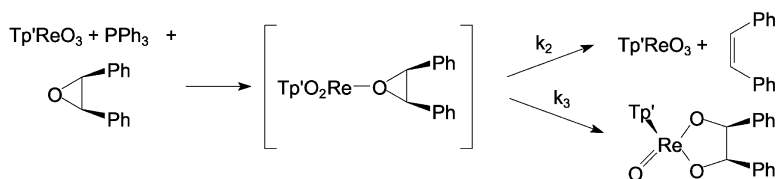


Kinetics and Mechanism of Rhenium-Catalyzed O Atom Transfer from Epoxides

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Kinetics and Mechanism of Rhenium-Catalyzed O Atom Transfer from Epoxides

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Abstract: O atom transfer from epoxides *cis*-stilbene oxide and styrene oxide to triphenylphosphine catalyzed by $\text{Tp}'\text{ReO}_3$ ($\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$) is shown to proceed via an unexpectedly complex combination of mechanisms. Reduction of $\text{Tp}'\text{ReO}_3$ with PPh_3 in THF is rapid above room temperature to form a highly reactive species suggested to be $\text{Tp}'\text{ReO}_2$. Spectroscopic examination and attempts to isolate this by chromatography lead only to $\text{Tp}'\text{Re}(\text{O})(\text{OH})_2$ (**1**); exposure of the crude reduction mixture to ethanol results in formation of $\text{Tp}'\text{Re}(\text{O})(\text{OEt})(\text{OH})$ (**3**). Both **1** and **3** are as efficient catalysts for O atom transfer as the unpurified mixture resulting from reaction of PPh_3 with $\text{Tp}'\text{ReO}_3$; all three rhenium reactants give the same turnover frequency to within 10% at identical $[\text{Re}]_{\text{total}}$ and $[\text{epoxide}]$. The kinetic behavior of the catalytic system (epoxide:Re = 20) is complex; an initial "burst" of alkene production is seen, which quickly tapers off and falls into a pseudo-zero-order reaction. The majority of rhenium is observed to exist as the *syn*- $\text{Tp}'\text{Re}(\text{O})(\text{diolate})$ complex, formed by ring expansion of the epoxide. However, cycloreversion of this diolate is incapable of accounting for the observed catalytic turnover frequency. An additional intermediate, a coordinated epoxide, is proposed to form and partition between ring expansion and direct fragmentation to alkene; eventually a steady-state concentration of diolate forms. Competition between direct atom transfer and ring expansion followed by diolate cycloreversion is demonstrated by reaction of **3** with excess *cis*-stilbene oxide and styrene oxide in the absence of reductant to give a 4:1 mixture of alkene and *syn*-diolate from *cis*-stilbene oxide or a 5.5:1 mixture of alkene and *syn*-diolate from styrene oxide under conditions where diolate cycloreversion is a negligible contributor.

Introduction

Metal-catalyzed O atom transfer reactions are important to a broad array of chemistry, from biologic processes to industrial synthesis.¹ Mechanistic understanding of these reactions is weak in many cases, and the search for this understanding is a topic of significant current interest. Among reactions receiving the most scrutiny are bishydroxylation and epoxidation of alkenes. Interest in these reactions is in part spurred by the capacity to introduce stereogenic centers into an achiral alkene, and by the ability to place new functionality at two adjacent carbon centers simultaneously. In general, reagents for accomplishing epoxidation are distinct and separate from the smaller group of bishydroxylation reagents,² although recent work³ and long-standing speculation⁴ have hinted at a connection between the two reactions.

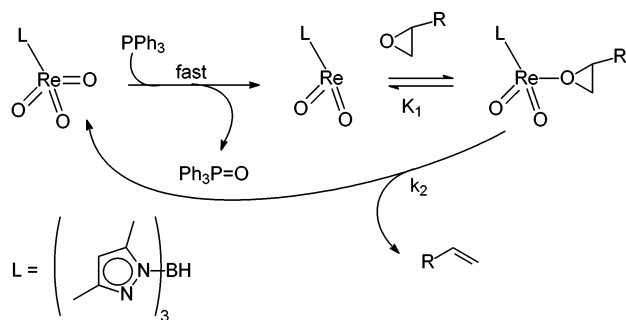
Work in our group has centered on metal-mediated C—O bond cleavage.⁵ The primary justification is that the principle of microscopic reversibility allows mechanistic investigations

of C—O bond cleavage to be related to C—O bond formation; rigorous application of this principle is seen in the ability of LReO_3 to undergo cycloaddition with strained alkenes ($\text{L} = \text{C}_5\text{Me}_5$, $\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3$).⁶ Thus, our focus is in using the rhenium platform as a mechanistic model for examining metal-mediated C—O bond transformations. The reactions are also of some technological interest of their own accord: removal of oxygen from organic compounds is key to selective transformations of biomass feedstocks;⁷ removal of an epoxide oxygen would offer completion of a protection/deprotection cycle for an alkene;⁸ an enantioselective version would provide a means of kinetic resolution for racemic epoxides or diols.⁹ Epoxide deoxygenation in general has received some attention over the past three decades; several phosphorus,¹⁰ silicon,¹¹ or selenium¹² based systems are known that lead (generally) to inversion of stereochemistry at one reaction center, while metal-mediated systems¹³ exhibit a broader spectrum of selectivity.

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Scheme 1



In the course of our examination of rhenium-mediated C–O bond formation and cleavage, we recently discovered a rhenium-catalyzed O atom transfer from epoxides to phosphines and phosphites that exhibited high stereoselectivity for retention of configuration.¹⁴ Preliminary investigations supported the assumption that the catalytically active species was a Re(V) complex, although no evidence for its nature was available at the time of our initial report. Of some interest was the fact that a common set of reaction conditions ($\text{LReO}_3 + \text{PPh}_3$) could lead to both reduction of a vicinal diol by cyclocondensation and cycloreversion, and epoxide deoxygenation. Thus, there was a potential, via microscopic reversibility, that in this system bishydroxylation and epoxidation were competing or even related mechanistic pathways. In this paper we describe the mechanistic investigation of this rhenium-catalyzed epoxide deoxygenation.

Results and Discussion

Characterization of the mechanism for a catalytic cycle requires two general accomplishments: structural identification of individual species lying on a catalytic cycle, and discovery of the rate constants for processes interrelating those species. The simplest mechanistic proposal for epoxide deoxygenation (Scheme 1) involves only two rhenium species, one the reactant, LReO_3 , the other a reduced rhenium complex, presumably LReO_2 . A minor variation includes equilibrium formation of a coordinated epoxide, but direct O atom transfer without formation of an intermediate is also possible.

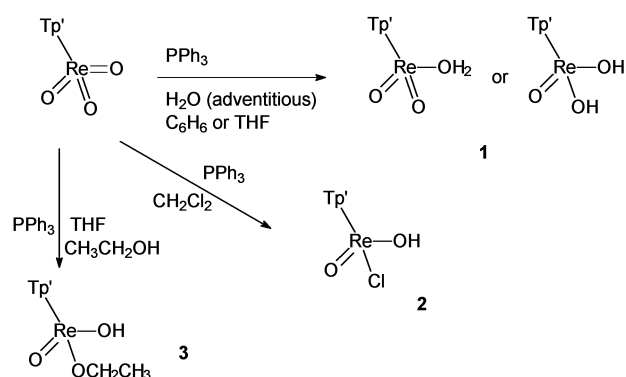
Reduction of $\text{Tp}'\text{ReO}_3$. An initial question was whether reduction of $\text{Tp}'\text{ReO}_3$ leads to a reactive $\text{Tp}'\text{ReO}_2$ complex, by analogy to Cp^*ReO_3 ¹⁵ and MeReO_3 .¹⁶ Such species have also been suggested for (pyrazolylborato)rhenium oxo systems.¹⁷ Such a species would be a d^2 *cis*-dioxo complex; on the basis of earlier discussions,¹⁸ this would be expected to be a highly reactive species largely because of electron–electron interactions between the metal lone pair and oxo π -donating electrons. Reduction of other LReO_3 complexes leads to dimeric, bridged oxo complexes for $L = \text{Cp}^*$, $\text{HB}(\text{pz})_3$, and $\text{B}(\text{pz})_4$. In the former case, there is NMR evidence for formation of the monomer at high temperatures, but because of the dynamic equilibrium with the dimer, full structural characterization is lacking.

Reaction of $\text{Tp}'\text{ReO}_3$ with PPh_3 in THF at room temperature or above leads to disappearance of the largely insoluble trioxo complex over 2–3 days, and formation of a pale blue solution. At higher temperature the reaction is complete in several hours. The crude NMR of this mixture shows formation of $\text{Ph}_3\text{P}=\text{O}$, and formation of a Tp' -containing species with C_s symmetry. Chromatography on silica gel with 1% acetone in dichloromethane led to isolation of a bright blue band that gave a blue microcrystalline solid on removal of solvent. The NMR spectrum was unchanged from signals seen in the crude mixture, and in addition to the signals from the Tp' ligand, a 2-H singlet was seen at 12.8 ppm. This latter signal disappeared on exchange with D_2O ; however, on exchange with 0.25 equiv of D_2O , a separate resonance approximately 15 Hz upfield was observed. No dynamic behavior was seen for the compound on either heating (to 50 °C) or cooling (to –83 °C). The IR spectrum showed only a single oxo stretch (966 cm^{-1}) and a broad O–H stretch centered at 3335 cm^{-1} in addition to expected bands from the Tp' ligand. (The trioxo complex shows a single $\text{Re}=\text{O}$ band at 908 cm^{-1} and similar ligand bands; a weak signal possibly indicating the presence of water is seen at 3422 cm^{-1} despite the complex having been dried at 150 °C under vacuum overnight.) The compound was moderately oxygen-sensitive and could be converted quantitatively to $\text{Tp}'\text{ReO}_3$ by exposing solutions to air for 15 h. The FAB mass spectrum was inconclusive in establishing composition; an intense signal envelope corresponding to $\text{Tp}'\text{ReO}_2$ was seen with a major peak at $m/z = 516$, but there was also a small but significant signal envelope with a major peak at $m/z = 534$; the latter could have been the parent ion of the compound, or it could have been a species formed in the ionization matrix. HRMS of this peak matched that expected for $\text{Tp}'\text{ReO}_2 + \text{H}_2\text{O}$. Attempts at direct thermal volatilization were unsuccessful. The available evidence for the structure of the reduced complex points to $\text{Tp}'\text{Re}(\text{O})(\text{OH})_2$ (Scheme 2), largely on the basis of the similarity of the visual spectrum ($\lambda_{\text{max}} = 606\text{ nm}$) with those of other $\text{Tp}'\text{Re}(\text{O})(\text{alkoxide})_2$ compounds. Preliminary computational modeling¹⁹ agreed with this assignment. The origin of the water

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Scheme 2



molecule that formally adds to $\text{Tp}'\text{ReO}_2$ is unknown; efforts to rigorously dry reaction samples did not suppress formation of the compound (best indicated by the 2-H OH signal at 12.8 ppm and also by the vinylic pyrazole signals in the ^1H NMR). One possible source is that $\text{Tp}'\text{ReO}_3$ may have a water of hydration; its synthesis involves a water rinse at one stage, and retention of adventitious water is certainly possible. Provided all other reagents were rigorously dried, $\text{Tp}'\text{ReO}(\text{OH})_2$ was as effective a catalyst for epoxide deoxygenation as was in situ reduction of $\text{Tp}'\text{ReO}_3$. Attempts to physically or chemically dehydrate $\text{Tp}'\text{ReO}(\text{OH})_2$ led to intractable mixtures.

Reduction of the trioxo complex in different solvents leads to different results (Scheme 2). Use of a chlorinated solvent led to the known $\text{Tp}'\text{Re}(\text{O})(\text{OH})\text{Cl}$ (2),²⁰ easily identified on the basis of its C_1 -symmetry ^1H NMR spectrum and its IR spectrum. This may be an artifact of HCl in the solvent, and deliberate addition of HCl to a THF reaction mixture also led to this chloride. Use of the hydroxylic solvent ethanol led, after chromatography, to $\text{Tp}'\text{Re}(\text{O})(\text{OEt})(\text{OH})$, identified by ^1H NMR and mass spectrometry. Particularly diagnostic, in addition to the C_1 -symmetry Tp' signals, are the signals for diastereotopic protons in the CH_2 group of the ethoxy ligand. The FAB mass spectrum was very similar to that of compound 1, except that in place of the $\text{Tp}'\text{ReO}_2 + \text{H}_2\text{O}$ peak envelope at $m/z = 534$, we now observe a $\text{Tp}'\text{ReO}_2 + \text{EtOH}$ peak envelope at $m/z = 562$. HRMS of this signal is consistent with a composition of $\text{Tp}'\text{ReO}_2 + \text{EtOH}$. The hydroxo chloride was moderately stable to oxygen, but the hydroxo ethoxide readily oxidized to the trioxide on exposure to air. The ethoxide was somewhat difficult to purify; small amounts of bishydroxide coeluted with it chromatographically, and overexposure to ethanol led to formation of the bisethoxide,¹⁷ which also coeluted and cocrystallized. The ethoxide also functioned as an equally effective catalyst for epoxide deoxygenation; observed pseudo-zero-order rate constants for catalytic turnover were identical for the two precatalysts.

Lacking crystals suitable for diffraction analysis, a final piece of evidence for the structure of $\text{Tp}'\text{ReO}(\text{OH})_2$ lay in its independent preparation. Cleavage of $\text{Tp}'\text{Re}(\text{O})(\text{OCH}_2\text{CH}_2\text{O})$ with HCl leads to the oxo dichloride $\text{Tp}'\text{Re}(\text{O})\text{Cl}_2$. Reaction of this compound with methanol and triethylamine (as base) was known to give bisalkoxide $\text{Tp}'\text{Re}(\text{O})(\text{OMe})_2$;²¹ use of water in place of methanol gave a compound identical to that formed by phosphine reduction of $\text{Tp}'\text{ReO}_3$.

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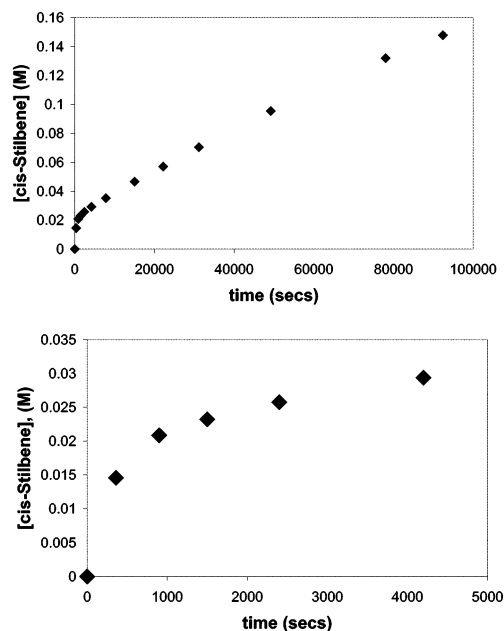


Figure 1. Upper plot: A typical pseudo-zero-order plot for production of *cis*-stilbene. The slope of the linear portion ($=k_{\text{obs}}$) is $(1.38 \pm 0.03) \times 10^{-6} \text{ M s}^{-1}$. Lower plot: Expansion of the initial phase of the reaction, showing the burst of alkene production initially. Reaction conditions: 8.4 mM $[\text{Re}]_{\text{total}}$, 0.175 M initial [*cis*-stilbene oxide], 0.199 M initial $[\text{PPh}_3]$, C_6D_6 , 75 °C.

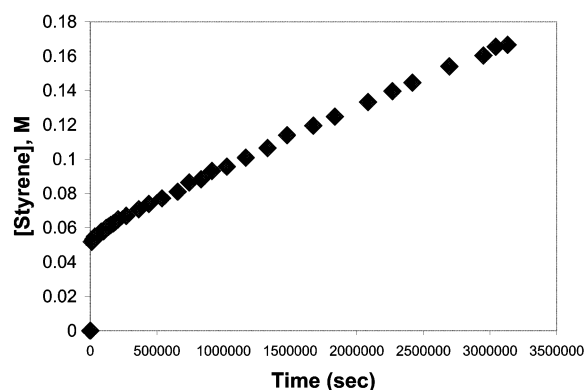


Figure 2. A typical plot for production of styrene. The slope of the linear portion ($=k_{\text{obs}}$) is $(3.69 \pm 0.02) \times 10^{-8} \text{ M s}^{-1}$. Reaction conditions: 8.4 mM $[\text{Re}]_{\text{total}}$, 0.175 M initial [styrene oxide], 0.199 M initial $[\text{PPh}_3]$, C_6D_6 , 75 °C.

Reaction Kinetics for Epoxide Reduction. Preliminary analysis of the kinetics was consistent with the above model. After a brief period during which the insoluble $\text{Tp}'\text{ReO}_3$ is converted to a reduced, soluble form, reaction mixtures exhibit pseudo-zero-order behavior for production of alkene (Figures 1 and 2). First-order behavior in $[\text{Re}]_{\text{T}}$ (Figure 3), zero-order dependence on $[\text{PPh}_3]$ (Figure 4), and saturation kinetics in [epoxide] for both *cis*-stilbene oxide (Figure 5) and styrene oxide all suggested reversible binding of epoxide to rhenium, followed by slow fragmentation (by any of several mechanisms) and rapid subsequent reduction of $\text{Re}(\text{VII})$ to $\text{Re}(\text{V})$.

The impact of several variations in reaction conditions was probed. Addition of excess $\text{Ph}_3\text{P}=\text{O}$ had no discernible impact on k_{obs} , nor did addition of coordinating solvent acetonitrile or ether. Use of $\text{P}(\text{OEt})_3$ as stoichiometric reductant marginally depressed k_{obs} ; it may be that this sterically less-hindered species may compete with epoxide for metal ligation, but the zero-order

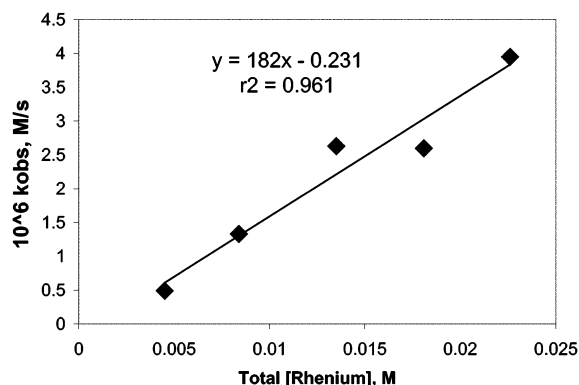


Figure 3. Dependence of turnover frequency on initial rhenium concentration. (The intercept is within 1 standard deviation, $3.2 \times 10^{-7} \text{ M s}^{-1}$, of zero.) For all samples, reaction conditions are 0.175 M initial [*cis*-stilbene oxide], 0.199 M initial [PPh₃], C₆D₆, and 75 °C.

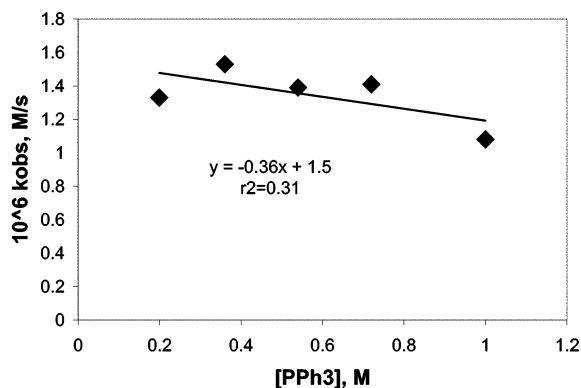


Figure 4. Dependence of turnover frequency on initial triphenylphosphine concentration. For all samples, reaction conditions are 8.4 mM [Re]_{total}, 0.175 M initial [*cis*-stilbene oxide], C₆D₆, and 75 °C.

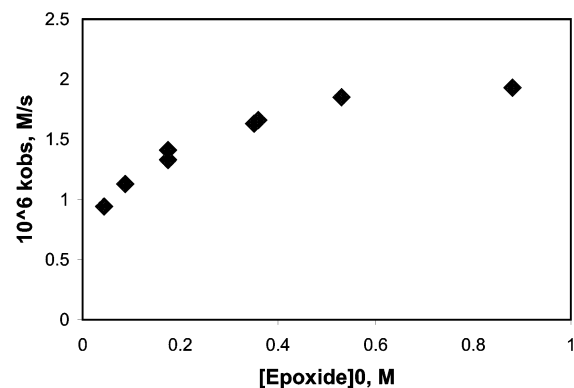


Figure 5. Dependence of turnover frequency on initial epoxide concentration. For all samples, reaction conditions are 8.4 mM [Re]_{total}, 0.199 M initial [PPh₃], C₆D₆, and 75 °C.

phosphine dependence noted above rules out participation of the phosphine in any rate-limiting process.

Electronic effects were probed by examining reduction rates for substituted styrene oxides. Both electron donors and electron acceptors accelerated the reaction, but the effect was modest; the fastest substituted styrene oxides (4-MeO and 4-CF₃) showed k_{obs} approximately twice that of the unsubstituted case. This provides prima facie evidence for a change in mechanism across the series, although further evidence below limits the conclusions that can be drawn.

However, there were several observations that cast some doubt on whether the initial model was complete. Competition

between styrene oxide and *cis*-stilbene oxide as substrates led to an unusual observation. In separate measurements, *cis*-stilbene oxide showed a much higher turnover frequency: $1.41 \times 10^{-6} \text{ M s}^{-1}$ for *cis*-stilbene; $3.90 \times 10^{-8} \text{ M s}^{-1}$ for styrene. However, a 1:1 mixture of the two led to production of styrene at a slightly higher rate ($4.71 \times 10^{-8} \text{ M s}^{-1}$) than normal. Formation of *cis*-stilbene, normally the faster process, was suppressed until late in the reaction. This would be consistent with a two-step process, in which binding was favorable for the less sterically encumbered styrene oxide, but either relief of steric compression or the added acceleration of the second aryl substituent caused fragmentation to be faster for stilbene.

Two other observations were critical. First, close examination of pseudo-zero-order plots for catalytic turnover (Figures 1 and 2) revealed that the zero-order behavior did not intercept the origin. While an induction period would not have been unexpected (as the insoluble trioxide was reduced to the active, soluble Re(V) species), this reproducible behavior indicated an initial “burst” of alkene formation, followed by a slower, steady-state system developing.

The second observation was that a new rhenium species appeared as the reaction proceeded, and that the symmetry of the compound (*C*₁ or *C*_s) matched what would have been imposed by the particular epoxide. Isolation of the stable compound from silica gel chromatography led to its identification as the *syn*-diolate **4s** from styrene oxide or **5s** from *cis*-stilbene oxide. The primary evidence for its structure was the match between the spectrum of new compound **4s** and that arising from a minor isomer in the crude reaction mixture from cyclocondensation of phenylethanediol with Tp⁺ReO₃ and PPh₃.^{6b} An earlier nuclear Overhauser enhancement experiment had established the *syn* stereochemistry for this.²² Confirmation of the *syn* stereochemistry for the diphenyl compound was also taken from the observation of NOEs; for **5s** irradiation of the pyrazole methyl signal at 2.21 ppm led to enhancement of the pyrazole vinyl signal at 5.52 ppm and the ortho aromatic protons at 7.33 ppm. Conversely, irradiation of the carbinolic diolate proton at 6.70 ppm led to enhancement of only the ortho phenyl protons at 7.33 ppm. The mass spectra for **4s** and **5s** were correct for the addition of the corresponding epoxide to Tp⁺ReO₂. The Re=O stretch in the IR spectrum also matched that of a large series of diolate complexes (957 cm⁻¹).

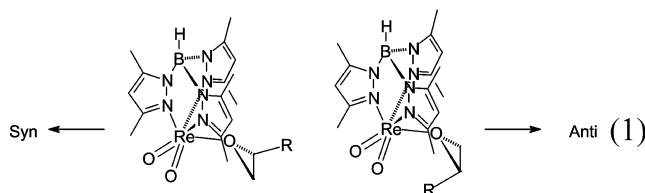
Ring expansion like this has been observed before in rhenium oxo chemistry, but with the much more Lewis acidic MeReO₃.²³ (Retention of stereochemistry is apparently seen in this case as well.) The substrates employed in this study are particularly vulnerable to Lewis and Bronsted acid-mediated ring opening by virtue of the phenyl substituents,²⁴ but the high degree of retention of stereochemistry (>95%) for *cis*-stilbene oxide in going to the diphenyldiolate argues against formation of a freely rotating carbocation. The rhenium center is not particularly Lewis acidic in these complexes in that neither phosphines nor coordinating solvents (ether, CH₃CN) appear to bind appreciably to the dioxo complex. One common explanation for retention of stereochemistry during rearrangements is a sequential “double

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inversion"; in this system likely candidates for mediating such a reaction can be ruled out. Attack by phosphine prior to the rate-limiting step would result in a kinetic dependence that is not observed. Also, reaction of a Re(V) species in the absence of phosphine (below) leads to the same diolates. Attack by adventitious water would result in a species similar to that likely formed in cyclocondensation of diols with LReO₂ compounds; this would certainly condense to an inverted diolate and generate the isomeric alkene to an observable extent. Attack by a pyrazole arm freed by $\kappa^3 \rightarrow \kappa^2$ isomerization is more difficult to rigorously exclude; however, such a reaction would be highly ionic in character, and again would lead to species that have good opportunity to expel the *trans*-alkene. Oxidative addition of the epoxide to form a metallaoxetane provides a solid rationale for retention of stereochemistry, but this would lead to a rare 7-coordinate Tp complex (again, barring $\kappa^3 \rightarrow \kappa^2$ isomerization) and provides no clear basis for expecting preferential production of the *syn* diastereomer of the diolate. Computational predictions have postulated a significant energy barrier for rearrangement of a metallaoxetane to a diolate.²⁵

Selective formation of the *syn* isomers **4s** and **5s** is a contrathermodynamic outcome and must be kinetic in origin. Demonstration comes from incubating the *syn-cis*-diphenyldiolate **5s** with an excess of 1,2-diphenylethanediol and *p*-toluenesulfonic acid, which leads to formation of *anti*-diolate; the converse reaction of the *anti*-diolate **5a** leads to no formation of the *syn* compound. A simple model can be devised to rationalize the kinetic preference for this compound (eq 1). If a



coordinated epoxide forms, there will be a steric bias to orient any epoxide substituent away from the oxo groups. If the oxygen retains sp³ hybridization, the epoxide substituent(s) will not yet interact with the Tp' ligand to any great extent. From this orientation, migration of either carbon to an oxo ligand with retention of stereochemistry will result in locking the resultant diolate into the *syn* stereochemistry. Preliminary experiments with alkyl-substituted epoxides indicate this phenomenon is general.

This observation forced a reevaluation of the initial mechanistic model in favor of one in which the diolate is the resting state of the catalyst. Cycloreversion of the diolate would be the rate-limiting step, followed by rapid reduction of rhenium and ring expansion of the epoxide. This model did not easily accommodate either the saturation behavior (ring expansion should be exothermic enough to preclude reversibility in diolate formation), nor did it easily explain the initial burst of alkene formation. Confirmation required measurement of the rate of cycloreversion of the *syn*-diolates. As expected, these com-

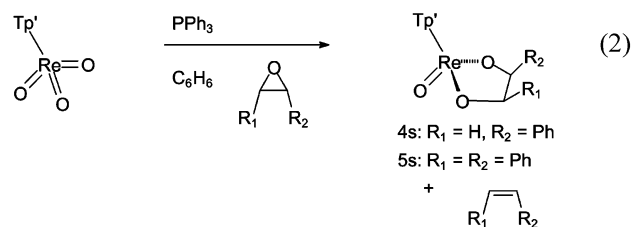
Table 1. Rates of Diolate Cycloreversion at 75 °C

compd	measured rate, ^a s ⁻¹	extrapolated rate, ^b s ⁻¹
4s	$(6.46 \pm 0.20) \times 10^{-7}$	
4a		5.53×10^{-6}
5s	$(6.04 \pm 0.23) \times 10^{-5}$	
5a	$(5.97 \pm 0.35) \times 10^{-6}$	6.29×10^{-6}

^a This work. Uncertainties are 95% confidence limits. ^b Reference 6b. Extrapolated from activation parameters.

pounds gave the corresponding alkene in a clean first-order process. *Anti* isomer **5a** was independently prepared and the rate of cycloreversion measured (see Table 1). The rate measured for the *anti-cis*-diphenyldiolate **5a** was identical to within experimental error to that extrapolated from earlier measurements, and so the extrapolated value for the *anti*-monophenyldiolate **4a** is used. Surprisingly, the impact of a second phenyl substituent differs considerably for the two diastereomers; for the *anti* isomer a second phenyl group has a marginal impact on rate, while the rate for the *syn* isomer is increased by 2 orders of magnitude. This effect is almost certainly steric in origin, though contribution from conformational effects is possible.

Having measured all diolate cycloreversion rates, it becomes clear that none of the diolates are kinetically competent to explain the observed turnover rate under catalytic conditions. The observed turnover frequency with 0.009 M total rhenium is 1.4×10^{-6} M s⁻¹ for formation of *cis*-stilbene; the fastest rate of formation from diolate, assuming *all* of the rhenium exists as diolate, is only one-third of that rate. (Attempting to account for alkene formation from some small amount of the *anti*-diolate, estimated to be no more than 1/10 the concentration of the *syn* diolate, fails to reconcile the discrepancy.) Analysis of the turnover frequency for styrene oxide at similar reactant concentration leads to a similar result; the *syn*-diolate is incapable of generating alkene as fast as it is forming. Here, the faster-reacting *anti*-diolate could be a contributor, but solution of the hypothetical rate expression still requires that the *anti*-diolate be present in at least the concentration of the *syn* isomer for diolate fragmentation to explain the rate of alkene production. Since it is not observed at all until very late in the reaction, we conclude that here too the diolates are kinetically incompetent to explain the rate of alkene formation. Consequently, we must conclude that there is an alkene-forming process that is independent of the diolates and propose that to be direct fragmentation of the coordinated epoxide complex.

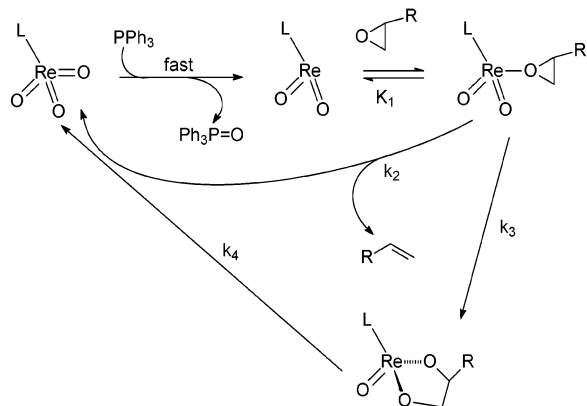


Stoichiometric reactions of Tp'Re(O)(OH)OEt (**3**) confirm this. A mixture of **3** and *cis*-stilbene oxide was allowed to react for 30 min at 75 °C. Formation of both free *cis*-stilbene and the diphenyldiolate **5s** was observed. In this period of time, any diolate formed could have undergone <5% fragmentation. Both stilbene and diphenyldiolate were observed; the majority of the epoxide had been converted to stilbene, and the stilbene:diolate

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Table 2. Rates of Alkene Production, 75 °C, C₆D₆ Solvent

[Re] _{total} , mM	alkene	[epoxide] ₀ , M	[PR ₃] ₀ , M	additive	k _{obs} , 10 ⁻⁶ M s ⁻¹
4.5	<i>cis</i> -stilbene	0.175	0.199		0.491
8.4	<i>cis</i> -stilbene	0.175	0.199		1.33
13.5	<i>cis</i> -stilbene	0.175	0.199		2.63
18.1	<i>cis</i> -stilbene	0.175	0.199		2.60
22.6	<i>cis</i> -stilbene	0.175	0.199		3.95
8.4	<i>cis</i> -stilbene	0.044	0.199		0.943
8.4	<i>cis</i> -stilbene	0.087	0.199		1.13
8.4	<i>cis</i> -stilbene	0.175	0.199		1.41
8.4	<i>cis</i> -stilbene	0.351	0.199		1.63
8.4	<i>cis</i> -stilbene	0.360	0.199		1.66
8.4	<i>cis</i> -stilbene	0.530	0.199		1.85
8.4	<i>cis</i> -stilbene	0.880	0.199		1.93
8.4	<i>cis</i> -stilbene	0.175	0.360		1.53
8.4	<i>cis</i> -stilbene	0.175	0.540		1.39
8.4	<i>cis</i> -stilbene	0.175	0.720		1.41
8.4	<i>cis</i> -stilbene	0.175	1.00		1.08
8.4	<i>cis</i> -stilbene	0.175	0.261	0.251 M Ph ₃ PO	1.22
8.4	<i>cis</i> -stilbene	0.175	0	0.199 M P(OEt) ₃	1.07
8.4	<i>cis</i> -stilbene	0.175	0.199	0.018 M CH ₃ CN	1.46
8.4	<i>cis</i> -stilbene	0.175	0.199	0.036 M Et ₂ O	1.48
9.1, Tp'ReO(OH) ₂	<i>cis</i> -stilbene	0.175	0.199		1.45
8.5, Tp'Re(O)(OH)(OEt)	<i>cis</i> -stilbene	0.175	0.199		1.29
8.4	styrene	0.175	0.199		0.039
8.4	styrene	0.175	0.199	0.17 M stilbene oxide	0.0471
8.4	4-methoxytyrene	0.175	0.199		0.0866
8.4	4-methylstyrene	0.175	0.199		0.0632
8.4	4-fluorostyrene	0.175	0.199		0.0424
8.4	4-(trifluoromethyl)styrene	0.175	0.199		0.0750
8.4	4-bromostyrene	0.175	0.199		0.0511

Scheme 3

ratio was 3.8. No trans isomer of either diolate or alkene was detected. Reaction of **3** with styrene oxide (in the absence of PPh₃) led to a 5.5:1 ratio of styrene:**4s**. A similar experiment run under catalytic conditions was performed on *cis*-stilbene oxide with Tp'ReO₃/PPh₃, heating to 75 °C for 6 min (to avoid rhenium turnover to the extent possible). A 17% conversion of the epoxide was seen; the stilbene:diolate ratio here was 4.4.

This new model (Scheme 3) appears to incorporate all known features of the catalytic system. Fast reduction of Tp'ReO₃ leads to a Re(V) complex. This may be hydrated as the bishydroxide, but loss of water to free the dioxo should be kinetically fast, given the ease of forming the ethoxy hydroxide complex **3**. Coordination of epoxide gives a metastable intermediate which can either ring expand or fragment directly to alkene and trioxide. Early in the reaction, the majority of rhenium exists as either free Tp'ReO₂ (or its hydrate) or as the bound epoxide complex; the stoichiometric reactions indicate that k_2/k_3 is approximately 4, so rapid formation of alkene is seen initially. However, because the diolate **4** or **5** cycloreverts slowly, this

compound accumulates and removes the more active rhenium dioxo complex from the system. Eventually a steady state is reached where the rate of diolate fragmentation equals its rate of formation from the epoxide complex, that is

$$k_3[\text{LReO}_2\text{-epoxide}] = k_4[\text{diolate}] \quad (3)$$

Under these conditions, the distribution of rhenium among various species is constant, and the overall turnover is given by the expression

$$d[\text{alkene}]/dt = k_2[\text{LReO}_2\text{-epoxide}] + k_4[\text{diolate}] \quad (4)$$

Substituting the above steady-state equality (eq 3), the rate expression reduces to

$$d[\text{alkene}]/dt = (k_2 + k_3)[\text{LReO}_2\text{-epoxide}] \quad (5)$$

At low epoxide concentrations, the epoxide complex is formed in equilibrium with free LReO₂, but at high concentrations of epoxide [LReO₂-epoxide] approaches a constant value, expressed by [Re]_T - [diolate]. Thus, the reaction will be first order in rhenium and zero order in phosphine and will show saturation behavior in epoxide, as observed.²⁶

By carefully measuring the diolate concentration formed under catalytic conditions, we can confirm the results of the experiment that showed competitive ring expansion and deoxygenation. The turnover rate was known to be 1.4×10^{-6} M s⁻¹. Quantitation of diolate (vs internal standard) showed that it accumulated to 4.9×10^{-3} M (average of 11 measurements over the course of the reaction); this compares to an estimated

(26) A reviewer has suggested that the origin of saturation lies in shifting the composition of the catalyst resting state from predominantly Tp'ReO₂ at low [epoxide] to primarily diolate at high [epoxide]. This hypothesis is ruled out because the observed rate at saturation significantly exceeds the rate of diolate cycloreversion under identical conditions.

total rhenium concentration of 8.5×10^{-3} M (2.4 ± 0.5 mg/0.5 mL based on $\text{Tp}'\text{ReO}_3$). The remaining 3×10^{-3} M rhenium could easily lie below detection limits given that the 0.18 M epoxide signals dominate the ^1H NMR spectrum. Finally, k_4 is known (Table 1) to be $6.0 \times 10^{-5} \text{ s}^{-1}$ for **5s**. Rearranging eq 4 above gives

$$k_2[\text{LReO}_2\text{-epoxide}] = \text{rate} - k_4[\text{diolate}] \quad (6)$$

Dividing eq 6 by eq 3 gives $k_2/k_3 = 3.8$, identical to the stilbene:diolate ratio observed when $\text{Tp}'\text{Re}(\text{O})(\text{OH})\text{OEt}$ reacts with *cis*-stilbene oxide.

Further, the model adequately explains the competition experiment between *cis*-stilbene oxide and styrene oxide. Because binding, ring expansion, and fragmentation are separate processes, the turnover rate for any individual epoxide will be a composite of all these individual processes. However, the outcome when there are different epoxides present will be determined by a combination of the competitive binding of each epoxide with rhenium, the relative rates of ring expansion and direct fragmentation for the two epoxide complexes, and the specific rate of diolate fragmentation for each of the diolate complexes. A rigorous attempt to fit the observed kinetic behavior to the model requires good estimates for epoxide binding; since we have not been able to conclusively identify an epoxide complex, this analytical fitting is not possible. Fitting the initial curve is also complicated by the heterogeneous reaction resulting in reduction of $\text{Tp}'\text{ReO}_3$.

The electronic effects on catalytic reduction of styrene oxides become somewhat clearer, in that *anti*-diolate cycloreversion has been shown to exhibit a bifurcated Hammett plot.²² At a minimum, parallel behavior for the *syn* diastereomer becomes a contributor to k_{obs} . Without separating the contribution by k_2 and k_4 for each substituent, further quantitative interpretation is not possible. However, variation in binding and in the competition between ring expansion and fragmentation provides ample qualitative explanation for the behavior.

Direct atom transfer to rhenium represents the microscopic reverse of a number of reactions of LReO_3 complexes.²⁷ In a sense it also parallels the O atom transfer from rhenium peroxo complexes to alkenes, although in this latter reaction there appears to be no stable intermediate in the O atom transfer process.²⁸ In our case, the reaction could be concerted, or it could proceed through a variety of intermediates. Competing formation of diolate strongly suggests that any intermediate would be diverted to this more stable species and supports concerted fragmentation as the direct atom transfer mechanism.

An important consequence of the mechanistic picture provided here is that interaction of LReO_3 with alkenes, known to proceed to diolate in the case of a strained alkene, must be capable of proceeding by either of two processes. The "normal" mechanism would be by the concerted but asynchronous [3+2] pericyclic mechanism involving interaction of two oxo ligands with the alkene,²² leading to the thermodynamically preferred diolate complex. The other would be an epoxidation reaction, arising from interaction of a single terminal oxo ligand with the alkene, followed by a ring expansion reaction. Detecting this possibility as a bishydroxylation mechanism remains a significant challenge

given that the diolate will always be thermodynamically preferred compared to the epoxide complex. Earlier attempts to detect crossover were not successful.²⁹ Some parallel is seen in the chemistry of dioxoruthenium(VI) complexes; alkenes are epoxidized, while alkynes produce enediolate species.³⁰ Earlier computational work has also considered the issue.³¹

Conclusions

Reduction of $\text{Tp}'\text{ReO}_3$ with PPh_3 leads to a reactive $\text{Re}(\text{V})$ species that efficiently removes oxygen from epoxides in a catalytic fashion. The isolated $\text{Re}(\text{V})$ compound is proposed to be $\text{Tp}'\text{Re}(\text{O})(\text{OH})_2$ on the basis of its spectroscopic and chemical behavior, and by prediction of computational modeling. This species can lose water easily to generate the more reactive $\text{Tp}'\text{ReO}_2$, which is proposed as the catalytically active species in solution. On the basis of the behavior toward styrene oxide and *cis*-stilbene oxide, this rhenium species can engage in at least two separate reactions with epoxides, each of which occurs after coordination of the epoxide. Ring expansion can form a diolate complex. Steric factors kinetically drive this reaction to the contrathermodynamic *syn* isomer; the *anti* isomer only forms to any identifiable extent late in the catalytic reaction. The independently measured kinetics of diolate cycloreversion make it impossible for this reaction and subsequent diolate cycloreversion to be primarily responsible for alkene formation under catalytic conditions; direct fragmentation of the coordinated epoxide is proposed to be the major source of alkene. Establishment of a steady-state distribution of rhenium between the diolate complex (major, but of low reactivity) and coordinated epoxide (highly reactive, but below detection limits) provides a good rationale for the overall kinetic behavior and of competition experiments between the two epoxides.

Experimental Section

General procedures have been described previously.^{6b} $\text{Tp}'\text{ReO}_3$ was prepared by a literature procedure and dried under vacuum at 150 °C for 15 h. Other compounds were used as purchased in synthesis (Aldrich, reagent grade); samples for kinetics were dried over CaH_2 (see below). Samples of <5 mg were weighed on a calibrated Cahn Model 29 microbalance.

[Hydridotris(3,5-dimethyl-1-pyrazolyl)borato]bishydroxyoxorhenium (1). **Method A.** Water (33.9 μL , 1.882 mmol) was added to a suspension containing $\text{Tp}'\text{ReO}_3$ (0.25 g, 0.47 mmol) and polymer-supported triphenylphosphine (0.204 g, 0.61 mmol) in THF (50 mL). The solution was then placed under reduced pressure to ensure the removal of any dissolved oxygen. The colorless solution was allowed to stir for 48 h and over time became dark blue. The solution was then filtered and concentrated under reduced pressure. Treatment of the solution with pentanes resulted in the precipitation of a light blue powder. Yield: 1.38 g (2.58 mmol, 55%). ^1H NMR (C_6D_6): δ 12.97 (br s, 2H), 5.52 (s, 2H), 5.24 (s, 1H), 2.81 (s, 6H), 2.41 (s, 3H), 2.15 (s, 6H), 1.87 (s, 3H). ^1H NMR (CD_2Cl_2): δ 12.8 (br s, 2H), 6.07 (s, 2H), 5.60 (s, 1H), 2.73 (s, 6H), 2.50 (s, 6H), 2.30 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (CD_2Cl_2): δ 156.1, 152.5, 148.1, 143.4, 108.1, 106.7, 14.0, 13.8, 12.6, 12.1. IR (KBr): 3335 (ν_{OH}), 2926, 2535 (ν_{BH}), 1543, 1450, 1202, 1070, 967 (ν_{ReO}), 865, 814, 786, 647 cm^{-1} . MS (FAB): $m/z = 534, 516$ ($[\text{ReO}]^+$). Exact mass: 534.1561, calcd for $\text{C}_{15}\text{H}_{24}\text{BN}_6^{187}\text{ReO}_3$ 534.1561.

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Method B. $\text{Tp}'\text{ReOCl}_2$ (0.049 g, 0.086 mmol) was placed in a 250 mL thick-walled glass bomb equipped with a magnetic stir bar. The vessel was evacuated, and 15 mL of CH_3CN was vacuum transferred. Then under a flow of argon, NEt_3 (0.087 g, 0.86 mmol) and H_2O (0.094 g, 5.25 mmol) were added. The solution was freeze–pump–thaw degassed and heated at 80 °C for 24 h. The reaction vessel was then opened in the glovebox, and its contents were poured into a 25 mL round-bottom flask attached to a fritted apparatus. The solution was filtered and concentrated under reduced pressure. Treatment of the solution with pentanes resulted in the precipitation of $\text{Tp}'\text{ReO}(\text{OH})_2$. The yield was 0.0064 g (0.012 mmol, 14%).

[Hydridotris(3,5-dimethyl-1-pyrazolyl)borato]chlorohydroxyoxorhenium (2). Concentrated aqueous HCl (30.0 μL , 0.51 mmol) was added to a solution containing $\text{Tp}'\text{ReO}_3$ (0.125 g, 0.235 mmol) and triphenylphosphine (0.111 g, 0.423 mmol) in THF (20 mL). The solution was then placed under reduced pressure to ensure the removal of any dissolved oxygen. The suspension was allowed to stir for 48 h and over time became dark blue. The solution was evaporated to dryness to yield a blue solid. Column chromatography on silica gel (Scientific Adsorbents Inc., 32–63) with CH_2Cl_2 as eluent yielded a deep blue product. Yield: 0.093 g (0.16 mmol, 71%). $^1\text{H NMR}$ (CDCl_3): δ 16.5 (br s, 1H), 6.062 (s, 1H), 6.054 (s, 1H), 5.63 (s, 1H), 2.91 (s, 3H), 2.80 (s, 3H), 2.62 (s, 3H), 2.58 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3): δ 158.1, 157.4, 153.9, 149.0, 147.0, 143.4, 109.1, 108.7, 107.9, 15.3, 15.2, 14.3, 12.81, 12.79, 12.6. IR (KBr): 3448 (ν_{OH}), 2929, 2546 (ν_{BH}), 1545, 1450, 1419, 1386, 1368, 1204, 1074, 971 (ν_{ReO}), 864, 814, 786, 690, 642, 616 cm^{-1} .

[Hydridotris(3,5-dimethyl-1-pyrazolyl)borato]ethoxyhydroxyoxorhenium (3). Ethanol (5.0 mL) was added to a solution containing $\text{Tp}'\text{ReO}_3$ (0.15 g, 0.282 mmol) and polymer-supported triphenylphosphine (0.188 g, 0.564 mmol) in THF (35 mL). The solution was then placed under reduced pressure to ensure the removal of any dissolved oxygen. The colorless solution was allowed to stir for 72 h and over time became blue. The solution was then filtered, and the volatiles were removed in vacuo, leaving a blue solid. Yield: 0.150 g (0.267 mmol, 95%). $^1\text{H NMR}$ (C_6D_6): δ 13.96 (br s, 1H), 5.86 (m, 1H), 5.58 (s, 1H), 5.50 (s, 1H), 5.38 (m, 1H), 5.31 (s, 1H), 2.92 (s, 3H), 2.63 (s, 3H), 2.49 (s, 3H), 2.18 (s, 3H), 2.16 (s, 3H), 1.90 (s, 3H), 1.60 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (C_6D_6): δ 156.8, 155.7, 153.8, 147.0, 146.2, 142.3, 108.1, 108.0, 106.9, 77.3, 18.9, 14.3, 14.1, 14.0, 12.4, 12.3, 12.0. IR (KBr): 3335 (ν_{OH}), 2924, 2540 (ν_{BH}), 1543, 1450, 1203, 1070, 961 (ν_{ReO}), 815, 643 cm^{-1} .

[Hydridotris(3,5-dimethyl-1-pyrazolyl)borato](syn-phenyl-1,2-diolato)oxorhenium (4s). Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed 30 mg of $\text{Tp}'\text{ReO}_3$ (0.057 mmol) and a magnetic stir bar. The vessel was evacuated, and 20 mL of dry benzene was vacuum transferred into it. The vessel was then filled with argon, and under a flow of argon, 33.8 μL of triethyl phosphite (0.282 mmol) and 19.3 μL of styrene oxide (0.169 mmol) were added. The solution was then freeze–pump–thaw degassed and heated at 75 °C for 90 min. The reaction vessel was opened to the air, its contents were poured into a round-bottom flask, and the volatiles were removed on a rotary evaporator. The product was then purified by chromatography on silica gel (Scientific Adsorbents Inc., 32–63). Initial elution with 1:1 hexane/dichloromethane was used to remove olefin and unreacted epoxide. Dichloromethane was used to elute the blue diolate. The dichloromethane solution was then dried with MgSO_4 and filtered and the solvent removed in vacuo to give a blue powder. Yield: 0.0138 g (0.0217 mmol, 38%). $^1\text{H NMR}$ (CDCl_3): δ 7.71 (d, $J = 7.50$ Hz, 2H), 7.43 (t, $J = 7.50$ Hz, 2H), 7.30 (t, $J = 7.50$ Hz, 2H), 6.01 (s, 1H), 5.98 (s, 1H), 5.89 (dd, $J = 7.68$, 9.70 Hz, 1H), 5.82 (dd, $J = 7.68$, 9.70 Hz, 1H), 5.49 (s, 1H), 5.40 (t, $J = 9.70$ Hz, 1H), 2.66 (s, 3H), 2.64 (s, 3H), 2.56 (s, 3H), 2.54 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H). $^1\text{H NMR}$ (C_6D_6): δ 7.83 (d, $J = 7.68$ Hz, 2H), 7.34 (t, $J = 7.68$ Hz, 2H), 7.19 (t, 1H), 6.13 (dd, $J = 7.68$, 9.61 Hz, 1H), 6.00 (dd, $J = 7.68$, 9.88 Hz, 1H), 5.59 (m, 3H), 5.10 (s, 1H), 2.83 (s, 3H), 2.81 (s,

3H), 2.27 (s, 3H), 2.17 (s, 6H), 1.86 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3): δ 157.7, 157.2, 154.2, 147.9, 147.3, 143.4, 143.1, 128.7, 127.1, 126.4, 108.1, 108.08, 107.5, 98.4, 89.4, 15.7, 14.5, 14.0, 12.93, 12.85, 12.8. IR (KBr): 2925, 2536 (ν_{BH}), 1545, 1451, 1420, 1384, 1204, 1071, 957 (ν_{ReO}), 814, 697, 646 cm^{-1} . MS (FAB): $m/z = 637.2$ [$\text{M}^+ + 1$].

[Hydridotris(3,5-dimethyl-1-pyrazolyl)borato](syn-cis-1,2-diphenyl-1,2-diolato)oxorhenium (5s). Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed 30 mg of $\text{Tp}'\text{ReO}_3$ (0.057 mmol), 33.2 mg of *cis*-stilbene oxide (0.169 mmol), and a magnetic stir bar. The vessel was evacuated, and 20 mL of dry THF was vacuum transferred into it. The vessel was then filled with argon, and under a flow of argon, 67.7 μL of triethyl phosphite (0.565 mmol) was added. The solution was then freeze–pump–thaw degassed and heated at 75 °C for 30 min. The reaction vessel was opened to the air, its contents were poured into a round-bottom flask, and the volatiles were removed on a rotary evaporator. The product was then purified by chromatography on silica gel (Scientific Adsorbents Inc., 63–200). Initial elution with 2:1 hexane/dichloromethane was used to remove olefin and unreacted epoxide. Pure dichloromethane was used to elute the blue diolate. The dichloromethane solution was then dried with MgSO_4 and filtered, and the volatiles were removed to give a blue powder. Yield: 0.016 g (0.022 mmol, 51%). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.32 (dd, 4H), 7.18 (m, 6H), 6.70 (s, 2H), 6.00 (s, 2H), 5.52 (s, 1H), 2.58 (s, 6H), 2.57 (s, 6H), 2.21 (s, 3H), 2.17 (s, 3H). $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 7.56 (d, 4H), 7.10 (m, 6H), 6.93 (s, 2H), 5.58 (s, 2H), 5.21 (s, 1H), 2.76 (s, 6H), 2.31 (s, 3H), 2.18 (s, 6H), 1.92 (s, 3H). $^{13}\text{C NMR}$ (400 MHz, CDCl_3): δ 158.0, 155.5, 147.6, 144.3, 142.8, 128.7, 127.7, 126.9, 108.1, 107.2, 99.8, 16.7, 14.2, 13.0, 12.9. IR (KBr): 2926, 2542 (ν_{BH}), 1544, 1451, 1383, 1204, 1073, 958 (ν_{ReO}), 943, 723, 698, 669 cm^{-1} . MS (FAB): $m/z = 711.2$ [$\text{M}^+ - 1$].

Kinetics. Kinetics were followed by measuring $^1\text{H NMR}$ integrations; where necessary 1,4-di-*tert*-butylbenzene was included as an integration standard, and all spectra were subjected to a relaxation delay of 15–30 s ($>5T_1$) per pulse to ensure accurate integration. All epoxide solutions were prepared by mixing epoxide, PPh_3 , and 1,4-di-*tert*-butylbenzene in the appropriate solvent and then predrying the mixture over CaH_2 before adding it to dry $\text{Tp}'\text{ReO}_3$. A representative procedure is given.

cis-Stilbene oxide (0.106 g, 0.542 mmol), triphenylphosphine (0.156 g, 0.596 mmol), and 1,4-di-*tert*-butylbenzene (1.61 mg, 0.0084 mmol) were dissolved in 3 mL of C_6D_6 and dried over CaH_2 . A 0.5 mL aliquot was then added to an NMR tube containing $\text{Tp}'\text{ReO}_3$ (2.41 mg, 0.0045 mmol), and the tube was sealed under vacuum. The tube was then submerged and heated to 75.3 ± 0.1 °C in a water/ethylene glycol bath. The sample tube was periodically removed and cooled to 25 °C, and the $^1\text{H NMR}$ spectrum was recorded. The concentration of stilbene oxide (versus di-*tert*-butylbenzene) was plotted versus time. Linear regression was applied to all points past $t = 0$; the slope of this line ($r^2 > 0.98$) was taken as k_{obs} .

Other kinetic measurements used analogous procedures.

Burst Experiment with $\text{Tp}'\text{ReO}(\text{OH})(\text{OEt})$. *cis*-Stilbene oxide (0.106 g, 0.542 mmol), triphenylphosphine (0.156 g, 0.596 mmol), and 1,4-di-*tert*-butylbenzene (1.29 mg, 0.0068 mmol) were dissolved in 3 mL of C_6D_6 and dried over CaH_2 . A 0.5 mL aliquot was then added to an NMR tube containing $\text{Tp}'\text{ReO}(\text{OH})(\text{OEt})$ (2.1 mg, 0.0038 mmol), and the tube was sealed under vacuum. The tube was then heated to 75.3 °C in a water/ethylene glycol bath. The sample tube was periodically removed and cooled to 25 °C, and the NMR spectrum was recorded.

Stoichiometric Reactions between $\text{Tp}'\text{ReO}(\text{OH})(\text{OEt})$ and Epoxides. Styrene oxide (10 μL , 0.083 mmol) was dissolved in 1.0 mL of C_6D_6 and dried for 30 min over CaH_2 . A 0.5 mL portion of this solution was added to 5 mg of $\text{Tp}'\text{ReO}(\text{OH})(\text{OEt})$ (0.0089 mmol) in an NMR tube under argon; the tube was evacuated, degassed with three freeze–pump–thaw cycles, and sealed under vacuum. After an initial NMR spectrum was recorded, the sample was heated to 75 °C for 20

min. The NMR spectrum after heating was recorded and showed complete conversion of the monoethoxide to diolate and Tp^*ReO_3 ; signals for styrene were also quite evident. Integration of peaks at 7.83, 6.13, 6.00, 5.59, and 5.10 ppm (for the *syn*-diolate) was compared to that of peaks at 6.63, 5.64, and 5.11 ppm (for styrene). The ratio of compounds, corrected for the requisite number of protons per molecule, was 5.5 styrene:diolate.

A similar procedure was used for stilbene oxide. A solution containing 17.7 mg of *cis*-stilbene oxide (0.09 mmol) in 0.5 mL of C_6D_6 was added to 5 mg of **3** (0.0089 mmol) in an NMR tube, and the tube was degassed and sealed under vacuum. The sample was heated

for 30 min. Here, the ratio of *cis*-stilbene:diolate was 3.8, on the basis of integration of signals at 5.58 and 5.21 ppm (for diolate) and 6.46 ppm (for stilbene).

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Supporting Information Available: Spectroscopic data for **1**, **3**, **4s**, and **5s** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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