Dihydroxylation of Alkenes using a Tp-Osmium Complex

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Dedicated to Jerry Trofimenko for his inspiration and enthusiasm, and for the Tp ligands.

Abstract

The reaction of $TpOs^{VI}(N)(OH)_2$ (**1**) [Tp = hydrotris(1-pyrazolyl)borate], *m*-chloroperbenzoic acid (*m*-CPBA), and *trans*-stilbene in C_6H_6 at room temperature gives the *trans*-diolate complex $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**) and *m*-chlorobenzoic acid (*m*-CBA). The *trans* configuration of the stilbene is retained in the diolate complex as shown in the crystal structure of **2**. Mechanistic studies rules out oxidation of **1** by *m*-CPBA to form $TpOs^{VIII}(N)(O)_2$, an Os^{VIII} intermediate, which subsequently reacts with *trans*-stilbene to form **2**. The reaction likely proceeds by a pre-equilibrium formation of a hydrogen bonding adduct between **1** and *m*-CPBA, which then reacts with *trans*-stilbene to give **2**. Adding 2 equiv of HCl to **2** in CD_2Cl_2 hydrolyzes to give *rac*-hydrobenzoin, a *cis*-diol and $TpOs^{VI}(N)Cl_2$. Other olefins such as *cis*-stilbene, styrene, cyclohexene, *trans*-dimethyl fumarate, *trans*-methyl cinnamate, and *trans*-4-dimethylamino-4′-nitrostilbene are converted to their corresponding free diol products under **1**/*m*-CPBA/HCl conditions in CD_2Cl_2. In aqueous HBF_4, oxidation of the water soluble olefin, 4-styrenesulfonic acid, by **1** is modestly catalytic (15 turnovers in 3 h) with excess PbO_2 as the oxidant. Under non-acidic conditions, the diolate complexes are inert and catalysis is precluded.

Keywords: Osmium; Oxidation; Hydroxide; Alkene; Dihydroxylation

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1. Introduction

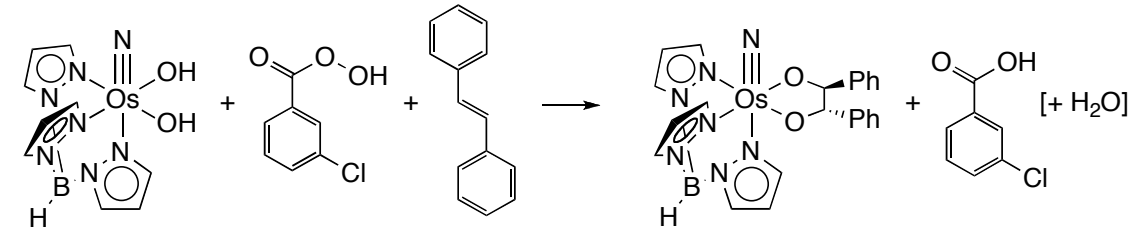
Metal-catalyzed olefin oxidations are important reactions, from the chiral *cis*-dihydroxylation by ligated osmium tetroxide ($Os^{VIII}O_4(L)$) to catalysts in the *cis*-dihydroxylation of olefins [1] to epoxidations with hydrogen peroxide over titanium silicalite TS1 [2] and many other processes [3]. While many metal systems accomplish olefin oxidations of various kinds, there are few examples of dihydroxylation and there has been much discussion of possible mechanistic pathways [4]. For the reaction of $OsO_4(L)$ with alkenes to give Os^{VI} diolates, experimental and theoretical studies indicate a concerted *[3+2]* mechanism involving a pericyclic direct addition of the alkene to an O=Os=O unit, a *[3+2]* pathway, rather than *[2+2]* addition to one Os=O bond to form an osmaoxetane followed by rearrangement [5,6,7,8]. The Os^{VI} diolate complex is then hydrolyzed to release the diol product and form Os^{VI} hydroxide species (osmate), which is then re-oxidized to regenerate the Os^{VIII} active catalyst.

We have been studying the oxidation chemistry of osmium compounds with a Tp ligand [Tp = hydrotris(1-pyrazolyl)borate] [9,10,11]. As part of these studies, we reported a Tp-Os^{VI} bis-hydroxide complex $TpOs^{VI}(N)(OH)_2$ (**1**) [12] that has the same osmium bis-hydroxide motif as osmate. Complex **1** is prepared from the known dichloride complex $TpOs^{VI}(N)Cl_2$ [9], with initial chloride metathesis to acetate using AgOAc to yield $TpOs^{VI}(N)(OAc)_2$ [10]. This is a rare example of a reaction of $TpOs^{VI}(N)Cl_2$ that does not occur at the electrophilic nitrido ligand [9,10,13]. Further reaction of $TpOs^{VI}(N)(OAc)_2$ with NaOH affords the bis-hydroxide complex **1**, by direct substitution of the acetates with hydroxides [12]. Complex **1** was prepared with the goal of oxidizing it to an Os^{VIII} species such as "$TpOs(N)O_2$". This paper presents our exploration of the oxidation chemistry of **1**, in particular the oxidations of olefins with **1** and *m*-chloroperbenzoic acid (*m*-CPBA) to give osmium(VI) diolate complexes. Some mechanistic studies are presented, which indicate that a reactive osmium species is responsible for the oxidation but the data do not support the intermediacy of "$TpOs(N)O_2$", in contrast with a very claim made by two of us some time ago [14].

2. Results and discussion

2.1. Synthesis and characterization of TpOs^{VI}(N)(trans-O$_2$C$_2$H$_2$Ph$_2$) (2)

Stirring TpOs^{VI}(N)(OH)$_2$ (**1**) with 1 equiv each of *m*-chloroperbenzoic acid (*m*-CPBA) and *trans*-stilbene in C_6H_6 at room temperature for 5 min yields *m*-chlorobenzoic acid (*m*-CBA) and the orange-red *trans*-diolate complex TpOs^{VI}(N)(*trans*-O$_2$C$_2$H$_2$Ph$_2$) (**2**) (Eq. (1)). Complex **2** is isolated in 95% yield using silica gel chromatography. *Trans*-stilbene oxidation occurs with retention of the *trans*-diolate configuration in **2** as revealed by ^{1}H NMR, which shows two different diolate protons (δ5.40, 5.48 in CD_2Cl_2) and nine pyrazole resonances (δ6.11–8.19), indicating that **2** has C_1 symmetry. This is in contrast with the related complexes TpOs^{VI}(N)X$_2$ (X = Cl, OAc, or OH), which show C_s symmetry, with six pyrazole peaks in a 2:2:2:1:1:1 ratio in the ^{1}H NMR [9,10,12]. It should be noted that under the conditions of reaction 1, the oxidation of *trans*-stilbene by *m*-CPBA alone is very slow.[OK@? Can we say something stronger?]



TpOs(N)(OH)$_2$ (**1**) *m*-CPBA TpOs(N)(O$_2$CH$_2$Ph$_2$) (**2**) *m*-CBA (1)

Crystals of **2** were grown from CH_2Cl_2/hexanes solutions, and the structure was solved by direct methods. The ORTEP of **2** is shown in Fig. 1, and the metrical parameters are shown in Tables 1 and 2 (See Section 4.4 for selected crystallographic data). The ORTEP of **2** shows a distorted octahedral molecule with all of the ligands bent away from the nitrido N(7), typical of complexes with a single nitrido or oxo group [15]. The Os≡N distance of 1.680(8) Å is within the 1.602(20)–1.70(2) Å range of such bond lengths in TpOs^{VI}(N)X$_2$ complexes (X = Cl, Me, Ph, O_2CCF_3, NO_3, or OH) [9a,10,12]. The Os–O distances in **2** (1.940(6) and 1.946(6) Å) are quite similar to those of **1** (1.956(7) and 1.941(8) Å) [12].

[Ahmad: Weren't there a variety of oxidants that would work to convert **1** to **2**? I seem to recall your using OsO_4, MnO_4^-, any others? Are they in your thesis?@]

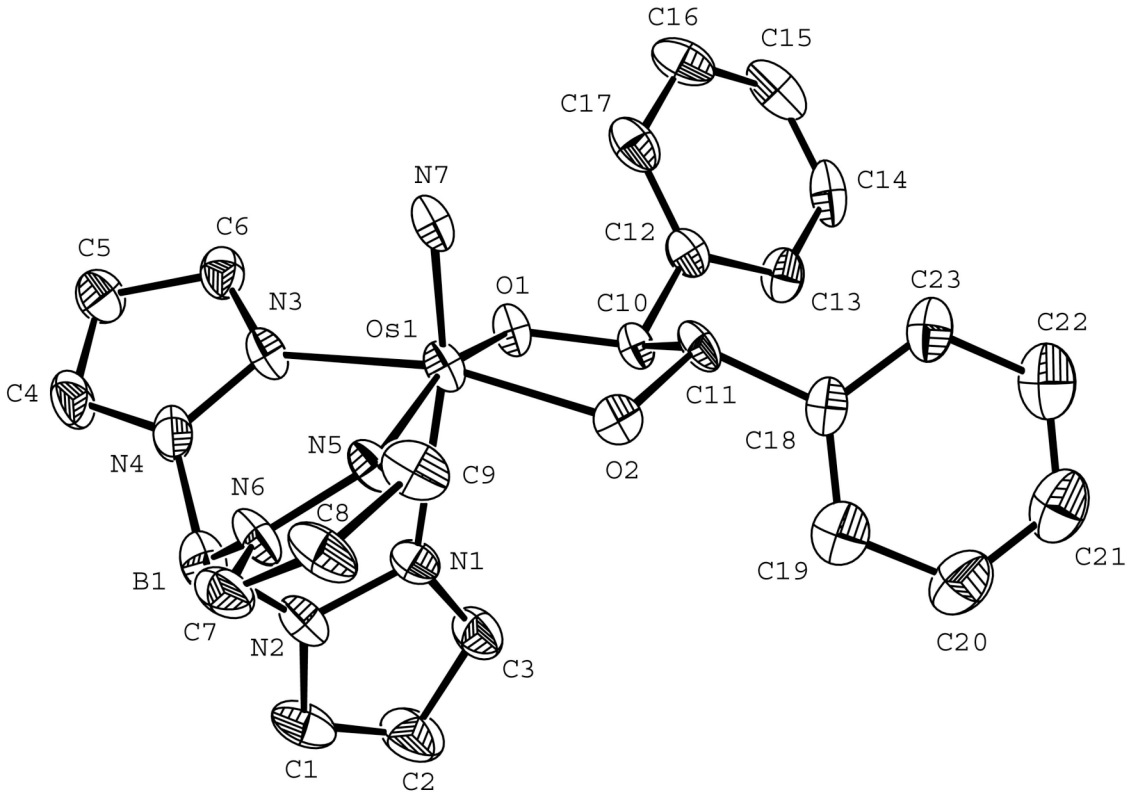


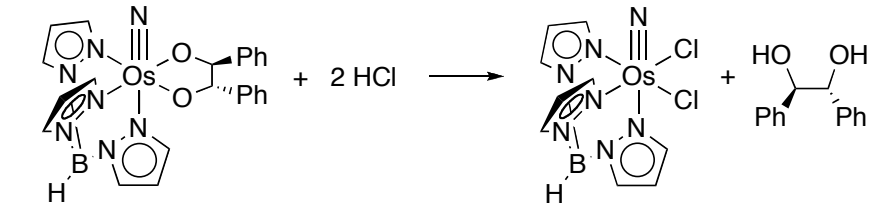
Fig. 1. ORTEP of $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**). Thermal ellipsoids are drawn at 30% probability level, and hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths and angles for $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**).

Bond	Length (Å) or Angle (˚)	Bond	Length (Å) or Angle (˚)
Os(1)–N(1)	2.296(8)	Os(1)–O(1)	1.946(6)
Os(1)–N(3)	2.084(8)	Os(1)–O(2)	1.940(6)
Os(1)–N(5)	2.080(8)	Os(1)≡N(7)	1.680(8)
N(3)–Os(1)–N(1)	78.2(3)	O(1)–Os(1)–N(1)	85.6(3)
N(5)–Os(1)–N(1)	78.2(3)	O(2)–Os(1)–N(1)	86.1(3)
N(3)–Os(1)–N(5)	91.2(3)	O(1)–Os(1)–N(3)	89.7(3)
N(1)–Os(1)–N(7)	166.1(3)	O(2)–Os(1)–N(3)	162.9(3)
N(3)–Os(1)–N(7)	93.3(3)	O(1)–Os(1)–N(5)	163.2(3)
N(5)–Os(1)–N(7)	91.2(3)	O(2)–Os(1)–N(5)	92.1(3)
O(1)–Os(1)–O(2)	82.3(3)	O(1)–Os(1)–N(7)	105.5(3)
		O(2)–Os(1)–N(7)	103.4(3)

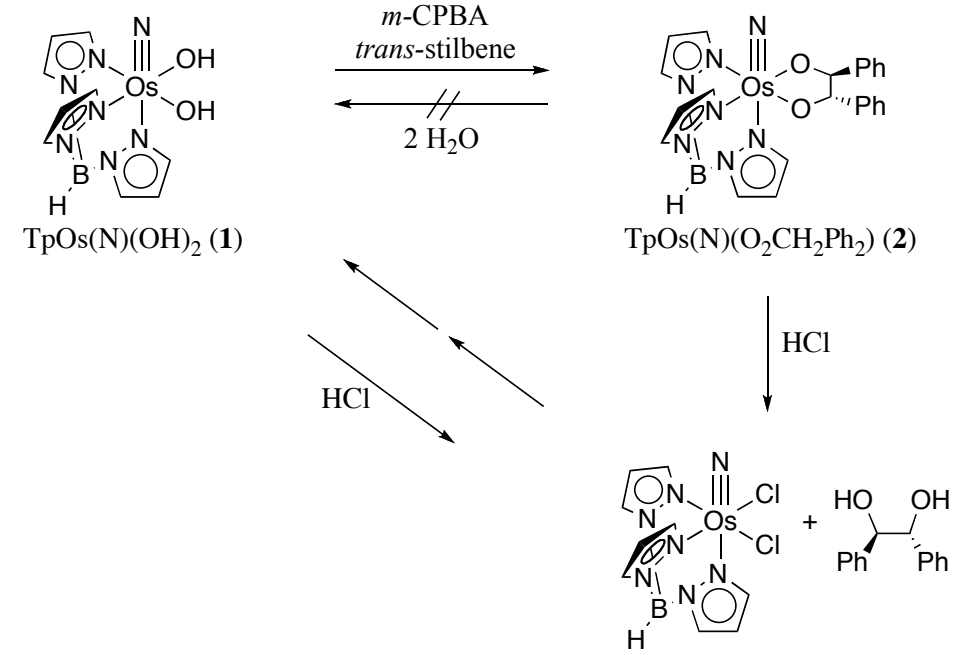
*2.2. The reaction of TpOs^{VI}(N)(trans-$O_2C_2H_2Ph_2$) (**2**) with HCl*

The reaction of **2** with 2 equiv of HCl in CD_2Cl_2 yields the Os^{VI} nitrido-dichloride complex TpOs^{VI}(N)Cl_2 [9], and *rac*-hydrobenzoin ([Eq. 2]), as observed by ^{1}H NMR [@How was *rac*-hydrobenzoin characterized?]. *Rac*-hydrobenzoin is the product of *cis*-dihydroxylation of *trans*-stilbene. Removal of the diolate requires strongly acidic conditions; no reaction is observed between **2** and H_2O in the absence of acid. In the presence of a variety of acids HX with coordinating anions, the bis(acetate) complex TpOs^{VI}(N)$(OAc)_2$ is converted to TpOs^{VI}(N)X_2 [10]. The hydroxide and diolate complexes appear to react similarly. Thus catalytic oxidations could not be simply achieved by adding H_2O, as described in Scheme 1; see Section 2.4 below.



TpOs(N)($O_2CH_2Ph_2$) (**2**) *rac*-hydrobenzoin (2)

Scheme 1.



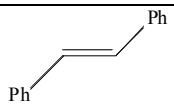
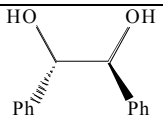
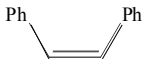
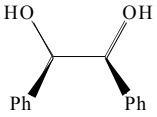
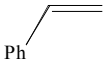
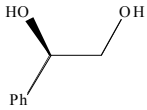
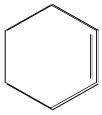
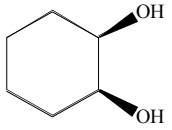
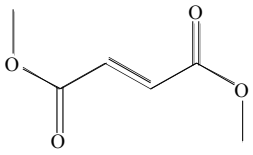
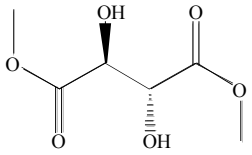
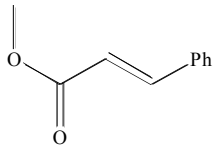
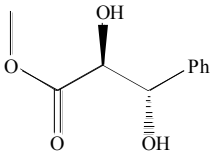
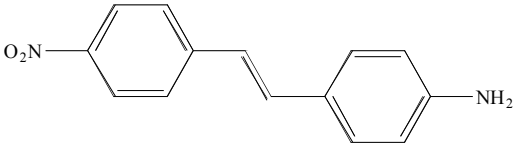
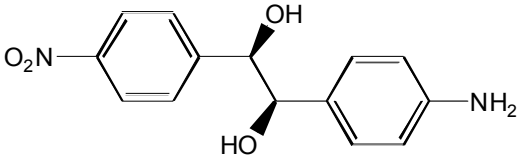
TpOs(N)$(OH)_2$ (**1**) TpOs(N)($O_2CH_2Ph_2$) (**2**)

2.3. Reactions with other olefins

The reaction of **1** with *m*-CPBA and other olefins also forms their corresponding diolate complexes. For example, reacting **1** with 1 equiv each of *m*-CPBA and *cis*-stilbene in CD_2Cl_2 gives $TpOs^{VI}(N)(cis\text{-}O_2C_2H_2Ph_2)$ (**3**). ^1H NMR spectra of the reaction show that **3** is a roughly 1:1 mixture of two diastereotopic diolate products. Twelve pyrazole resonances are observed, in two sets of the characteristic peaks for C_s symmetry of the Tp compounds: 2 doublets + 1 triplet of intensity 2 plus 2 doublets + 1 triplet of intensity 1. The isomers have the phenyl substituents are on the same or opposite side of the diolate ring as the nitrido ligand. Addition of 2 equiv of HCl gives $TpOs^{VI}(N)Cl_2$ and *meso*-hydrobenzoin (by ^1H NMR@?).

The same reactivity as for the stilbenes is observed with other alkenes. *Trans*-alkenes give a single diolate isomer, while *cis*- and unsymmetrical alkenes give mixtures of diolate products.[Ahmad: OK?@] After treatment with HCl, styrene and cyclohexene are converted to their *cis*-dihydroxylated products, and the reaction proceeds well even with an dimethylaniline substituent, with *trans*-4-dimethylamino-4′-nitrostilbene (Table 2).[The text here and the first column of Table 3 refer to this as the "dimethylamino" but the drawings in the Table and the name in the second column indicate just the NH_2 compound. Ahmad: do you recall? Rebecca: can you tell and fix the text/drawings?@] The electron deficient olefins *trans*-dimethyl fumarate and *trans*-methyl cinnamate are also converted to their corresponding free diol products with **1**/*m*-CPBA/HCl conditions in CD_2Cl_2.

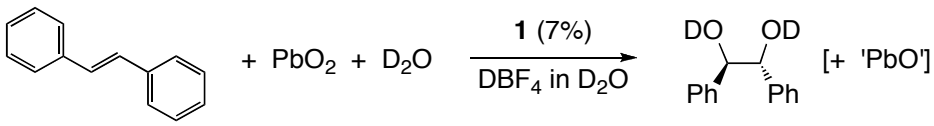
Table 3. *Cis*-dihydroxylation of olefins by $TpOs^{VI}(N)(OH)_2$ (**1**) + *m*-CPBA, then HCl, in CH_2Cl_2.

Olefin Substrates	*Cis*-diol Products
 *trans*-stilbene	 *rac*-hydrobenzoin
 *cis*-stilbene	 *meso*-hydrobenzoin
 stilbene	 *rac*-1-phenylethylene glycol
 cyclohexene	 *meso*-cyclohexane-1,2-diol
 *trans*-dimethyl fumerate	 *rac*-dimethyl 2,3-dihydroxysuccinate
 *trans*-methyl cinnamate	 *rac*-methyl 2,3-dihydroxy-3-phenylpropanoate
 *trans*-4-dimethylamino-4'-nitrostilbene	 (*R,S*)- and (*S,R*)-1-(4-aminophenyl)-2-(4-nitrophenyl)ethane-1,2-diol

[why is the drawing of the last product so different from all the other drawings?@]

2.4. Catalytic oxidation of olefin to cis-diol in aqueous acidic media

The formation of the *cis*-diol from its corresponding olefin by **1**/*m*-CPBA/HCl in CD_2Cl_2 is stoichiometric. To complete a catalytic cycle for alkene dihydroxylation requires hydrolysis of the diolate back to the bis-hydroxide complex (Scheme 1), which we have been unable to achieve by adding acids in organic solvents. Catalysis has been achieved in acidic aqueous solutions, using the non-coordinating acid HBF_4. A solution of 1 mM **1** in 100 mM HBF_4 (pH ~1) with excess PbO_2 solid (50 mg) in D_2O, quantitatively converted 15 mM 4-styrenesulfonic acid sodium salt (15 mM) to the corresponding free *cis*-diol (15 turnovers) over 3 h at room temperature (eq 3). This oxidation can also be accomplished with *m*-CPBA.[true@? This seems to be implied by the next sentences.] When more olefin is present than oxidizing equivalents, the catalytic reaction continues until all of the oxidant is consumed, and the solution containing **1**, olefin, diol, and *m*-CBA is stable. When there is more oxidant (*m*-CPBA) than olefin, however, once all of the olefin had been converted to *cis*-diol decomposition of **1** is observed, forming unidentified pyrazole products. Apparently **1** is decomposed by its slow oxidation by *m*-CPBA, as discussed in the next section. [Rebecca: would you be willing to try a few more catalytic reactions? I'd be interested in things like (1) 1% **1** with styrene sulfonate, *m*CPBA in D_2O/100 mM HBF_4, and in a sealed NMR tube, and (2) catalytic oxidation of stilbene by *m*CPBA in 50% CD_3CN/50% D_2O/100 mM $HBF_4$with 5% **1**.@]



(3)

2.5. Mechanistic Studies

The alkene oxidations reported here are accomplished by osmium complex(es). The direct oxidation of stilbene and the other alkenes by *m*-CPBA alone is very slow under these conditions[can we say anything stronger, *e.g.*, that no reaction is observed under these conditions?@]. Furthermore, the *trans*-stilbene epoxide that would be formed from *m*-CPBA + *trans*-

stilbene does not react with **1** to give the diolate **2**. In additional control experiments, neither *trans*-stilbene nor *rac*-hydrobenzoin, PhCH(OH)CH(OH)Ph, react with **1** under these conditions. Thus neither the epoxide nor the diol can be intermediates in the formation of **2**.

The reaction of **1** (2.2 mM), *m*-CPBA (22 mM), and *trans*-stilbene (6.6 mM) in CD_2Cl_2 was monitored by ^1H NMR at room temperature, as shown in Fig. 2. Spectrum A, after 9 minutes of reaction, shows that **1** is the major species, from the well separated pyrazole triplets at

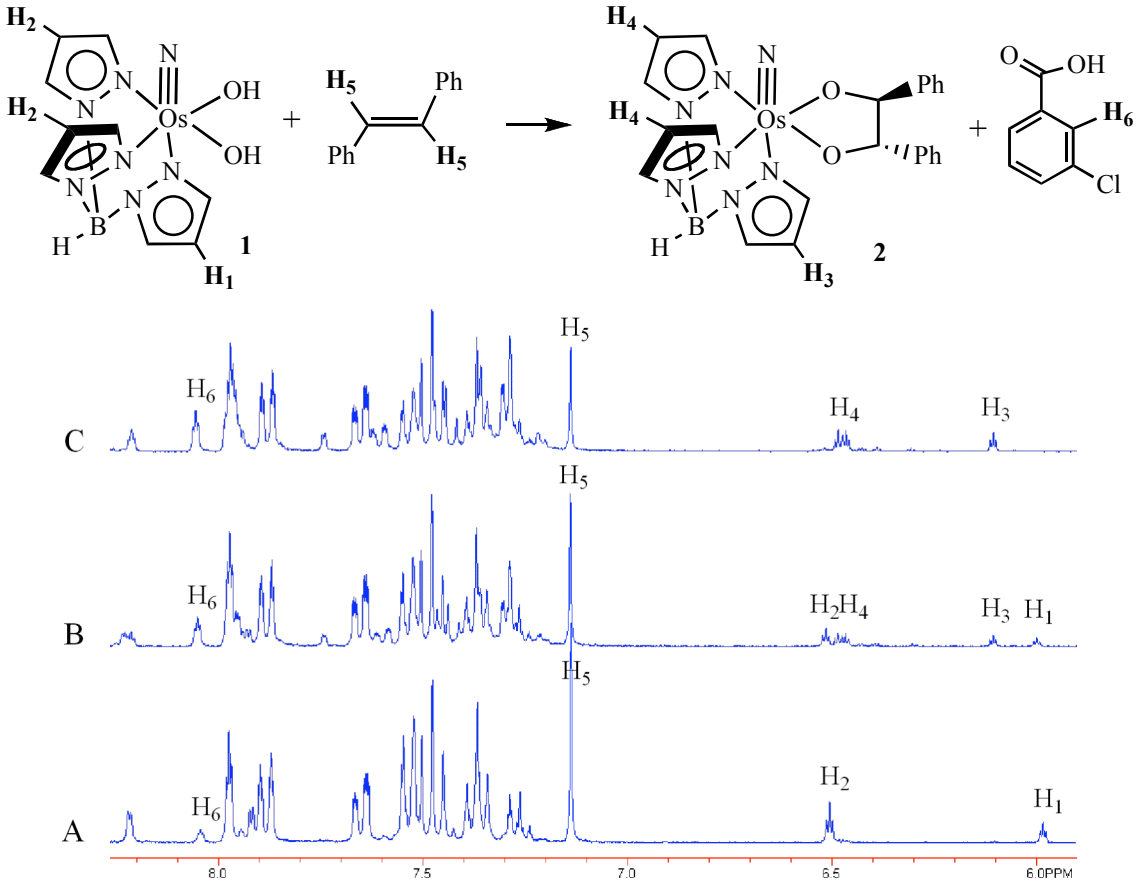


Fig. 2. Partial ^1H NMR spectra in CD_2Cl_2 at room temperature for the reaction of **1** (2.2 mM), *m*-CPBA (22 mM), and *trans*-stilbene (6.6 mM) to generate **2** and *m*-CBA at 9 (A), 49 (B), and 101 min (C). Selected proton resonances are labeled corresponding to the structures above.

δ 5.99 (H_1) and 6.50 (H_2). After 49 minutes, spectrum B shows approximately equal amounts of **1** and **2**, with the latter identified by its characteristic three (1:1:1) triplets at 6.10 ppm (H_3), 6.46 (H_4), and 6.48 (H_4). Spectrum C, at 101 minutes of reaction shows almost complete

consumption of **1** as the reaction nears completion. Over the course of the reaction, the *trans*-stilbene vinyl resonance (H_5 at δ 7.14) decreases, and an *m*-CBA resonance (H_6 at 8.05 ppm) increases. These resonances are unobstructed for quantifying the species concentrations.

Two similar versions of reaction 1 were done with different initial *trans*-stilbene concentrations, 6.6 or 22 mM, and were monitored by ^{1}H NMR (Fig. 3**A**). Peak integrations relative to a capillary C_6Me_6 resonance (δ 2.20) were used to determine the concentrations of each species; good mass balance was observed.[@is this true? Adam, can you send me a new version of Figure 3A that shows the mass balance, as well as the [**1**] and [**2**]? My question is whether 2 is formed during the induction period and therefore there is good mass balance during the early stage of the reaction (as it appears from Fig 3), or whether the induction period is simply the decomposition of 1 + mCPBA, without formation of **2**?] While this is not a full kinetic study, both reactions appear to show an induction period. After this initial slow phase, the decay of **1** is roughly first order in **1**. Modeling this portion of the data with an exponential decay, eq 4, plotting $\ln([\mathbf{1}]/[\mathbf{1}]_o)$ *vs.* $(t - t_{induction})$ (Figure 3**B**), yields k_{obs} values of 0.55×10^{-3} s^{-1} and 1.6×10^{-3} s^{-1} for [*trans*-stilbene]$_o$ = 6.6 and 22 mM. Thus an approximate three-fold increase in [*trans*-stilbene] gives about three-fold increase in k_{obs}. This suggests that the main portion of the reaction is first order in [*trans*-stilbene]. The induction times were estimated to be 1140 and 660 s for the two reactions, to fit $\ln([\mathbf{1}]/[\mathbf{1}]_o) \sim 0$ at time 0 s.

$$-\frac{d[\mathbf{1}]}{d(t-t_{induction})} = k_{obs}[\mathbf{1}] \qquad (4)$$

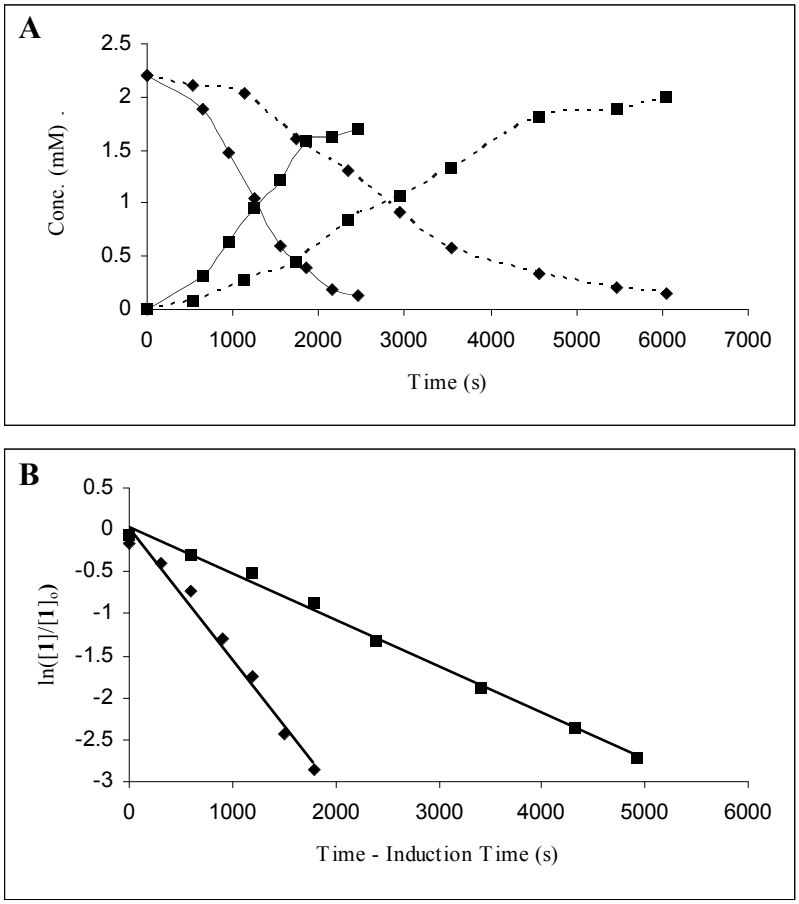


Fig. 3. Kinetic data for reactions with [**1**]$_o$ = 2.2 mM, [*m*-CPBA]$_o$ = 22 mM, and [*trans*-stilbene]$_o$ = 6.6 or 22 mM. In plot **A**, the lower stilbene concentration is indicated by - - -, the higher concentration by —, and the concentrations of [**1**] (♦) and [**2**] (■) are indicated. **B** shows first-order plots of ln([**1**]/[**1**]$_o$) vs. (time – induction time), with [*trans*-stilbene]$_o$ = 6.6 (■) and 22 mM (♦); the induction times were estimated to be 1140 (■) and 660 s (♦).

Reactions of **1** with *m*-CPBA in CD_2Cl_2 at room temperature, under the same conditions as in Figure 2 but without any *trans*-stilbene, were also monitored by ^{1}H NMR (Fig. 4**A**). Over a couple of hours, **1** decomposed over time and precipitates deposited in the NMR tube. More than 1 equiv of *m*-CBA is formed, likely because of further reaction of *m*-CPBA with the decomposition products of **1** (Fig. 4**B**). The high initial [*m*-CBA] (1.6 mM at 9 min) is due, at least in part, to the presence of the acid as an impurity in the *m*-CPBA.

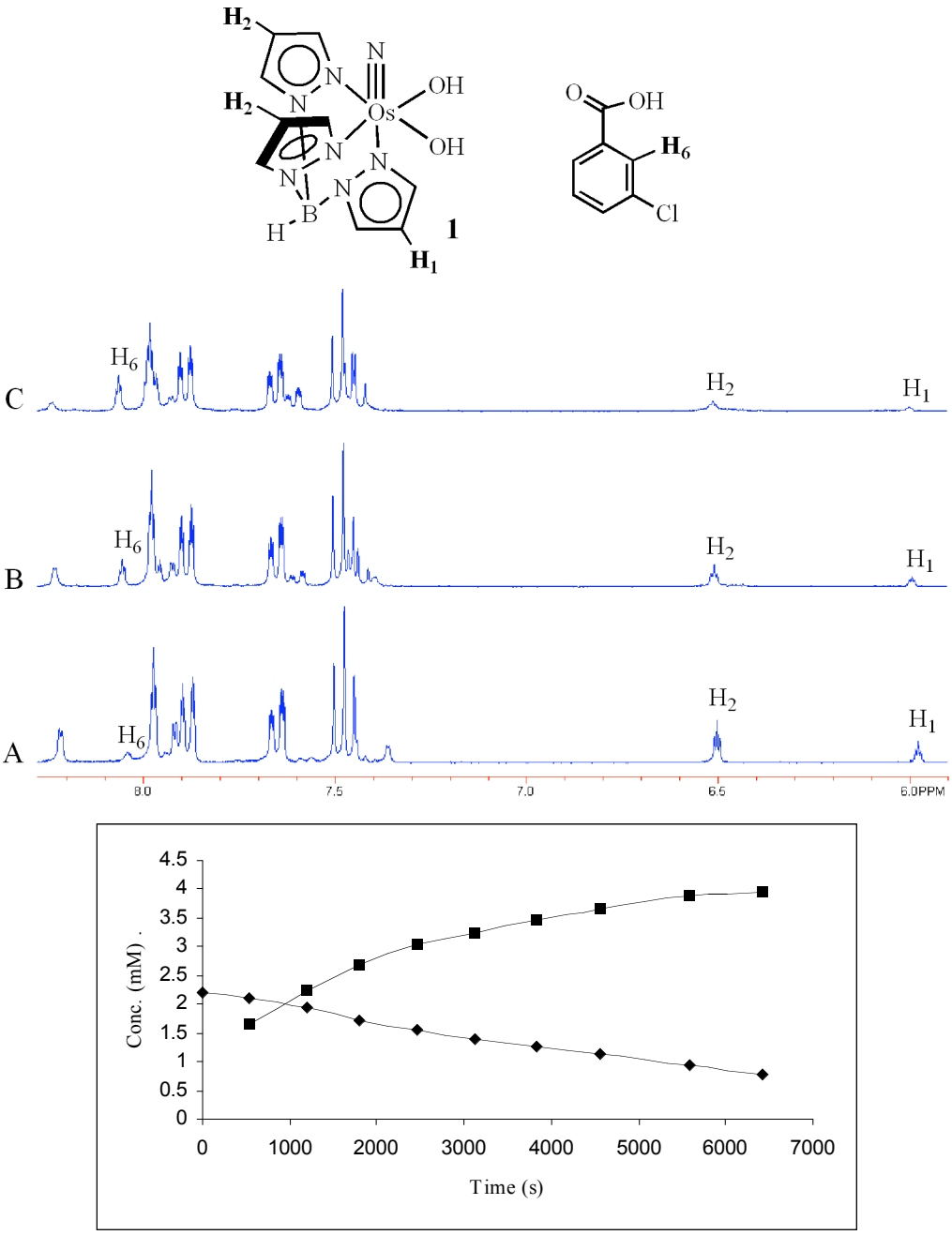


Fig. 4. Data from a reaction of **1** (2.2 mM) and *m*-CPBA (22 mM) in CD_2Cl_2 at room temperature. **Top:** Partial ^{1}H NMR spectra at 9 (A), 52 (B), and 107 min (C), with selected proton resonances labeled corresponding to the structures above. **Bottom:** Plots of [**1**] (♦) and [*m*-CBA] (■) versus time, for the reaction described in part where $[\mathbf{1}]_o$ = 2.2 mM and $[m\text{-CPBA}]_o$ = 22 mM.

Qualitatively, the rate of decay of **1** is slower in the absence of *trans*-stilbene than the rate in the presence of *trans*-stilbene (Fig. 3). At 6000 s, ~39 % of the initial **1** was still visible in the reaction without *trans*-stilbene, compared to ~7 % of when $[trans\text{-stilbene}]_o$ = 6.6 mM. For $[trans\text{-stilbene}]_o$ = 22 mM, **1** was completely consumed before 3000 s. However, the rate of decay of **1** in the absence of stilbene could be fast enough to account for the decay of **1** during the apparent induction period of the reaction, although only very limited data are available (Figure 3A).

These results rule out initial rate limiting oxidation of the bis-hydroxide complex **1** to the related dioxo compound "$TpOs^{VIII}(N)(O)_2$". This species would be, in a way, an octahedral analog of $OsO_4(L)$ and might therefore be expected to react with alkenes to give diolate products. However, rate limiting formation of "$TpOs^{VIII}(N)(O)_2$" is inconsistent with the decay of **1** being dependent on the alkene concentration (Fig. 3). Pre-equilibrium formation of "$TpOs^{VIII}(N)(O)_2$" is also very unlikely because reactions of peroxides are almost invariably thought to be irreversible, given the difficulty of re-forming the O–O bond [16]. Thus our previous brief suggestion of the intermediacy of "$TpOs^{VIII}(N)(O)_2$" [14] is indicated to be incorrect.

[Becca: can you try the following set of reactions? First make a little bit of the $^{n}Bu_4N^+$ salt of *m*-chlorobenzoate (probably easiest from $^{n}Bu_4N^+OH^-$ and *m*-CBA). Then make a solution of **1** + *trans*-stilbene in CD_2Cl_2, similar to the cases above, and split it into four NMR tubes. One tube will be your control. To the 2nd tube, add about 4 equiv (vs. Os) of *m*-CBA, to test for reversibility in O–O bond cleavage. To the third, please add ~0.3 equiv of $^{n}Bu_4N^+$*m*-CBA^-, to test for trace acid catalysis. Finally to the fourth, add 1 equiv of water, as I'm thinking that water could be the accelerant after the induction period. Then add a concentrated solution of *m*-CPBA in equal amounts to both tubes, to make a solution that is close to those above, with $[\mathbf{1}]_o$ = 2.2 mM, $[m\text{-CPBA}]_o$ = 22 mM, and = 6.6 < $[trans\text{-stilbene}]_o$ < 22 mM. I think you should pick the alkene concentration to give you a convenient rate, so that you can just sit at the NMR for a couple of hours and monitor all four tubes at the same time. If you have the patience for it, there's one more thing that would be interesting. Once the alkene has been pretty well consumed

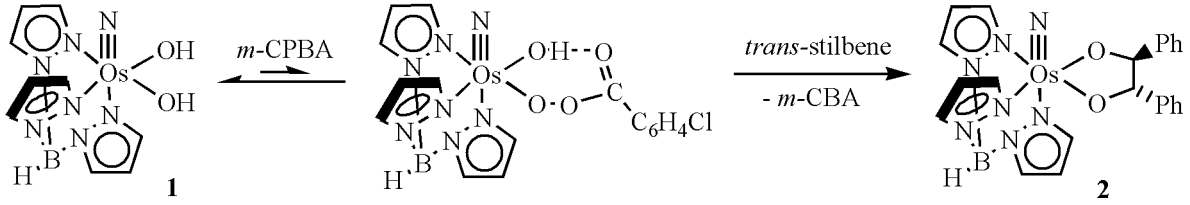
in the control tube, add a second shot of alkene and *m*-CPBA to go back to your starting concentrations. It would be interesting to see if there is still an induction period, or if something made in the first run that is still in solution will eliminate that. Thanks@]

The presence of an induction period and the decomposition of **1** in the absence of alkene indicate a fairly complex reaction pathway. The simple pre-equilibrium kinetic scheme **1** + *m*-CPBA $\rightleftharpoons$ X (k_1, k_{-1}), X + stilbene $\longrightarrow$ **2** (k_2) does not give an induction period, because it can never proceed faster than the initial k_1 step.[is this true? Jim should ask Karen@] It is possible that a decomposition or side product formed from the reaction of **1** + *m*-CPBA accelerates the reaction, although this must involve only a small amount of **1** since **2** is formed even during the induction period and good mass balance is observed throughout.[true?@] While no intermediate osmium species is observed by ^{1}H NMR, it seems likely that stilbene is reacting with some sort of oxidizing osmium in equilibrium with **1** + *m*-CPBA, perhaps a species with a bound *meta*-chloro-perbenzoate anion. Recently, it has been suggested that a related Os^{VI}-oxo-^{t}butylperoxo complex can *cis*-dihydroxylate alkenes prior to O–O bond formation [17]. However, it should be noted that *cis*-dihydroxylation is also accomplished by **1** + PbO_2 in acidic water, showing that an O–O bond is not required for reactivity.[any other oxidants to mention@?]

[Adam: As you can see, I'm happy to include your proposal in the text but hesitant to write it out as a Scheme, because it doesn't explain the induction period. Here's your text; let me know if you want to push to include more of it.@ The following mechanism is proposed in Scheme 2 for the reaction of **1**, *m*-CPBA, and *trans*-stilbene [Eq. 1]. The first step involves a fast pre-equilibrium of an hydrogen-bonded adduct of **1** and *m*-CPBA, which then reacts with *trans*-stilbene in the rate determining step to produce **2** and *m*-CBA. The equilibrium in the first step lies to the left, where the intermediate does not accumulate to a high enough concentration to be observed, as no new Tp-Os species has been observed by ^{1}H NMR during reaction 1. As *trans*-stilbene concentration increases, the increased consumption of the intermediate shifts the equilibrium to the right and increases the decay rate of **1**. This is consistent with the *trans*-

stilbene dependence on the disappearance rate of **1**, and the simultaneous growth of **2** and *m*-CBA with the decay of **1**.

Scheme 2.]



3. Conclusions

Alkenes are stoichiometricaly oxidized by $TpOs^{VI}(N)(OH)_2$ (**1**) + *m*-chloroperbenzoic acid (*m*-CPBA) to give isolable Os^{VI} diolate complexes. With *trans*-stilbene, the *trans*-diolate complex $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**) is formed and has been structurally characterized. The diolate complexes release the organic diol product upon treatment with HCl. For all of the alkenes, dihydroxylation occurs in a *cis* fashion. In acidic aqueous solutions with PbO_2 as the oxidant, **1** catalyzes the conversion of 15 equivalents of the water soluble olefin, 4-styrenesulfonic acid to its corresponding diol. Mechanistic studies with m-CPBA in CD_2Cl_2 suggest a complex mechanism, and argue against the intermediacy of an Os^{VIII} species such as "$TpOs(N)(O)_2$", favoring an oxidant with the O–O bond intact. An Os^{VIII} complex could be involved, however, in the aqueous [and other@?] oxidations that do not involve a peroxide oxidant.

4. Experimental

All reactions were conducted under air, unless stated otherwise. ^{1}H NMR spectra were recorded on Bruker spectrometers (300 and 500 MHz) at ambient temperatures and referenced to a residual solvent peak: δ (multiplicity, number of protons, assignment). All pyrazole resonances display $^3J_{HH}$ = 2 Hz. Electrospray ionization mass spectra (ESI/MS) were obtained on a Applied Biosystems Mariner API-TOF Mass Spectrometer. Samples were introduced in CH_3CN/H_2O mixture with a nozzle potential set at 140 V. UV-vis spectra were acquired with a Hewlett-Packard 8453 diode array spectrophotometer in anhydrous CH_2Cl_2, and reported as λ_{max}, nm (ε, M^{-1} cm^{-1}). Elemental analyses were performed by Atlantic Microlab.

All reagent grade solvents were purchased from Fisher Scientific or EMD Chemicals. Deuterated solvents were obtained from Cambridge Isotope Laboratories. CD_2Cl_2 was dried over CaH_2 and vacuum transferred. PbO_2, *m*-CPBA, *trans*-stilbene, HBF_4 (48 wt % in H_2O), *cis*-stilbene, styrene, cyclohexene, *trans*-dimethyl fumarate, *trans*-methyl cinnamate, *trans*-4-dimethylamino-4′-nitrostilbene, and 4-styrenesulfonic acid were purchased from Aldrich. *m*-CPBA was purified according to a literature method [18]. $TpOs^{VI}(N)(OH)_2$ (**1**) was prepared according to literature procedure [12].

*4.1. $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**).*

Trans-stilbene (0.020g, 0.11 mmol) was added to a solution of **1** (0.050 g, 0.11 mmol) and *m*-CPBA (0.023g, 0.13 mmol) in C_6H_6 (5 mL) and stirred for 5 min. The solvent was removed *in vacuo*, and the residue was loaded onto a silica gel column with 80:20 CH_2Cl_2/hexanes to collect the orange red **2** (0.060 g, 0.140 mmol, 95% yield). ^{1}H NMR (CD_2Cl_2): δ 6.11 (1H, t, pz), 6.45 (1H, t, pz'), 6.49 (1H, t, pz''), 7.52, 7.73 (each 1H, d, pz), 7.94, 7.97 (each 1H, d, pz'), 8.17, 8.19 (each 1H, d, pz''); 7.27–7.33 (m, 10H, Ph); 5.40, 5.48 (d, 6 Hz, 1H each, HCCH'). ESI/MS^+: 630 (M^+). UV-Vis: 425 (280). Anal. Fnd: C, 43.90%; H, 3.53%; N, 15.45%. Calcd for $C_{23}H_{22}B_1N_7O_2Os$: C, 44.02%; H, 3.21%; N, 15.63%.

4.2. $TpOs^{VI}(N)(cis\text{-}O_2C_2H_2Ph_2)$.

The same procedure was used as described above for **2**, using *cis*-stilbene instead of *trans*-stilbene. The ^{1}H NMR spectrum of *$TpOs^{VI}(N)(cis\text{-}O_2C_2H_2Ph_2)$* shows two diastereotopic diolate products: ^{1}H NMR (CD_2Cl_2): δ 6.10 (t), 6.12 (t), 7.62 (d) 7.65 (d), 7.75 (d), 7.79 (d) (each 1H, pz); 6.49 (t), 6.51 (t), 7.93 (d) 7.95 (d), 8.17 (d), 8.19 (d) (each 2H, pz'); 4.67 (s, 2H, CH), 4.69 (s, 2H, CH'). The overlapping phenyl resonances are at δ 7.2–7.7.

*4.3. Mechanistic studies for the reaction of **1**, m-CPBA, and trans-Stilbene by ^{1}H NMR.*

Complex **1** (2.0 mg), *m*-CPBA (7.7 mg), and C_6Me_6 (~ 0.5 mg) were charged into a 2 mL volumetric flask, and CD_2Cl_2 was added to make a 2 mL solution. Each (2 × 1 mL) solution was immediately pipetted into an NMR tube containing *trans*-stilbene (1.2 or 4.0 mg) to make a solution of **1** (2.2 mM), *m*-CPBA (22 mM), and *trans*-stilbene (6.6 or 22 mM) in CD_2Cl_2. Both reactions were monitored by ^{1}H NMR at room temperature using two spectrometers; the spectra were recorded in 5-min intervals. The reaction of **1** (2.2 mM) and *m*-CPBA (22 mM) was performed analogously in the absence of *trans*-stilbene. The relative concentrations were determined by peak integration against a capillary standard of C_6Me_6 (δ 2.20). Data analyses and plots were prepared using Microsoft Excel.

*4.4. X-ray structural determination of $TpOs^{VI}(N)(trans\text{-}O_2C_2H_2Ph_2)$ (**2**)*

Crystals of **2** were obtained from slow evaporation of CH_2Cl_2/hexanes solutions and were mounted onto a glass capillary with oil. The data were collected on a Nonius Kappa CCD diffractometer. Selected crystallographic data for $TpOs(N)(O_2C_2H_2Ph_2)$: $C_{23}H_{22}BN_7O_2Os$, fw = 629.51, 0.19 × 0.17 × 0.10 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 14.5100(12), b = 11.2880(9), c = 15.0910(15) Å, β = 106.896(4)°, V = 2365.0(4) Å^3, ρ_{calc} = 1.768 Mg·m^{-3}, Z = 4, $2\theta_{max}$ = 2.78–28.22°, MoKα radiation (λ = 0.71073 Å), F(000) = 1224, T = 130(2) K, total/independent reflections = 33126/5050 (R_{int} = 10.11%), observed data = 8387 ($I > 2\sigma(I)$), restraints/parameters = 0/307, absorption correction: semi-empirical (hkl-SCALEPACK [19]),

max(min) transmission: 0.6129(0.4254), R_1 (wR_2) = 5.12 (11.97)% for $I > 2\sigma(I)$, GOF = 0.910, largest diff. peak (hole) = 1.269 (–1.398) e Å^{-3}. Solution by direct methods (SIR92) produced a complete heavy-atom phasing model consistent with the proposed structure [20]. The heavy atoms were refined anisotropically by full matrix least-squares, and the hydrogen atoms were placed using a riding model [21].

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Supporting information

CCDC ###### contains the crystallographic data for **2**. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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