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Oxidation of Tertiary Silanes by Osmium Tetroxide

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In the presence of an excess of pyridine ligand L, osmium tetroxide oxidizes tertiary silanes (Et_3SiH, $^iPr_3SiH$, Ph_3SiH, or $PhMe_2SiH$) to the corresponding silanols. With L = 4-*tert*-butylpyridine (^{t}Bupy), $OsO_4(^tBupy)$ oxidizes Et_3SiH and $PhMe_2SiH$ to yield 100 ± 2% of silanol and the structurally characterized osmium(VI) μ-oxo dimer $[OsO_2(^tBupy)_2]_2(\mu\text{-}O)_2$ (**1a**). With L = pyridine (py), only 40–60% yields of R_3SiOH are obtained, apparently because of coprecipitation of osmium(VIII) with $[Os(O)_2py_2]_2(\mu\text{-}O)_2$ (**1b**). Excess silane in these reactions causes further reduction of the Os^{VI} products, and similar osmium "over-reduction" is observed with $PhSiH_3$, Bu_3SnH, and boranes. The pathway for $OsO_4(L) + R_3SiH$ involves an intermediate, which forms rapidly at 200 K and decays more slowly to products. NMR and IR spectra indicate that the intermediate is a monomeric Os^{VI}-hydroxo-siloxo complex, *trans*-*cis*-*cis*-$Os(O)_2L_2(OH)(OSiR_3)$. Mechanistic studies and density functional theory calculations indicate that the intermediate is formed by the [3 + 2] addition of an Si–H bond across an O=Os=O fragment. This is the first direct observation of a [3 + 2] intermediate in a σ-bond oxidation, though such species have previously been implicated in reactions of H–H and C–H bonds with $OsO_4(L)$ and RuO_4.

Selective oxidations of σ bonds are both practical and fundamental goals in current chemistry. In particular, the conversion of C−H bonds selectively to COH groups has long been a "holy grail" of catalysis.[1] Silanes have often been used as imperfect models for the less-reactive alkanes in reactions of transition-metal complexes.[2] Reported here are stoichiometric oxidations of Si−H bonds in tertiary silanes to R_3SiOH by $OsO_4(L)$ (L = 4-*tert*-butylpyridine (^{t}Bupy) or pyridine (py)). Although there are better methods to prepare silanols,[3] this reaction extends the scope and provides mechanistic insight into an interesting class of σ-bond oxidations.

The activation of σ bonds can occur by a variety of mechanisms. Among the fundamental reactions of organometallic chemistry are the additions of X−Y to a metal center (oxidative addition), to an M−Z bond (σ-bond metathesis), or to an M=Z π bond ([2 + 2] cycloaddition).[4] High oxidation state metal complexes can also oxidize C−H and

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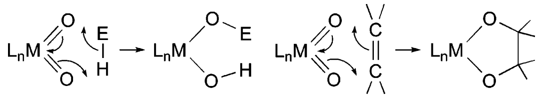
Chart 1. [3 + 2] Mechanisms for E−H and Alkene Oxidations[a]



[a] See refs 8−14.

other σ bonds by hydrogen atom transfer,[5,6] hydride transfer,[5] or direct insertion.[7]

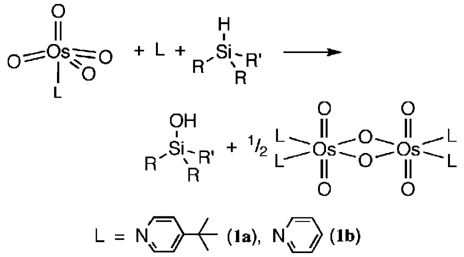
Alkane oxidation by ruthenium tetroxide has been suggested to proceed via the [3 + 2] addition of a C−H bond across an O═Ru═O unit (Chart 1).[8] This mechanism, in which no new bonds to the metal are formed, is analogous to the now widely accepted pathway[9] for alkene dihydroxylations by OsO_4 (right side of Chart 1).[10] It appears to be the favored pathway for alkane oxidations by RuO_4[8,11] and perhaps OsO_4[12] and for reactions of H_2 with RuO_4, MnO_4^-,[13] and OsO_4.[14]

Reactions of silanes with osmium tetroxide have not previously been reported, although recent papers describe reactions of silanes with rhenium-oxo complexes that are novel hydrosilation catalysts.[15,16] A [2 + 2] pathway has been suggested for some of these reactions based on the observation of a rhenium hydride intermediate and on density functional theory (DFT) calculations.[15] Silanes are also well-known to undergo oxidative addition and σ-bond metathesis with transition-metal compounds.[2]

We find that the oxidation of tertiary silanes to silanols by $OsO_4(L)$ in the presence of excess ligand proceeds via an intermediate, $L_2(O)_2Os(OSiR_3)(OH)$, which is the formal product of [3 + 2] addition of the Si−H bond across an O═Os═O unit. Mechanistic and computational studies indicate that the intermediate is formed by a [3 + 2] pathway. Although intermediates of this kind have been proposed in the oxidations of H_2 and alkanes by tetraoxo metal complexes,[8,11−14] this is the first direct observation of such a species in a σ-bond oxidation.

Results

The reaction of 1 equiv of a tertiary silane ($PhMe_2SiH$, Et_3SiH, $^iPr_3SiH$, or Ph_3SiH) with OsO_4 in CD_2Cl_2 in the presence of a pyridine ligand in excess forms $R_2R'SiOH$ and $[OsO_2(L)_2]_2(\mu\text{-}O)_2$[17] (eq 1). In the absence of a pyridine ligand, OsO_4 is still rapidly reduced by $R_2R'SiH$ in CD_2Cl_2, but a black insoluble material forms and no silicon products are observed. Thus, our studies have focused on reactions in the presence of either py or ^{t}Bupy.


(1)

I. OsO_4 + L. The addition of pyridine bases to OsO_4 in organic solvents is well-known to form yellow $OsO_4(L)$ complexes (eq 2).[18,19] Monitoring the formation of $OsO_4(L)$ in CH_2Cl_2 at 25 °C by optical spectroscopy yields $K_L = 166 \pm 20\ M^{-1}$ for $OsO_4(^tBupy)$ and $26 \pm 3\ M^{-1}$ for $OsO_4(py)$ (see the Experimental Section). The literature values for $OsO_4(py)$ are $34 \pm 2\ M^{-1}$ in MeCN and $79 \pm 7\ M^{-1}$ in toluene.[19] ^1H NMR spectra of CD_2Cl_2 solutions containing OsO_4 and excess ^{t}Bupy or py show only one set of resonances for the organic base, even at 200 K. Thus, the exchange of bound and free ligand is fast on the NMR time scale.

$$OsO_4 + L \overset{K_L}{\rightleftharpoons} OsO_4(L) \qquad (2)$$

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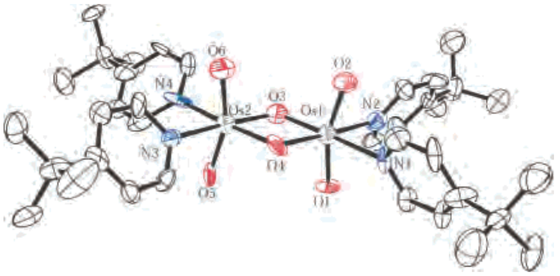

Figure 1. *ORTEP* diagram of **1a** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for **1a**

formula	$C_{42}H_{64}Cl_{12}N_4O_6Os_2$
fw	1526.77
T (K)	130 (2)
λ (Å)	0.71073
space group	$P2_1/c$
a (Å)	12.2650 (13)
b (Å)	23.736 (3)
c (Å)	21.737 (3)
β (deg)	114.251 (7)
V (Å^3)	5769.7 (12)
Z, D_{calcd} (Mg m^{-3})	4, 1.758
θ range for data collection (deg)	2.11−28.37
index ranges	$-12 \leq h \leq 15$ $-31 \leq k \leq 27$ $-29 \leq l \leq 28$
μ (mm^{-1})	5.001
reflns collected/unique	15 030/10 865
R_{int}	0.1176
Params/restraints	607/54
R_1 [$I > 2\sigma(I)$]^a	0.087
$R_2{}^b$ (all data)	0.216
GOF (on F^2)	0.994

^{a} R_1 [$I > 2\sigma(I)$] = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} R_2 (all data) = $\{(\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1a**

Os(1)−O(1)	1.740(11)	Os(2)−O(5)	1.745(13)
Os(1)−O(2)	1.743(13)	Os(2)−O(6)	1.756(13)
Os(1)−O(3)	1.939(13)	Os(1)−O(4)	1.966(13)
Os(2)−O(3)	1.989(13)	Os(2)−O(4)	1.977(12)
Os(1)−N(1)	2.209(14)	Os(2)−N(3)	2.120(18)
Os(1)−N(2)	2.221(18)	Os(2)−N(4)	2.156(16)
O(1)−Os(1)−O(2)	161.9(5)	O(1)−Os(1)−N(1)	81.5(6)
N(1)−Os(1)−N(2)	89.3(5)	O(1)−Os(1)−O(3)	95.3(6)
O(3)−Os(1)−O(4)	80.5(5)	O(3)−Os(2)−O(4)	80.0(6)

II. Reactions of OsO_4 + $R_2R'SiH$ + Pyridines. The addition of 100 mM $R_2R'SiH$ to a yellow equimolar solution of OsO_4 in CD_2Cl_2 and 0.4−1.0 M py or ^{t}Bupy forms a pinkish-brown solution rapidly at 200 K. Excess ligand was used to ensure that essentially all of the Os^{VIII} in solution was present as OsO_4(L). The color change is due to an intermediate that is discussed below. Within hours at 200 or 298 K, the color of the solution turns brown and the silanol and osmium products are formed (eq 1). The reactions proceed similarly in CD_2Cl_2, $CDCl_3$, acetone-d_6, and toluene-d_8. When excess silane was used, OsO_4(L) was converted to black insoluble material and no silicon-containing products were identifiable. This is most likely due to further reduction of the Os^{VI} products by the silane (as observed in independent experiments).

The tertiary silanol, R_3SiOH, is the only observed silicon product in the OsO_4(L) oxidations of $PhMe_2SiH$, Et_3SiH, $^iPr_3SiH$, and Ph_3SiH. The silanols were identified by ^1H and $^{13}C\{^1H\}$ NMR, including spiking with authentic samples. With ^{t}Bupy as the ligand, quantitative yields of $PhMe_2SiOH$ and Et_3SiOH were obtained (100 ± 2%). In contrast, using py as the ligand gave lower yields, which never exceeded 75%; e.g., $PhMe_2SiOH$, 64 ± 10%; Et_3SiOH, 44 ± 5%; $^iPr_3SiOH$, 52 ± 5%; Ph_3SiOH, 61 ± 10%. In these cases, the final reaction mixtures contained R_3SiOH and unreacted silane, which together accounted for all of the R_3SiH present initially.

The OsO_4/^{t}Bupy reactions yield a single osmium product, the μ-oxo Os^{VI} dimer $[OsO_2(^tBupy)_2]_2(\mu\text{-}O)_2$ (**1a**, eq 1). Complex **1a** is analogous to the well-known pyridine derivative $[OsO_2(py)_2]_2(\mu\text{-}O)_2$ (**1b**), first prepared by Griffith in 1972.[17] It has been characterized spectroscopically and by an X-ray crystal structure (Figure 1, Tables 1 and 2). The diffraction data were of below-average quality, probably due to partial loss of CH_2Cl_2 from the crystal, and refinement required that the thermal parameters for nine atoms be constrained to positive values. Still, the osmium complex is well-defined, and its structural parameters are similar to those of **1b**[20] and a related $OsO_2(^tBupy)_2$-heterobimetallic complex.[21] Complex **1a** was independently prepared by the reduction of $OsO_4(^tBupy)$ with ethanol, following the procedure for **1b**.[17] The ^1H and $^{13}C\{^1H\}$ NMR spectra, which showed one set of ^{t}Bupy resonances, are the same for **1a** whether prepared with silanes (eq 1) or with ethanol. IR spectra of the different samples of **1a** are also identical and are very similar to the IR spectrum of **1b**.

When pyridine is used as the ligand, all of the osmium precipitates at the end of the reaction, leaving a colorless supernatant. The precipitate was originally thought to be pure **1b** since its IR spectrum in KBr and ^1H NMR spectrum in CD_3OD were similar to those of an authentic sample (which is only soluble in CD_3OD). However, the incomplete conversion of the silane should have left some yellow OsO_4(py) in the supernatant. Vigorous stirring of the isolated precipitate in fresh CH_2Cl_2 gave a yellow solution, the IR spectra of which showed a characteristic OsO_4(py) band at 909 cm^{-1}. Adding R_3SiH to this yellow solution caused further production of R_3SiOH and **1b**. These results suggest that the precipitate is a mixture of or a complex between **1b** and some Os^{VIII} species such as OsO_4(py). This coprecipitation could remove the oxidant from the solution and thus account for the low yields of silanol. With ^{t}Bupy, all of the osmium compounds are soluble and the conversion to $R_2R'SiOH$ is quantitative.

III. The Intermediate. The addition of the colorless silane to a yellow solution of OsO_4(L) rapidly forms a pinkish-brown intermediate, $Os(O)_2L_2(OH)(OSiR_2R')$ (Chart 2). The nature of this intermediate and its formation and decay have been studied by NMR at 200 K. $PhMe_2SiH$ is a particularly convenient substrate because the methyl signals are distinct

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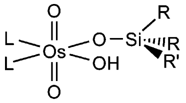
Chart 2



2a: L = ^{t}Bupy, SiR_2R' = $SiMe_2Ph$
2b: L = py, SiR_2R' = $SiEt_3$

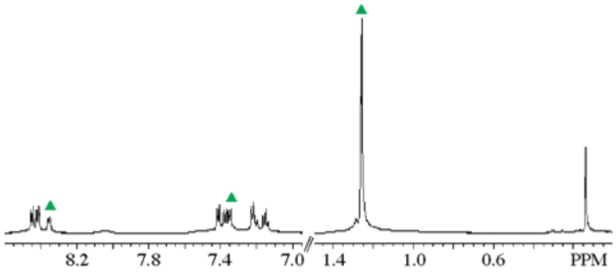


Figure 2. ^{1}H NMR spectrum of **2a** at 200 K; ▲ (green) = OsO_4(^{t}Bupy)/^{t}Bupy (peaks at δ 1.2 and 7.3 also have contributions from **2a**).

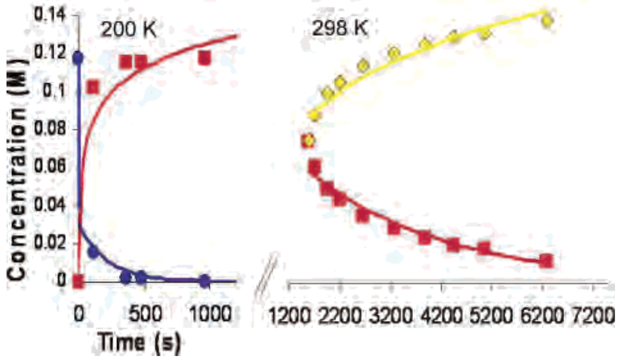


Figure 3. Time course of a reaction of OsO_4(^{t}Bupy) (117 mM), $PhMe_2SiH$ (117 mM), and ^{t}Bupy (322 mM) in CD_2Cl_2, at 200 K from 0 to 1000 s and at 298 K from 1200 s onward, showing $PhMe_2SiH$ (●, blue), **2a** (■, red), and $PhMe_2SiOH$ (◊, yellow).

for the silane, silanol, and intermediate, whereas for other silanes, overlapping resonances are observed.[16c]

^{1}H NMR spectra of the intermediate from $PhMe_2SiH$, $Os(O)_2L_2(OH)(OSiMe_2Ph)$ (**2a**), at 200 K in CD_2Cl_2 show one set of $PhMe_2Si$ peaks, a broad singlet at 8.2 ppm, and two sets of ^{t}Bupy peaks (Figure 2). The relative integration of these resonances was constant throughout the formation and decay of **2a**, and nuclear Overhauser effect cross-peaks[22] were observed between resonances of different pyridines, indicating that all of these resonances result from the same species. The bound ^{t}Bupy ligands do not exchange with free ^{t}Bupy on the NMR time scale at 200 K. The silyl methyl groups appear as a singlet (δ 0.12), indicating that they are equivalent and that a proton is not attached to the silicon center. (Free $PhMe_2SiH$ shows a doublet for the methyl groups at δ 0.29 with $^3J_{HH}$ = 4 Hz.) The ^{1}H NMR and parallel $^{13}C\{^1H\}$ NMR results indicate that the structure of **2a** has a single plane of symmetry, which makes the silicon substituents equivalent but leaves the ^{t}Bupy ligands inequivalent. The data thus indicate that **2a** is *trans-cis-cis*-$Os(O)_2L_2(OH)(OSiR_3)$ (Chart 2).

The broad ^{1}H NMR resonance at δ 8.2 ppm is assigned to the OH ligand in **2a**. Exchange between this singlet and the water peak at 2.0 ppm was shown by a ^{1}H NMR exchange spectroscopy (EXSY) spectrum[22] at 250 K. (The water resonance was confirmed in all experiments by spiking because its chemical shift was variable.) In a reaction of the deuterated silane $PhMe_2SiD$, the δ 8.2 signal was not observed in a ^{1}H NMR spectrum taken 2 min after mixing at 250 K, though all of the other peaks for **2a** were present. After 8 min, the δ 8.2 resonance had grown in and an EXSY spectrum showed faint cross-peaks between this resonance and the water singlet. Thus the hydrogen at δ 8.2 derives from the silicon hydride and exchanges with water, supporting its assignment as a hydroxide ligand. The chemical shift of 8.2 ppm is reasonable for a hydroxide ligand and would be unusual for an osmium hydride resonance.[23] In $OsH(OH)(CO)(P^tBu_2Me)_2$, for instance, $\delta(OsH) = -27.2$ and $\delta Os(OH) = 4.09$.[23a]

Similar intermediates are formed in all of the silane reactions. With Et_3SiH and pyridine as the ancillary ligand, the ^{1}H NMR spectra show inequivalent py ligands and ethyl resonances that do not have diastereotopic methylene hydrogens. Thus, a similar *trans-cis-cis*-$Os(O)_2py_2(OH)(OSiEt_3)$ structure (**2b**) is implicated. In the reaction of Et_3SiH, $OsO_4(py)$, and py in pentane at 200 K, intermediate **2b** precipitates as a pink solid. This pink material has the same ^{1}H NMR spectrum as in situ generated **2b**, and its IR spectrum (KBr) displays a broad band at 3379 cm^{-1} for the OsOH group. Solutions of the isolated pink solid, under the same conditions of excess pyridine as the reaction, decay on the same 1−2 h time scale at 298 K as that observed in the reaction mixtures. Thus, the isolated pink material is both spectroscopically consistent and kinetically competent to be the intermediate in the reaction of $OsO_4(py)$ with Et_3SiH. Attempts to grow crystals of this material have not been successful.

The intermediates form very rapidly at 200 K, then slowly decay to **1a**/**1b** and R_3SiOH. In a reaction of $PhMe_2SiH$ and OsO_4 (both 117 mM) and excess mM ^{t}Bupy in CD_2Cl_2, **2a** is ~80% formed after 2 min at 200 K and completely formed after 6 min (Figure 3). After warming to 298 K, **2a** quantitatively converts to $PhMe_2SiOH$ and **1a** (Figure 3, right side). Reactions initiated at 298 K show complete formation of **2a** within 2 min and some conversion to $PhMe_2SiOH$ and **1a** at 3 min. The formation of **2a** at 200 K occurs at a rate of ~8 × 10^{-4} M s^{-1} and, assuming second-order behavior (and zero-order in ^{t}Bupy under these saturating conditions), the rate constant is ca. 10^{-1} M^{-1} s^{-1} at 200 K. The initial rate of formation of **2a** at 200 K was essentially the same in CD_2Cl_2, $(CD_3)_2CO$, and $C_6D_5CD_3$ despite the differing polarity of these solvents. An analogous reaction in CCl_4 showed complete formation of **2a** within ~2 min at 250 K.

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[23] (a) Renkema, K. B.; Bosque, R.; Streib, W. E.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1999**, *121*, 10895−10907. (b) Wilton-Ely, J. D. E. T.; Wang, M.; Honarkhah, S. J.; Tocher, D. A. *Inorg. Chim. Acta* **2005**, *358*, 3218−3226. (c) Esteruelas, M. A.; Hernándes, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989−6000. (d) Sellmann, D.; Prakash, R.; Heinemann, F. W. *J. Chem. Soc., Dalton Trans.* **2004**, 3991−3996. (e) Sánchez-Delgado, R. A.; Rosales, M.; Esteruelas, M. A.; Oro, L. A. *J. Mol. Catal. A: Chem.* **1995**, *96*, 231−243.

Table 3. Calculated Energies, Enthalpies, and Free Energies (kcal mol^{-1}) of Products and Transition Structures, Relative to $OsO_4 + R_3SiH$

	ΔE	ΔH^{298}	ΔG^{298}
	$OsO_4 + SiH_4$		
$Os(O)_2(OSiH_3)(OH)$	−52.8	−49.0	−40.2
[3 + 2] transition state	8.7	8.2	18.1
$Os(O)_3(H)(OSiH_3)$	−1.5	0.2	9.1
[2 + 2] transition state	43.1	43.0	53.2
$Os(O)_3(SiH_3)(OH)$	−4.0	−0.9	8.8
[2 + 2] transition state	62.2	60.5	67.7
	$OsO_4 + Me_3SiH$		
$Os(O)_2(OSiMe_3)(OH)$	−63.5	−60.0	−51.4
[3 + 2] transition state	4.4	4.0	13.1
$Os(O)_3(H)(OSiMe_3)$	−12.4	−10.9	−2.8
[2 + 2] transition state	33.6	34.4	42.9
$Os(O)_3(SiMe_3)(OH)$	−14.1	−11.0	−1.7
[2 + 2] transition state	55.0	53.9	61.8

Reactions with py instead of ${}^tBupy$, at similar concentrations, proceeded at comparable rates.

The decay of **2a**, generated in situ, was monitored at 298 K by both ${}^1H$ NMR and UV−vis spectroscopies. Both the ${}^1H$ NMR data ([Os] = 8.4−25 mM) and UV−vis spectra ([Os] = 2.3−38 mM) indicate that the decay of **2a** is second order. Plots of 1/[**2a**] vs time from NMR data yield $k_d = 0.025 \pm 0.009$ M^{-1} s^{-1}, in good agreement with the $k_d = 0.030 \pm 0.007$ M^{-1} s^{-1} value derived from global analysis of the UV−vis spectra using *Specfit*.[24] Preliminary data suggest that an excess of pyridine slows the conversion of **2** to **1**. These data are consistent with a monomeric intermediate undergoing hydrolytic condensation to give **1a** and $PhMe_2SiOH$.

IV. Reactions with Other Reducing Agents. OsO_4(py) and $OsO_4({}^tBupy)$ react rapidly with Bu_3SnH, 9-borabicyclo-[3.3.1]nonane (9-BBN), and pinacolborane at 200 K in CD_2Cl_2, exhibiting color changes within seconds and producing insoluble black material over 1 h. The reaction of $PhSiH_3$ with OsO_4(py) at 298 K in CD_2Cl_2 is similar. No boron, tin, silicon, or organic products could be identified in the complex ${}^1H$ NMR spectra of reaction mixtures. Reactions of isolated **1a** and **1b** with these reducing agents similarly formed insoluble black materials within 30 min. Such "over-reduction" was also observed, as noted above, when more than 1 equiv of R_3SiH was mixed with OsO_4(L).

OsO_4(L) does not react with *n*-heptane, cyclohexane, or methylcyclopentane, under air or in air-free conditions, in CD_2Cl_2 or $CDCl_3$, and at 298 or 323 K. The solutions did not change color, and no products were observed by ${}^1H$ NMR. $SiMe_4$ is similarly unreactive. Hexamethyldisilane ($Me_3SiSiMe_3$) does react with $OsO_4({}^tBupy)$. After 24 h at 298 K in CD_2Cl_2, three new Si*Me* resonances were observed in the ${}^1H$ NMR spectrum. These product(s) have not been identified ($Me_3SiOSiMe_3$ was not present).

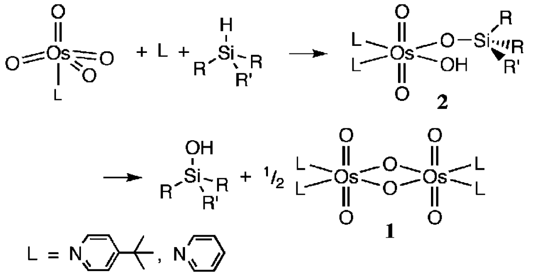
V. Computational Studies. The reactions of OsO_4 with SiH_4 and Me_3SiH were studied at the B3LYP level of DFT. The methodology was essentially the same as that used in our previous study of the reaction of OsO_4 with H_2.[14] Details are given at the end of the Experimental Section. Computed gas-phase reaction energies and enthalpies at 298 K are shown in Table 3, and optimized geometries and absolute energies in hartrees are given in the Supporting Information.

The [3 + 2] additions of $H_3Si{-}H$ and $Me_3Si{-}H$ to OsO_4 in the gas phase are predicted to be very exothermic and to proceed with low barriers. For Me_3SiH, $\Delta H^{\ddagger} = 4.0$ kcal mol^{-1}.

The addition of an Si−H bond in a [2 + 2] fashion across an Os═O bond can occur in two different orientations, to make a hydride-siloxide $Os(O)_3(H)(OSiR_3)$ or a silylhydroxide $Os(O)_3(OH)(SiR_3)$. The formation of both types of [2 + 2] addition products is computed to be enthalpically much less favorable than the formation of the [3 + 2] addition products. Consequently, the barriers calculated for the formation of the [2 + 2] addition products are much higher than the barriers calculated for the formation of the [3 + 2] addition products.[25]

Discussion

OsO_4(L) complexes rapidly oxidize the Si−H bond in tertiary silanes, forming a siloxide intermediate, which decays to silanol and the Os^{VI} μ-oxo dimers **1a** or **1b** (eq 3). At ~100 mM concentrations, silane oxidation is complete within minutes at 200 K. This is a quite rapid oxidation of a σ bond, particularly since OsO_4 is predominantly known for its oxidations of π bonds.[26] These results extend previous experimental and computational studies of H−H and C−H σ-bond oxidations by OsO_4[12,14] and RuO_4.[8,11,13] Non-tertiary silanes, boranes, and ${}^nBu_3SnH$ also react rapidly with OsO_4(L), but the osmium is apparently reduced beyond Os^{VI} and a complex mixture of oxidation products is formed. Similar over-reduction apparently occurs when tertiary silanes are present in excess over OsO_4, which would appear to limit the catalytic applications of these reactions. OsO_4(L) reacts slowly with $Me_3SiSiMe_3$ (1 day at 298 K), and no reaction has been observed with Me_4Si or alkanes in CD_2Cl_2 solution.



(3)

All of the OsO_4(L) + R_3SiH reactions proceed via an intermediate (**2**), which is the product of net [3 + 2] addition of the Si−H bond across an O═Os═O unit and the binding of a second pyridine ligand (eq 3). Such an intermediate has been suggested in H−H and C−H oxidations by OsO_4(L)

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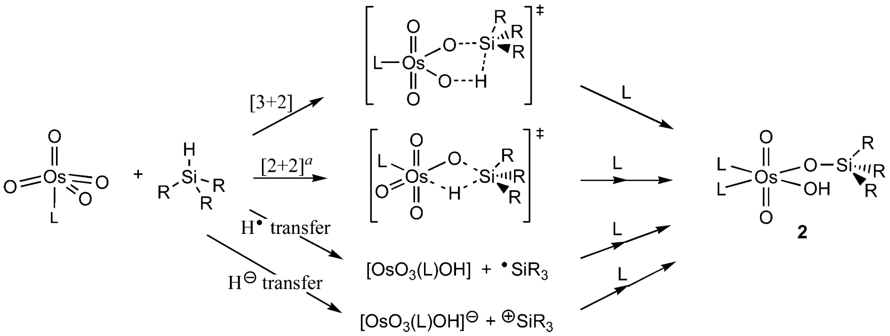
[24] Binstead, R. A.; Zuberbühler, A. D.; Jung, B. *Specfit*, version 3.0.36 (32-bit Windows); Spectrum Software Associates: Chapel Hill, NC, 2004.

[25] Our previous study found that the kinetic and thermodynamic preference for [3 + 2] over [2 + 2] product formation was similar for both OsO_4 and OsO_4(L),[14] so we did not perform calculations on OsO_4(L) reactions for this study.

[26] (a) References 10 and 18. (b) OsO_4 oxidations of C−H bonds in alcohols and amines are thought to involve prior coordination of the substrate: (c) Toyoshima, K.; Okuyama, T.; Fueno, T. *J. Org. Chem.* **1980**, *45*, 1600−1604. (d) Singh, H. S.; Singh, V. P.; Pande, D. P. *Chem. Scr.* **1977**, *12*, 166−170.

Scheme 1. Mechanisms of Silane Oxidation by $OsO_4(L)$



and RuO_4 but had not previously been observed.[8,11−14] It is more easily observed in this system because of the rapid initial reaction, whereas the H−H and C−H additions are slower than the decay of the intermediate. DFT calculations show that the [3 + 2] addition of R_3Si-H bonds to OsO_4 is very exothermic: $\Delta H° = -60$ kcal mol^{-1} for R = Me. This is perhaps not surprising, since silanes are thermodynamically strong reducing agents and OsO_4 is a good oxidant.

The key mechanistic question is how the intermediate is formed. Following Collman et al.[13a] and our previous study of H_2 addition,[14] four types of pathways can be envisioned (Scheme 1). The Si−H bond could be cleaved by hydrogen atom abstraction, hydride transfer, or [2 + 2] or [3 + 2] mechanisms.[5,6b,8,11,16,27−30] Very recently, ozonation of Si−H bonds has been suggested to occur by a 1,3-dipolar insertion mechanism closely related to the [3 + 2] pathway.[27]

H-atom transfer, to make the $\bullet SiR_3$ radical, is a common reaction of silanes;[28] and many metal-oxo complexes are good H-atom abstractors.[5a] However, the observation that the reactions are unaffected by CCl_4 solvent or the presence of CBr_4 rules out this pathway. $Et_3Si^\bullet$ reacts with CCl_4 to make Et_3SiCl at close to the diffusion limit: $k = (4.6 \pm 0.8) \times 10^9$ M^{-1} s^{-1}.[29] If $Et_3Si^\bullet$ were formed in these reactions, Et_3SiCl would have to be formed because a ≤0.1 M osmium species could not react faster than 10 M CCl_4.

The hydride transfer pathway involves charge separation at the transition state and forms charged intermediates such as silyl cations.[2a,30] This path should therefore be very sensitive to solvent polarity.[2b,14,31] However, the rate of formation of the intermediate is not discernibly different in CD_2Cl_2, acetone, or toluene at 200 K. This indicates that hydride transfer is an unlikely mechanism.

The [2 + 2] and [3 + 2] pathways are often difficult to distinguish experimentally, as evidenced by the extensive debate over the mechanism of alkene oxidation by $OsO_4(L)$.[9,10] Toste et al. observed a hydride intermediate by ^1H NMR (δ_{ReH} 6.60) in the reaction of silanes with $Re^V(O)_2I(PPh_3)_2$, and in part on that basis suggested a [2 + 2] mechanism of silane addition to an Re═O unit.[15,16] In the chemistry reported here, the observed intermediate is the product of [3 + 2] addition, but this could be formed by [2 + 2] addition and 1,2-hydride migration.[8−16]

DFT calculations have been quite definitive in distinguishing [2 + 2] vs [3 + 2] mechanisms, for both alkene and σ-bond oxidations.[9,11−14] On this basis, the previous studies of H−H and C−H bond oxidations by OsO_4 and RuO_4 were suggested to proceed via [3 + 2] pathways. DFT calculations are similarly definitive for the oxidations of silanes described here. $\Delta H^\ddagger$ for [3 + 2] addition of Me_3Si-H to OsO_4 is computed to be 4 kcal mol^{-1} whereas the most favorable [2 + 2] pathway has $\Delta H^\ddagger = 34$ kcal mol^{-1}. The low barrier calculated for the [3 + 2] path is consistent with the observations of silane oxidation by osmium tetroxide within minutes at 200 K. For R_3SiH and $OsO_4(L)$ in CD_2Cl_2, the rough estimate of $k \approx 10^{-1}$ M^{-1} s^{-1} implies $\Delta G^\ddagger \approx 12$ kcal mol^{-1}. $OsO_4(L)$ likely reacts by a [3 + 2] path because it is strongly oxidizing and has four oxo groups, whereas the rhenium(V) complexes examined by Toste and Abu-Omar may use the redox-neutral [2 + 2] addition because they are not very oxidizing and have only one or two oxo groups.[15,16]

Conclusions

The reaction of $OsO_4(L)$ (L = 4-^{t}Bupy, py) with tertiary silanes produces silanols and the osmium(VI) dimers $[Os(O)_2L_2]_2(\mu\text{-}O)_2$ (**1**). This extends the known σ-bond oxidation reactivity of OsO_4 from H−H and C−H to Si−H bonds. B−H, Sn−H, and Si−Si bonds were also observed to be reactive. Many of these reagents, including R_3SiH when it is in excess, appear to further reduce the Os^{VI} product, which limits the utility of this $OsO_4(L)$ oxidation of silanes. When $OsO_4(^tBupy)$ is used, Et_3SiH and $PhMe_2SiH$ are quantitatively converted to Et_3SiOH and $PhMe_2SiOH$, respectively. The silanol yields are significantly lower (∼50%) when pyridine is the supporting ligand, apparently due at least in part to coprecipitation of Os^{VIII} with $[OsO_2(py)_2]_2(\mu\text{-}O)_2$.

$OsO_4(L)$ reacts with R_3SiH within minutes at 200 K to form an intermediate, $L_2Os(O)_2(OSiR_3)(OH)$ (**2**), which is the product of net [3 + 2] addition of an Si−H bond to an O═Os═O group followed by addition of a second ligand (eq 3). Mechanistic studies rule out H$^\bullet$ and H$^-$ transfer as the Si−H bond cleaving step, since silyl radicals are not trapped by CCl_4 or CBr_4 and the reactions do not proceed

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(28) (a) Chatgilialoglu, C. *Organosilanes in Radical Chemistry: Principles, Methods and Applications*; Wiley: New York, 2004. (b) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

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(30) (a) Carey, F. A.; Tremper, H. S. *J. Am. Chem. Soc.* **1968**, *90*, 2578. (b) Whitmore, F. C.; Pietrusza, E. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1947**, *69*, 2108.

(31) Stewart, R. *J. Am. Chem. Soc.* **1957**, *79*, 3057−3061.

faster in more polar solvents. Gas-phase DFT calculations indicate that the [3 + 2] additions of silanes to OsO_4 are very exothermic and proceed with very small barriers. In contrast, [2 + 2] additions are computed to have high barriers and to be roughly thermoneutral. The computational results, together with the mechanistic experiments, implicate a [3 + 2] mechanism for silane oxidation by osmium tetroxide.

Experimental Section

***Caution**! OsO_4 is volatile, a strong oxidant, and highly toxic. It is very hazardous to eyes, lungs, and skin and should be handled with great care.*

OsO_4 (Colonial Metals) was sublimed before use. Pyridine and 4-^{t}butylpyridine (Aldrich) were dried over CaH_2 and vacuum-transferred before use. CH_2Cl_2 was dried using a Seca Solvent System (GlassContour).[32] Silanes, silanols, Et_3SiCl, $PhMe_2SiCl$, Bu_3SnH, 9-BBN, pinacolborane, hexamethyldisilane, protio solvents (Aldrich, ACRŌS organics, or Fisher), and deuterated solvents (Cambridge Isotope Laboratories) were used as received. $PhMe_2SiD$ was prepared from $PhMe_2SiCl$ and excess $LiAlD_4$.[33] Reactions were conducted under air in Norell XR-55 thin-walled NMR tubes unless otherwise stated. Solution transfers typically used VWR pipettors.

^1H NMR spectra were acquired on a 500 MHz Bruker spectrometer (for kinetics) or on a DRX 499 spectrometer (for spectra at 200−250 K). Spectra are reported as chemical shift, δ (multiplicity, J_{HH}, no. protons) relative to TMS by referencing the residual solvent peak. IR spectra were recorded on Perkin-Elmer 1720 or Bruker Vector 33 FT-IR spectrophotometers, with KBr pellets or CH_2Cl_2 solutions, and are reported in cm^{-1}. GC-MS data were acquired on a Hewlett-Packard 5971A/5890, with identification using both Wiley07 and NIST05 libraries. UV−vis spectra were acquired at room temperature in a capped 1 cm path quartz cell using a Hewlett-Packard 8453 UV−vis spectrophotometer. Elemental analysis was performed by Atlantic Microlab, Inc.

K_1 for OsO_4(L). A 3 mL cuvette was charged with 40 μL of an OsO_4 solution (64.2 mg in 5 mL CH_2Cl_2) and 2.96 mL of CH_2Cl_2 ($[OsO_4] = 0.673$ mM). After an initial spectrum ($\lambda_{max} = 320$ nm), py was added in microliter increments and UV−vis spectra were acquired until the maximum absorbance was reached. Half of the absorbance change occurred at [py] = 38.5 mM. The experiment was repeated at $[OsO_4] = 6.73$ mM. Plots of $(A - A_0)/(A_{max} - A_0)$ vs free [py] (M) gave straight lines indicating $K_{eq} = 26 \pm 3$ M^{-1} for OsO_4(py). Similar titrations were done for ^{t}Bupy with $[OsO_4]$ = 0.773, 3.87, 7.73, and 64.5 mM in CH_2Cl_2, yielding $K_1 = 166 \pm 20$ M^{-1}.

$[OsO_2(^t\mathrm{Bupy})_2]_2(\mu\text{-}O)_2)$ (1a). A vial was charged with 100 μL of an OsO_4(^{t}Bupy) solution (41.5 mg OsO_4, 0.163 mmol, 163.3 mM; 100 μL of ^{t}Bupy, 0.676 mmol, 677 mM in 1 mL CH_2Cl_2) and then 66 μL of a $PhMe_2SiH$ solution (0.1685 g $PhMe_2SiH$, 1.24 mmol, 0.247 M in 5 mL of CH_2Cl_2). After 2 h at 298 K and standing overnight at ∼248 K, a brown precipitate formed, which was isolated by decanting the mother liquor and drying under a stream of N_2 while still cold. ^1H NMR (CD_2Cl_2): 8.73 (d, 6.5 Hz, 2H, py), 7.42 (d, 6.5 Hz, 2H, py), 1.31 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 292.1, 149.2, 122.3 (py); 35.26 (CMe$_3$); 30.85 (CMe_3). IR (CH_2Cl_2): 840 (ν Os═O), 693 (ν μ-O). Elemental Anal. (C, H, N) Calcd: 42.5, 5.12, 5.51. Found: 42.9, 5.24, 5.51.

OsO_4(py) + py + Et_3SiH. These reactions in CD_2Cl_2 deposited a precipitate which was identified as in large part $[OsO_2(py)_2]_2(\mu\text{-}O)_2$ (**1b**) by comparison with an authentic sample.[17] ^1H NMR (CD_3OD): 8.77 (m, 2H, 6.5 Hz), 7.94 (m, 1H, 6.5 Hz), 7.53 (m, 2H, 6.5 Hz). IR (KBr) : 875 (m), 835 (s, O═Os═O), 645, 447 (s, $Os_2(\mu\text{-}O)_2$). IR for **1b** from OsO_4(py) + py + EtOH[17] (KBr): 875 (m), 833 (s), 640 (s), 445 (s).

OsO_4(^{t}Bupy) + $PhMe_2SiH$. An NMR tube was charged with 400 μL of a 117 mM OsO_4 solution (0.1488 g, 0.585 mmol in 5 mL CD_2Cl_2) and 20 μL of ^{t}Bupy (to make a 322 mM solution). ^1H NMR (200 K): 8.36 (d, 6.0 Hz, 2H, py), 7.35 (d, 6.0 Hz, 2H, py), 1.22 (s, 9H, ^{t}Bu), 4.0 (s, 2H, H_2O). $PhMe_2SiH$ (29 μL of a cooled solution, 0.2450 g in 5 mL CD_2Cl_2, 1.798 M) was added to the NMR tube at 77 K. The mixture was thawed, shaken, and reinserted into the spectrometer. A ^1H NMR spectrum was acquired after 2 min, followed by $^{13}C\{^1H\}$ NMR and COSY spectra.[22] A subsequent EXSY spectrum[22] at 250 K indicated exchange between peaks at δ 8.2 (s) and 2.8 (s) with $k = 80$ s^{-1} ($EXSY_{calc}$).[34] **1a** formed during the acquisition of the NMR spectra. After 24 h at room temperature, the yield of $PhMe_2SiOH$ was 100 ± 2% by integration vs a calibrated capillary standard (Me_4Si in CD_2Cl_2). Spiking with an authentic sample confirmed the identity of $PhMe_2SiOH$.

NMR spectra of $OsO_2(^t\mathrm{Bupy})_2(OSiMe_2Ph)(OH)$ (2a) (in the presence of ^{t}Bupy, from the procedure above): ^1H NMR (CD_2Cl_2, 200 K): 8.44 (d, 6.5 Hz, 2H, py), 8.41 (d, 6.5 Hz, 2H, py), 7.37 (d, 7.0 Hz, 2H, py), 7.22 (d, 6.0 Hz, 2H, py), 1.25 (s, 18H, ^{t}Bu), 7.42 (d, 7.5 Hz, 2H, Ph), 7.34 (m, 1H, Ph), 7.15 (m, 2H, Ph), 0.124 (s, 6H, $Si(CH_3)_2$), 8.1 (OsOH); also, 2.8 (s, H_2O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 200 K): 165.7, 165.0, 149.5, 149.3, 122.8, 122.6 (py); 34.85, 34.73 (CMe$_3$); 30.16, 30.12 (CMe_3); 142.6, 134.0, 128.5, 127.4 (PhMe$_2$Si); −3.9 (PhMe_2Si).

Other ^1H NMR reactions followed the procedure above and are described in the Supporting Information. The ^1H NMR yields of Et_3SiOH and $^iPr_3SiOH$ were verified by GC/MS using a calibration curve.

$Os(O)_2(py)_2(OSiEt_3)(OH)$ (2b). OsO_4 (21.1 mg, 83 μmol, 16 mM), and py (14 μL, 173 μmol, 35 mM) in 5 mL of pentane was cooled to ∼200 K, and a separate cooled solution of Et_3SiH (14 μL, 88 μmol, 18 mM) in 5 mL pentane was added dropwise over 1 h. The fluffy pink material that formed was isolated by decanting the excess pentane and drying with N_2. ^1H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$ (250 K) and CD_2Cl_2 (200 K) were identical within 0.01 ppm to those observed for **2b** from OsO_4(py) + Et_3SiH. A ^1H EXSY spectrum[22] at 230 K showed exchange between the singlet at δ 8.2 ppm and the H_2O peak at δ 2.1 ppm.

Kinetics of OsO_4(^{t}Bupy) + $PhMe_2SiH$. Following the procedure above, reactions of OsO_4 (119−122 mM), ^{t}Bupy 731 mM), and $PhMe_2SiH$ (119−122 mM) in CD_2Cl_2, $(CD_3)_2CO$, and $C_6D_5CD_3$ were monitored by ^1H NMR at 200 K. Initial rates of formation of **2a** were $(7 \pm 3) \times 10^{-4}$ M s^{-1}, $(8 \pm 2) \times 10^{-4}$ M s^{-1}, and $(9 \pm 3) \times 10^{-4}$ M s^{-1}, respectively, derived from the integrals for PhMe_2Si vs those of a TMS capillary. The reactions were warmed to 298 K in the spectrometer and monitored for 1 h. Plots of 1/[**2a**] vs time were linear, yielding $k = 0.028 \pm 0.009$, 0.031 ± 0.008, and 0.026 ± 0.009 M^{-1} s^{-1}, respectively. A separate set of eight NMR experiments monitored the decay of **2a**, using 8.4−25 mM OsO_4 in 400 μL of CD_2Cl_2 (using a stock solution of 0.1488 g OsO_4 in 5 mL of CD_2Cl_2) and ^{t}Bupy (60 μL, 863 mM). After the initial ^1H NMR spectra were obtained, 10 μL of $PhMe_2SiH$ was added to

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each tube ([$PhMe_2SiH$] = 136 mM) and 100 spectra were acquired over ~100 min. Plots of 1/[**2a**] vs *t* yielded $k_d = 0.025 \pm 0.01$ $M^{-1}s^{-1}$. UV−vis kinetic data were obtained similarly ([Os] = 2.25−37.9 mM) and fitted to a 2A → B model with *Specfit*,[24] yielding $k_d = 0.030 \pm 0.007$ M^{-1} s^{-1}.

Crystal Structure of [$OsO_2(^tBupy)_2]_2(\mu\text{-}O)_2$ (1a). A single crystal of **1a** was obtained from a reaction of $OsO_4(^tBupy)$ and $PhMe_2SiH$ in CH_2Cl_2 at 273 K and was mounted with paratone-*N* oil (Exxon). X-ray data acquired at −143 °C had $R_{int} = 0.118$, indicating that the data were of less than average quality (av. = 0.07). The low crystal quality may be due to loss of some of the CH_2Cl_2 of crystallization, as there are six such molecules in the unit cell, or to an unresolved twinning. Indexing and unit cell refinement indicated space group $P2_1/c$ (No. 14). The data were integrated and scaled using *hkl-SCALEPACK*. Solution by direct methods (*SIR97*) produced a complete heavy-atom phasing model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares analysis. All hydrogen atoms were located using a riding model. To complete the refinement of this noisy data, the thermal parameters were constrained to positive values for atoms O1, C5, C14, C17, C23, C27, C29, C38, and C39 (with 6 per atom, there were 54 restraints).

Computational Methodology. Using *Gaussian03*,[35] DFT at the Becke3LYP (B3LYP) level[36] was used to optimize the geometries of all compounds. The effective core potentials of Hay and Wadt with a double-valence basis set (LanL2DZ)[37] were used to describe the Os atom,[38] whereas the 6-31+G(d,p) basis set[39] was used for all other atoms. Vibrational frequencies were calculated for all stationary points, to verify whether each was a minimum (NIMAG = 0) or a transition state (NIMAG = 1) on the potential energy surface. The wavefunctions for all calculated species were checked for stability, with respect to the unrestricted (UB3LYP) wave functions.

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Supporting Information Available: Crystallographic data for **1a**, additional ^1H NMR experiments, IR spectra, and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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