprotonation of hydrogen peroxide and coordination of hydroperoxide gives Cp$^*$W(O)$_2$(R)(OOH), which is higher in energy than 1 by 10 and 13 kcal mol$^{-1}$. Conversion of Cp$^*$W(O)$_2$(R)(OOH) to complex 2 through an intramolecular proton transfer and dissociation of hydroxide are calculated to occur with overall activation barriers of 28 and 27 kcal mol$^{-1}$. Thus, the calculations do not reveal any obvious advantage to base-promoted conversion of 1 and hydrogen peroxide to complex 2.
Scheme 9. Calculated Free Energy for the Conversion of Cp^\text{5}\text{W}(\text{O})_2(\text{CH}_3\text{SiMe}_3) (1) and H_2O_2 to Cp^\text{5}\text{WO}(-\text{O})_2(\text{CH}_2\text{SiMe}_3) (2)\text{A}

\text{\textsuperscript{a}Numbers are free energies (kcal mol\textsuperscript{-1}) for 1,4-dioxane/water and are relative to complex 2.}

\section*{SUMMARY AND CONCLUSIONS}

Insertion of oxygen atoms into metal–hydrocarbyl bonds is a potential key step in catalytic oxidation of hydrocarbons. Despite the potential importance of such oxygen atom insertion reactions, there are few examples of nonradical conversion of M–R bonds and oxygen atom transfer reagents to M–OR, and detailed studies of nonradical oxygen atom insertion into M–R bonds are rare. We have established that Cp^\text{5}W\text{VI} complexes can undergo clean oxygen atom insertion reactions by at least three different pathways (Scheme 10). Oxy-insertion from \eta^3-peroxide complexes can be promoted by addition of hydroxide or Brønsted acid. DFT calculations lead to the suggestion that protonation of the \eta^3-peroxide ligand facilitates allyl migration to the unprotonated oxygen atom. Our calculations suggest that the addition of base leads to a similar TS in which the allyl group migrates to the unprotonated oxygen of an \eta^3-hydroperoxide ligand; however, the base-promoted TS is overall anionic and has a second oxo ligand (Scheme 11).

\textbf{Scheme 10. Summary of Pathways for the Oxygen Atom Insertion into W–C Bonds of Cp^\text{5}W(\text{O})_2(\text{CH}_3\text{SiMe}_3) (1) and Cp^\text{5}W(\text{O})(\text{\textsuperscript{\text{-}}\text{O})_2(\text{CH}_3\text{SiMe}_3) (2)\text{)}

\textbf{Scheme 11. Comparison of TSs Based on DFT Calculations for Base- and Acid-Promoted Conversion of Cp^\text{5}W(\text{O})(\text{\textsuperscript{\text{-}}\text{O})_2(\text{CH}_3\text{SiMe}_3) (2) to the Oxy-Insertion Products}

Experiments clearly show that the base-promoted oxy-insertion is faster than the acid-catalyzed reaction. Quantification of such effects is important, since most successful transition-metal-catalyzed alkane oxidations incorporate electrophilic late transition metals that tolerate acidic conditions but are not likely to be amenable to alkaline conditions.\textsuperscript{a,c} Some caution is advised when comparing these calculated values, since most computations use an implicit water solvation model and calculations for the reaction of 1 and IO\textsubscript{4} with explicit water demonstrate that hydrogen bonding can be important. The third oxy-insertion follows an OMBV pathway. To our knowledge, this is only the second example of an oxygen atom
insertion into a M–R bond that likely proceeds by this concerted process.\(^5\) Importantly, the OMBV reaction with \(I\) occurs in neutral water/1,4-dioxane, suggesting that catalysts with nucleophilic hydroxycarbonyl groups that are tolerant of water should be amenable for this oxy-functionalization process.

**EXPERIMENTAL SECTION**

**General Methods.** Unless otherwise noted, all synthetic procedures were performed under anerobic conditions in a nitrogen bubbled glovebox or by using standard Schlenk techniques. Globoxew purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer (O<sub>2</sub> < 15 ppm for all reactions). Tetrahydrofuran and 1,4-dioxane were dried by distillation from calcium hydride and P<sub>2</sub>O<sub>5</sub>, respectively. Distilled ether was distilled over CaH<sub>2</sub> THF-d<sub>4</sub> 1,4-dioxane-d<sub>4</sub> D<sub>2</sub>O and H<sub>2</sub>18O were used as received and stored under a N<sub>2</sub> atmosphere over 4 Å molecular sieves (except water). 1H NMR spectra were recorded on a Varian Mercury 300 or Varian Inova 500 MHz spectrometer. All 1H spectra are referenced against residual proton signals of the deuterated solvents. GC/MS was performed using a Shimadzu GCMS-QP2010 Plus system with a 30 mm × 0.25 mm SHRX-5MS column with a 0.25 mm film thickness using negative chemical ionization (NCI), which also allows for simulated electron impact (SEI) ionization. The preparation, isolation, and characterization of Cp"W(O)₂(CH₂SiMe₃)" and Cp"W(O)(O=O)(CH₂SiMe₃)" have previously been reported.\(^3\) All other reagents were used as purchased from commercial sources.

**Computational Methods.** DFT calculations with the B3LYP\(^{48}\) functional employed the Gaussian 09 program\(^{49}\) in conjuction with the pseudopotentials and valence basis sets of Steever and co-workers\(^{50}\) for W, Si, and I. All 2p elements plus hydrides were modeled with the 6-31+G(d,p) all-electron basis set. All species were singlet spin states and optimized within the restricted Kohn–Sham formalism with the exception of I and [IO₄]⁻, which are doublets and optimized with unrestricted Kohn–Sham methods. For the latter, spin contamination was minimal. All stationary points were optimized in the gas phase without symmetry constraint and identified as minima or TSs through the calculation of the energy Hessian. Solvents effects were incorporated implicitly through the use of the CPCM\(^{51}\) model for water and 1,4-dioxane.

**Reaction of Cp"W(O)₂(CH₂SiMe₃)" (1) with NaO₄.** Complex 1 (2.1 mg, 5.0 µmol) was dissolved in 300 µL of THF-d₄ in an NMR tube. NaO₄ (3.3 mg, 15 µmol) was dissolved in 300 µL of D₂O and transferred to the solution of 1. The reaction was monitored by 1H NMR spectroscopy until completion. The production of TMSCH₄OH was confirmed using two methods. First, 5 µL of the reaction mixture was analyzed by GC/MS, and TMSCH₄OH was detected (and compared with GC/MS of an authentic sample). Second, 1 µL of TMSCH₄OH was added to the reaction mixture. The intensity of the product peaks increased in the 1H NMR spectrum. Cp"W(O)₂(CH₂SiMe₃)" (3): 1H NMR (THF-d₄/D₂O 1:1), δ: 4.17 (CH₆H₆), 2.04 (CH₆H₆), -0.05 (Si(CH₃)₄) ppm.

**Kinetics of Reactions of Cp"W(O)₂(CH₂SiMe₃)" (1) with NaO₄.** A representative kinetic experiment is described. Complex 1 (32.0 mg 75.0 µmol) was dissolved in 4.5 mL of THF-d₄. Two drops of benzene were added to the solution as an internal standard for 1H NMR integration. A 300 µL aliquot (0.0166 mol/L) was transferred to an NMR tube. NaO₄ (143 mg, 0.667 mol/L) was dissolved in 2.0 mL of D₂O (0.33 mol/L). D₂O (225 µL) was added to the solution of 1 by syringe and 25 s later, 0.0015 K and 1 atm were added resulting in unscaled vibrational frequencies.

**Erying Plot of Reaction of Cp"W(O)₂(CH₂SiMe₃)" (1) with NaO₄.** A representative kinetic experiment is described. Complex 1 (13.5 mg, 32.0 µmol) was dissolved in 4.8 mL of THF-d₄. Two drops of benzene were added to the solution as an internal standard for 1H NMR integration. A 300 µL aliquot (0.0067 mol/L) was transferred to an NMR tube by syringe. NaO₄ (4.48 mg, 0.200 mmol) was dissolved in 6.0 mL of D₂O (0.033 mol/L). The solution of complex 1 was cooled in ice water. Then, 300 µL (5.0 equiv) of the NaO₄ solution was added to the solution of complex 1. The reaction mixture was monitored by 1H NMR spectroscopy on a 500 MHz spectrometer at 10.7 ppm. 1H NMR spectrum was acquired every 2 min. Integration of the methylene peak of complex 1 gave the variation in concentrations. Similar reactions were set up at -1.3, 22.7, and 34.7°C. The time between every 1H NMR spectrum in the array was adjusted according to the rate of the reaction. To ensure reproducibility, every concentration was repeated at least twice for a minimum of three total experiments under each set of conditions.

**Oxygen Labeling of Reaction of Cp"W(O)₂(CH₂SiMe₃)" (1) with NaO₄.** NaO₄ (10.7 mg, 50.0 µmol) was dissolved in 300 µL of H₂O and allowed to equilibrate at 1 h at room temperature with sonication (the exchange of H₂O and H₂O under such condition is extremely fast). Complex 1 (4.2 mg, 10 µmol) was dissolved in 300 µL of THF, and the solution was transferred to the NaO₄ solution. After 20 min at room temperature, the color of the solution faded from pale yellow to colorless. A 3.0 µL aliquot of the reaction mixture was analyzed by GC/MS for TMSCH₄OH content. The fragmentation pattern of TMSCH₄OH produced from the reaction was compared to patterns of TMSCH₄OH and TMSCH₄OH by GC/MS. Reaction of Cp"W(O)₂(CH₂SiMe₃)" (1) with PhIO. Complex 1 (4.2 mg, 10 µmol) was dissolved in 400 µL of 1,4-dioxane-d₄ in a 1-mL Young tube. The tube was then taken out of the box and sonicated for 30 min. 1H NMR spectroscopy was used to monitor the reaction.

**Reaction of Cp"W(O)₂(CH₂SiMe₃)" (1) with [Bu₄N][IO₄].** Complex 1 (4.3 mg, 10 µmol) and [Bu₄N][IO₄] (12.9 mg, 30 µmol) were dissolved in 300 µL of dry THF-d₄. 1H NMR spectroscopy was used to monitor the reaction at room temperature. No reaction was observed after 24 h. D₂O (300 µL) was added to the reaction mixture. 1H NMR spectrum was acquired after 2 h, and quantitative formation of TMSCH₄OH was observed.

**Kinetics of Water Dependence in the Reaction of Cp"W(O)₂(CH₂SiMe₃)" (1) with [Bu₄N][IO₄].** A representative kinetic experiment is described. Complex 1 (32.0 mg 75.0 µmol) and [Bu₄N][IO₄] (487 mg, 1.12 mmol, 15 equiv) were dissolved in 60 mL of THF-d₄. Two drops of benzene were added to the solution as an internal standard for 1H NMR integration. A 400 µL aliquot was transferred to a 1-mL Young tube. D₂O (5.0 µL, 50 equiv) was added to the solution of 1 and [Bu₄N][IO₄] by syringe. The reaction mixture was then monitored by 1H NMR spectroscopy on a 500 MHz spectrometer at 50°C in a NMR tube. The reaction mixture was acquired every 20 min. Integration of the methylene peak of complex 1 gave the variation in concentrations. Similar procedures were used to set up the reaction of 1 and 15 equiv of [Bu₄N][IO₄] with 10.0, 20.0, 30.0, 40.0, 60.0, and 100 µL of D₂O (the reaction with 60.0 and 100 µL of D₂O, the same amount of 1 and [Bu₄N][IO₄] were dissolved in 300 µL of THF-d₄ instead of 400 µL). To ensure reproducibility, every concentration was repeated in triplicate.

**Reaction of Cp"W(O)(O=O)(CH₂SiMe₃)" (2) with NaOH.** Complex 2 (4.3 mg, 10 µmol) was dissolved in 300 mL of THF-d₄ in an NMR tube. NaO₄ (1.2 mg, 30 µmol) was dissolved in 300 µL of D₂O and transferred to the solution of complex 2. The reaction mixture was monitored by 1H NMR spectroscopy until completion. The production of TMSCH₄OH was confirmed using two methods. First, 5 µL of the reaction mixture was analyzed by GC/MS, and TMSCH₄OH was detected (and compared with GC/MS of an authentic sample). Second, 1 µL of TMSCH₄OH was added to the reaction mixture. The intensity of the product peaks increased in the 1H NMR spectrum.

**Kinetics of Cp"W(O)(O=O)(CH₂SiMe₃)" (2) with NaOH.** A representative kinetic experiment is described. Complex 1 (330 mg, 0.080 mmol) was dissolved in 4.5 mL of THF-d₄. Two drops of benzene were added to the solution as an internal standard for 1H NMR integration. A 300 µL aliquot (0.0166 mol/L) was transferred to an NMR tube. NaO₄ (143 mg, 0.667 mol/L) was dissolved in 2.0 mL of D₂O (0.33 mol/L). D₂O (225 µL) was added to the solution of 1 by syringe and 25 s later, 0.0015 K and 1 atm were added resulting in unscaled vibrational frequencies.

**Kinetics of Reactions of Cp"W(O)(O=O)(CH₂SiMe₃)" (2) with NaOH.** A representative kinetic experiment is described.
75.0 (µmol) was dissolved in 4.5 mL of THF-d₈. Several milligrams of hexamethylbenzene were added to the solution as an internal standard for ¹H NMR integration. A 300 µL aliquot (0.0166 mol/L) was transferred to an NMR tube. NaOH (2.67 g, 0.067 mmol) was dissolved in 2.0 mL of D₂O (0.33 mol/L). D₂O (225 µL) was added to the solution of complex 1 by syringe and cooled in ice water. Then, 75 µL (5.0 equiv) of the NaOH solution was added to the complex 1 solution. The reaction mixture was then monitored by ¹H NMR spectroscopy on a 500 MHz spectrometer at 10.7 C. A ¹H NMR spectrum was acquired every 2 min. Integration of the ¹H methyl peak of complex 1 and the methylene peak of TMSCHN₂ gave the variation in concentrations. Similar reactions were set up for 10.0, 15.0, and 20.0 equiv of NaOH by adjusting the amounts of the D₂O and NaOH solutions. The time between every ¹H NMR spectrum in the array was adjusted according to the rate of the reactions. To ensure reproducibility, every concentration was repeated in triplicate.

Eyring Plot of Reaction of Cp²W(O)(O₂)(CH₂SiMe₃) (2) with NaOH. A representative kinetic experiment is described. Complex 2 (35.2 mg, 80.4 µmol) was dissolved in 4.8 mL of THF-d₈. Several milligrams of hexamethylbenzene were added to the solution as an internal standard for ¹H NMR integration. A 300 µL aliquot (0.0166 mol/L) was transferred to an NMR tube by syringe. NaOH (2.02 g, 0.058 mmol) was dissolved in 6.0 mL of D₂O (0.083 mol/L). The solution of complex 1 was cooled in ice water. Then, 300 µL (5.0 equiv) of the NaOH solution was added to the solution of complex 1. The reaction mixture was then monitored by ¹H NMR spectroscopy on a 500 MHz spectrometer at 10.7 C. A ¹H NMR spectrum was acquired every 2 min. Integration of the ¹H methyl peak of complex 1 and the methylene peak of TMSCHN₂ gave the variation in concentrations. Similar reactions were set up at −1.3, 22.7, and 34.7 C. The time between every ¹H NMR spectrum in the array was adjusted according to the rate of the reaction. To ensure reproducibility, every concentration was repeated in triplicate.

Oxygen Labeling of Reaction of Cp²W(O)(O₂)(CH₂SiMe₃) (2) with LiOH. H₂O (300 µL) was transferred to a vial and frozen in an −50°C/−70°C dry ice bath. CH₂I₂ in diethyl ether solution (1 M, 30 µL) was added to the frozen H₂O. The −30°C dry ice bath was then removed, and the mixture was warmed up to room temperature to generate the LiOH in H₂O solution. Complex 2 (4.3 mg, 10 µmol) was dissolved in 300 µL of THF; and the solution was added to the LiOH solution. After 30 min at room temperature, a 3.0 µL aliquot of the reaction mixture was analyzed by GC/MS for TMSCHN₂ content. The fragmentation pattern of TMSCHN₂ from the reaction was compared to patterns for TMSCHN₂ and TMSCHN₂O.

Reaction of Cp²W(O)(O₂)(CH₂SiMe₃) (2) with Bronsted Acid. A representative reaction is described. Complex 2 (2.2 mg, 5.0 µmol) was dissolved in 400 µL of 1,4-dioxane-d₈ in a 10 mL round-bottom flask and HCl in diethyl ether solution (1N, 15 µL) was added to the solution of 2. The reaction was then monitored by ¹H NMR spectroscopy. The reaction was complete after approximately 2 days.

Kinetcs of Reaction of Cp²W(O)(O₂)(CH₂SiMe₃) (1) with H₂O/NaOH. Complex 1 (4.2 mg, 10 µmol) was dissolved in 300 µL of 1,4-dioxane-d₈ in an NMR tube. Hydrochloric acid (35%, 3.0 µL, 33 µmol) and H₂O (30%, 3.0 µL, 29 µmol) were added to 300 µL of D₂O. The mixture of H₂O and HCl was then added to the complex 2 solution. ¹H NMR spectroscopy was used to monitor the reaction at room temperature.

Kinetics of Reaction of Cp²W(O)(O₂)(CH₂SiMe₃) (1) with H₂O/NaOH. Complex 1 (4.2 mg, 10 µmol) was dissolved in 300 µL of THF-d₈ in an NMR tube. NaOH (2.0 mg, 50 µmol) was dissolved in 300 µL of D₂O and 5 µL (48 µmol) of 30% H₂O solution was added to the NaOH solution. Both starting materials were cooled in ice water. The mixture of H₂O and NaOH was then added to the solution of 2. The reaction mixture was then monitored by ¹H NMR spectroscopy on a 500 MHz spectrometer at −1.3 C. A ¹H NMR spectrum was acquired every 26 s.

**ASSOCIATED CONTENT**

* Supporting Information

Kinetics and GC/MS data, additional experimental details, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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