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Reaction of Strained-Ring Heterocycles with a Rhenium(V) Dioxo Complex

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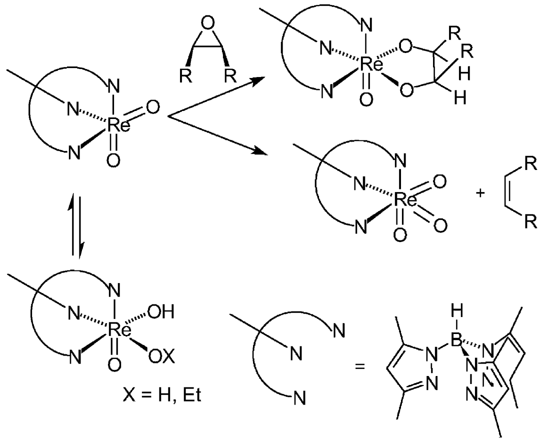
Epoxides and episulfides react stereospecifically with $Tp'ReO_2$, generated in situ from $Tp'ReO_3$ and PPh_3 (Tp' = hydrido-tris(3,5-dimethylpyrazolyl)borate). A combination of direct atom transfer, resulting in alkene, and ring expansion, resulting in a five-member rhenacycle, is observed. When epoxides *cis*- and *trans*-cyclooctene oxide are used, the ring-expanded product is exclusively the corresponding Re(V) diolate. However, when an episulfide such as ethylene sulfide or *ci*s- or *trans*-cyclooctene sulfide is used, the predominant observed rhenium product is a dithiolate. Retention of initial stereochemistry is observed in all cases. Selectivity between atom transfer and ring expansion is measured for each substrate, and a mechanistic model is proposed to account for the reaction outcome.

Atom transfer reactions have gained recognition as a particularly useful class of transformations. Catalyzed atom transfer reactions such as epoxidations in particular represent a particularly efficient means of utilizing inexpensive, readily available reagents for making highly versatile functional groups such as epoxides and vicinal diols.[1] In a broader view, atom transfer to or from organic substrates can have other applications; removal of oxygen from an epoxide "deprotects" the alkene product;[2] utilizing carbohydrates for fine chemical synthesis usually requires removal of an oxygenated functionality.[3] Removal of sulfur from organic compounds is key to hydrodesulfurization reactions in the petrochemical industry.[4]

In the course of investigating the mechanism of a rhenium-catalyzed O atom transfer from epoxides to phosphines, both direct observation and indirect measurement of kinetics demonstrated that the reactive Re(V) intermediate interacting with epoxide led to two competitive processes:[5] one led to alkene via what was apparently direct atom transfer, while the second was an unusual stereospecific ring expansion to give a diolate complex. While the diolate was known to generate alkene on thermolysis,[6] measurement of kinetic behavior rigorously demonstrated that this latter fragmentation was responsible for only a fraction of the alkene formed. Stoichiometric reaction of precursors to $Tp'ReO_2$ ($Tp'Re(O)(OH)_2$, **1**, or $Tp'Re(O)(OH)(OEt)$, **2**) in the absence of PPh_3 under conditions of minimal diolate cycloreversion (eq 1) also gave a mixture of alkene and diolate.



(1)

The ring expansion is unusual in two respects. First, it proceeds with a high degree of stereoselectivity with retention of configuration at the migrating carbon. The substrates used in the earlier study (styrene oxide and *cis*-stilbene oxide) are more prone to Lewis- or Bronsted-acid-catalyzed heterolysis of the C−O bond than most epoxides, but it could be that rapid trapping by the Re═O group occurs more rapidly than single bond rotation occurs in a putative carbocation intermediate. We thus wished to rigorously test the capacity for maintaining high stereospecificity in this reaction. Another unusual facet was that it occurred to give the less thermodynamically preferred syn diastereomer. While a basic hypothesis for understanding controlling steric interactions was proposed, further insight would be useful.

Sulfur atom transfer is an interesting contrast both in terms of potential technologic applications and also

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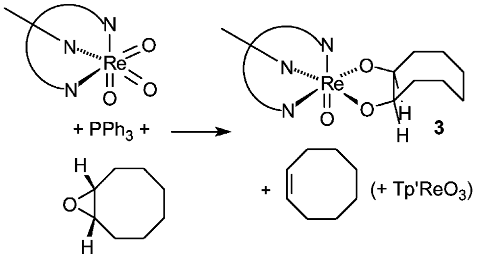
in terms of periodic comparisons between S and O.[7] Preliminary work had strongly suggested that the thermodynamics of S atom transfer in this system were notably different than for O atom transfer in that mono- and dithiolates were thermally stable to the alkene fragmentation seen for diolates.[8] This opened the question of whether episulfides would undergo direct atom transfer by analogy with epoxides, or whether the thermodynamic preference for monothiodiolate would drive ring expansion to that species. Further, the stereochemical outcome from episulfides need not parallel that for epoxides and thus might probe questions of mechanism.

We report here results of several related investigations. Consistent with earlier work, cyclooctene epoxides undergo competitive, stereospecific atom transfer and ring expansion. Unexpectedly, episulfides engage in both direct atom transfer and net ring expansion, but the ultimate rhenium-containing product is a dithiolate of the same configuration as the episulfide.

Results

cis-Cyclooctene oxide reacts with Tp′ReO$_3$/PPh$_3$ (which generates **1** in situ) at 75 °C in benzene to give a mixture of *cis*-cyclooctene and Tp′Re(O)(O−C$_8$H$_{14}$−O) **3** (eq 2). The latter was shown to be the cis compound on the basis of the C_s symmetry in the ^{1}H NMR spectrum. Comparison of the chemical shifts of the diolate to that prepared by cyclocondensation of *cis*-cyclooctanediol, in addition to NOE experiments, clearly showed exclusive formation of the syn isomer (carbinol CH proton at δ 5.51; Tp′ vinyl proton at δ 5.19) and the absence of the anti isomer (carbinol proton at δ 5.60, vinyl Tp′ proton at δ 5.22). Using initial concentrations of 23 mM epoxide, 23 mM PPh$_3$, and 6.0 mM rhenium, the reaction proceeded to 25% conversion after 15 h at 75 °C and 80% conversion after 5 days at the same temperature.



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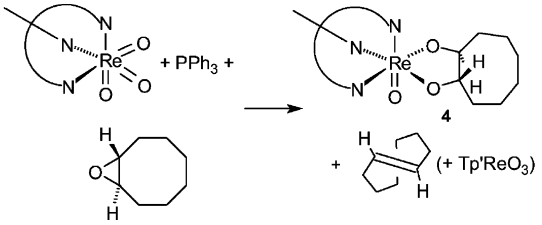
(2)

The selectivity for alkene:diolate drops from 38:1 after 15 h to 24:1 after 5 days at 75 °C, on the basis of integration of ^{1}H NMR signals. Prior work had established that this diolate would thermally fragment to form *cis*-cyclooctene, but the extrapolated rate constant at 75 °C was 2.30×10^{-7} s^{-1} ($t_{1/2} = 800$ h), and we thus conclude that little cycloreversion occurs during the 120 h of reaction.

A control experiment examined interaction of *cis*-cyclooctene oxide with PPh$_3$ in C$_6$D$_6$. After 5 days at 75 °C, no change was seen.

trans-Cyclooctene oxide (prepared by rhenium-mediated epoxidation[9] of *trans*-cyclooctene[10]) reacts under the same conditions to give, likewise, a mixture of *trans*-cyclooctene and the trans diolate **4** (eq 3). The diolate **4** was identical to that prepared by reductive cyclocondensation of *trans*-cyclooctane-1,2-diol with Tp′ReO$_3$/PPh$_3$. This compound is stable at 135 °C for more than two weeks in toluene-d_8 under vacuum. Conversion at this point was 75%; the alkene:diolate ratio seen from the epoxide was 0.53:1 after 45 h at 75 °C. Care must be taken in interpreting this ratio, in that *trans*-cyclooctene reacts with the Tp′ReO$_3$ liberated from direct atom transfer to also give diolate. (Attempted reaction with *cis*-cyclooctene gives no diolate.) The alkene:diolate ratio thus decreased to 0.35:1 after an additional 6 days at 75 °C.



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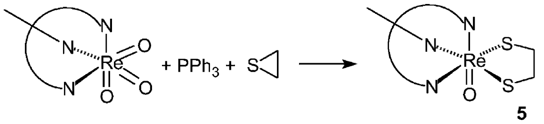
(3)

A control experiment with *trans*-cyclooctene oxide and PPh$_3$ in C$_6$D$_6$ showed no change after 5 days at 75 °C.

Ethylene sulfide reacts under the same conditions to give Tp′Re(O)(S−CH$_2$CH$_2$−S) **5** as the only identifiable rhenium-containing product (eq 4). The material is identical spectroscopically to that made from reductive cyclocondensation of HSCH$_2$CH$_2$SH with Tp′ReO$_3$/PPh$_3$ and is distinctly different from that (**6**) made by cyclocondensation of HOCH$_2$CH$_2$SH with Tp′ReO$_3$/PPh$_3$.[8a] Several specific features confirm this observation. First, the product **5** is C_s-symmetric, while **6** has C_1 symmetry. Sulfur is less electronegative than oxygen, and thus the chemical shifts of the carbinolic CH proton are different for an O-bearing versus an S-bearing carbon: the former appear 0.5−1.0 ppm downfield from the latter. Finally, mass spectrometry clearly shows the added mass of sulfur versus oxygen; **5** has a parent ion at m/z 592, while **6** has a parent ion at 576. Ethylene is presumably a byproduct of the reaction, but only a minor peak at δ 4.5 is apparent in the sealed-NMR-tube reaction for this volatile product and no quantitation of selectivity was attempted.



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(4)

Episulfides are known to react with PPh$_3$ in the absence of any other reagent and are known to give direct atom transfer by what is presumed to be a concerted reaction on the basis of stereochemical studies and the absence of solvent effects.[11] A control experiment with *cis*-cyclooctene episulfide (prepared from *cis*-

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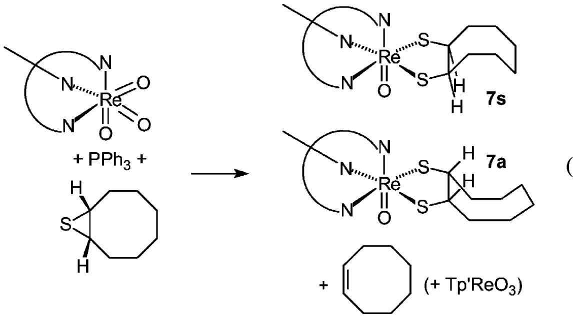
cyclooctene oxide and elemental sulfur with $NaBH_4$)[12] showed that at 75 °C this reaction had proceeded to 20% conversion after 3 h. When Tp′ReO_3 was added to a similar mixture, reaction at room temperature was complete after the same 3 h (eq 5). The rhenium-containing product was the *cis*-1,2-cyclooctanedithiolate **7**, which was isolated from column chromatography of the reaction mixture. Both syn and anti isomers were present, as demonstrated by 2D and NOE NMR experiments; the syn/anti ratio was initially 0.7:1. On heating the purified mixture of isomers to 75 °C for 6 days (under vacuum in C_6D_6), the isomeric ratio changed to 10:1 anti/syn. The structures were proved by the C_s symmetry exhibited in the ^1H and ^{13}C NMR spectra and by observation of the molecular ion at *m*/*z* 674 in the mass spectrum. NOE studies showed weak enhancement of ring methylene protons at 3.03 and 2.64 ppm on irradiation of a methyl signal at 2.46 ppm for the less stable isomer; irradiation of the nearby methyl signal at 2.43 ppm resulted in enhancement of the thiocarbinolic protons in the more stable anti isomer at 4.63 ppm (and no enhancement in the syn isomer at 4.19 ppm). After correcting for the amount of alkene generated in a parallel control reaction (and quantitated relative to 1,4-di-*tert*-butylbenzene internal standard), the alkene:dithiolate selectivity was 4:1.

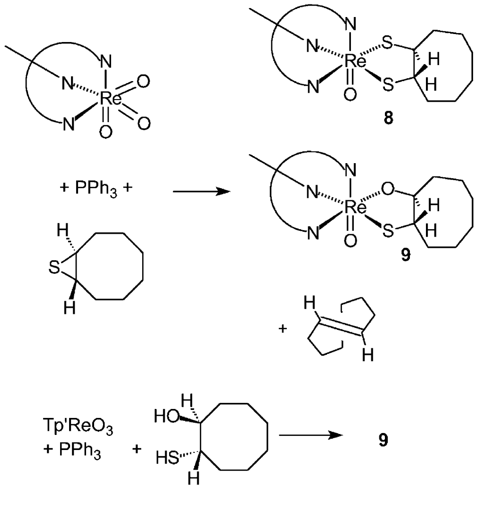


(5)

Reaction of *trans*-cyclooctene episulfide (prepared by molybdenum-catalyzed sulfidation of *trans*-cyclooctene)[13] with PPh_3 does not proceed at an appreciable rate (presumably due to the influence of steric interactions imposed by the ring conformation). However, in the presence of Tp′ReO_3, a complex mixture was produced that included *trans*-dithiolate **8** and *trans*-cyclooctene (Scheme 1). *trans*-Monothiodiolate **9** was also noted. The alkene:**8**:**9** ratio after 1 h at 75 °C was 1.0:0.82:0.17. The dithiolate was isolated by column chromatography and its structure demonstrated by 2D and NOE experiments; particularly noteworthy is the observation of enhancement of the methyl signal at δ 2.43 ppm on irradiation of the thiocarbinolic proton at δ 4.13, but the absence of any enhancement on irradiating the second thiocarbinolic proton at δ 3.59. The mass spectrum of the purified compound also confirmed the presence of two sulfurs; the parent ion was clearly present at *m*/*z* 674.

Given that **9** was not isolated from the above reaction in sufficient amounts to definitively characterize it, independent synthesis was performed. Reductive cyclocondensation of Tp′ReO_3 with *trans*-mercaptocyclooctanol followed by chromatographic purification gave the monothiodiolate in low yield. Significant properties include the absence of symmetry, as expected; NOE enhancement of a single methyl signal (δ 2.35 ppm) on irradiation of the more upfield thiocarbinolic proton at δ 3.95 ppm; no similar enhancement on irradiation of the downfield carbinol proton at δ 4.90 ppm; and a parent ion in the mass spectrum showing a single sulfur at *m*/*z* 658. Only the single diastereomer shown ("*syn*-O; *anti*-S") was observed.

Scheme 1. Reactions Forming *trans*-Thio- and Dithiolates 8 and 9



Earlier work had shown that Tp′ReO(OH)(OEt), formed by reduction of Tp′ReO_3 in the presence of ethanol, was an effective phosphine-free source of Tp′ReO_2. Reaction of this compound with an excess of cyclooctene episulfides gave, for both cis and trans isomers, a mixture of rhenium products. The cis isomer reacted quite rapidly, being complete in 5 min at 75 °C. One of the rhenium products is clearly the dithiolate syn-**7**, based on the location of the thiocarbinolic proton at δ 4.19 ppm; none of the anti isomer is seen at δ 4.63 ppm. A second species is present having signals at δ 3.92 and 5.23 (coupled to each other as shown by a 2D COSY experiment); this is presumed to be one of the *cis*-monothiodiolate isomers **10**. The ratio of cyclooctene:**7**:**10** is 10.0:1.9:1.1. Unfortunately, the rhenium compounds were inseparable by column chromatography. The same experiment with *trans*-cyclooctene is more definitive in that all species present have been previously characterized; the ratio of *trans*-cyclooctene:**8**:**9** was 1.00:0.69:0.36 after 24 h at 75 °C. The reaction had proceeded only to 40% completion, judged from the remaining rhenium ethoxide complex.

Discussion

The chemo- and stereoselectivity of the O atom transfer from cyclooctene oxides is a critical confirmation of the chemistry reported earlier for styrene and *cis*-stilbene oxides. The thermodynamics of the two (cyclooctene + Tp′ReO_3) systems are quite clear, in that the *cis*-diolate preferentially cycloreverts, and the *trans*-alkene preferentially cycloadds to the trioxide, while the converse mixtures (*trans*-diolate, or *cis*-alkene + Tp′ReO_3) are thermally stable well above 100 °C. The fact that *trans*-cyclooctene oxide results in selective formation of

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trans-cyclooctene and the *trans*-diolate emphatically underscores that both direct atom transfer and ring expansion processes avoid intermediates such as radicals or carbocations that would be expected to invert in order to relieve ring strain. (Small amounts of *cis*-cyclooctene are observed after extended reaction of the trans epoxide, but this is consistent with the slow rate of thermal isomerization that occurs in control reactions in the absence of $Tp'ReO_3/PPh_3$.[14])

Estimates of the double bond strain energy in *trans*-cyclooctene range from 9[15] to 12[16] kcal/mol based on comparison with *cis*-cyclooctene; the most recent study gave a value of 11.4 kcal/mol based on heats of hydrogenation in hexane.[17] Experimental thermodynamic data for the epoxides and episulfides is less readily available, but generally reliable computational methods (B3LYP/6-31G**; see Supporting Information) indicate a similar difference for the epoxide ($\Delta E = 9.7$ kcal/mol) and somewhat less for the episulfide ($\Delta E = 6.0$ kcal/mol). This difference effectively disappears for isomers of the diol, monothiodiol, and dithiol. The inherent reaction enthalpy of diolate cycloreversion in the absence of strain is near zero,[18] and all of these systems behave consistently in that the unstrained *cis*-cyclooctene prefers to fragment from the diolate, and strained *trans*-cyclooctene can overcome the effect of entropy to add to $Tp'ReO_3$. Formation of dithiolates represents a thermodynamic sink for the episulfides, because the weaker Re=S bond can now attack both strained and unstrained alkenes. The fate of the system (monothio- or dithiolate) is determined by the relative amounts of alkene, $Tp'ReO_2S$, and $Tp'ReOS_2$ present at various points over the course of the reaction.

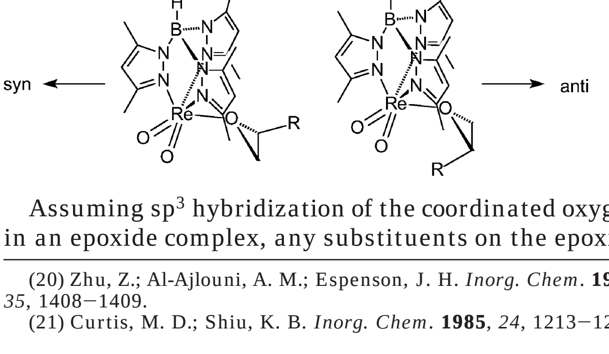
The unusual result, from a thermodynamic point of view, is that in all cases an energetically intermediate result is seen to compete with the ultimate fate of the system. In the case of *trans*-cyclooctene oxide, the unstable alkene is generated competitively with the thermodynamically preferred diolate, while in reactions of the *cis*-epoxide, diolate formation competes with production of the alkene that is preferred here. Likewise, all of the episulfides generate alkene prior to thiodiolate formation.

Fully concerted reactions (branching from a common rhenium epoxide complex) represent the simplest mechanistic explanation for each. Direct atom transfer is the microscopic reverse of the commonly accepted mechanism by which late metal oxo complexes epoxidize alkenes;[19] this mechanism assigns electrophilic "oxene" character to the metal oxo ligand and presumes some analogy to organic carbene-alkene cycloadditions.

The ring expansion reaction is somewhat more problematic with regard to locating concerted analogues. The only direct analogy is another example mediated by high-valent rhenium.[20] The formal description in Woodward−Hoffmann terms is a [1,3]-sigmatropic rearrangement; for it to be thermally allowed it would have to be either $\sigma 2s + \pi 2a$ (invoking an antarafacial interaction along the Re=O π system) or would have to involve an antarafacial interaction between the breaking C−O σ bond and an orbital on rhenium. Neither provides an experimentally testable feature, in that each invokes a nondetectable "inversion" at oxygen. As with other pericyclic reactions, one may propose a biradical or zwitterionic pathway, provided C−O bond formation occurs faster than the bond rotations that would result in isomerized product. In the current context, *trans*-cyclooctene oxide in particular should invert rapidly if any ring-opened intermediate formed, but cis product is notably undetected until after extensive thermolysis.

An interesting alternative for either reaction would be oxidative addition of the C−O bond. Such a direct insertion reaction would preserve stereochemistry in both formation of the metallaoxetane intermediate and its fragmentation to alkene and migration of carbon from Re to O. Three problems exist for this rationale. One minor issue is that tris-pyrazolylborate ligands have a marked tendency to enforce octahedral geometries.[21] This objection is fairly easy to accommodate, though, in that the putative metallacycle is a higher-energy species to begin with (no intermediates are observed), and the Tp′ ligand can lose one arm via $\kappa^3 \rightarrow \kappa^2$ isomerization. A second objection to the metallaoxetane is that extensive computational work[22] has consistently proposed that barriers of more than 30 kcal/mol exist for the proposed transformations of rhenaoxetanes. While current computational methodology does result in fairly good optimized structures for such complexes based on extensive comparisons between optimized structures and crystallographically determined structures, the comparison of gas-phase activation barriers with solution-phase rate constants is less extensive. Further, the comparison between osmaoxetanes and rhenaoxetanes noted that the calculated barriers into and out of the metallacycle were smaller for the rhenaoxetane, enough so that the impact of structural features (substituent electronics, steric interactions, or the impact of strain on a reacting carbon) could alter the actual barrier. Thus computational results cannot rigorously exclude the metallacycle as an intermediate in either reaction.

A third objection is more difficult to accommodate; this deals with the diastereoselectivity of the ring expansion process to give the syn isomer. A concerted reaction offers a coherent steric argument for this outcome (eq 6).



(6)

Assuming sp^3 hybridization of the coordinated oxygen in an epoxide complex, any substituents on the epoxide

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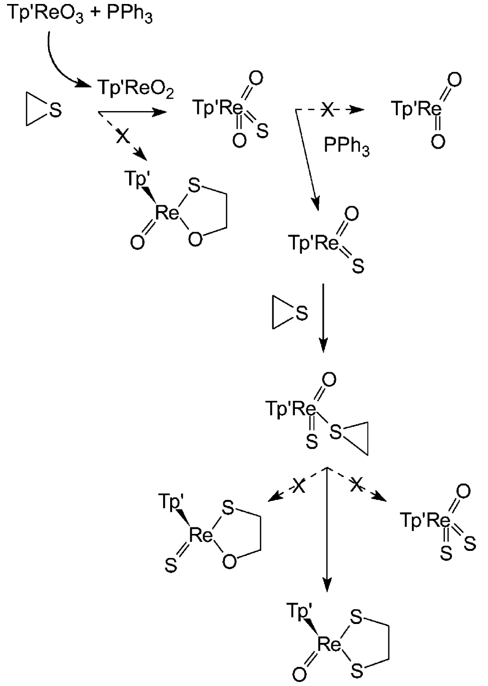
can point either away from the complex (left) or in toward the metal (right). Given the distance between pyrazole methyl groups and the R groups, one presumes the former would be preferred on the basis of poor steric interactions in the latter. If this is the case, then migration of carbon to an oxo ligand (regardless of which carbon moves) effectively locks the stereochemistry into the syn form. A notable supporting observation is that trans substrates react more slowly than cis; presumably the latter can avoid steric clash with the ligand while the former are forced to accommodate some steric strain. However, such a reaction represents at least formally a substitution with retention of configuration. Some formal analogy might be drawn from the vinylcyclopropane rearrangenment, a process suspected to proceed through a biradical that gets trapped as product prior to stereorandomization.[23] The polarization of bonds in our system suggests a more polar transition state, but the absence of significant solvent effects would demand that formation of the incipient new C−O bond accompany to some degree the opening of the epoxide. In any event, the observation of rigorous retention of stereochemistry can be explained adequately by concerted processes for both atom transfer and ring expansion.

Reactions of the episulfides lead to several conclusions. Here in all cases, observation of the alkene provides strong evidence for a direct atom transfer pathway, in that mono- and thiodiolates are thermally resistant to fragmentation of the alkene.[8a] Further, the preservation of stereochemistry eliminates the possibility of generating an intermediate with an invertable carbon.

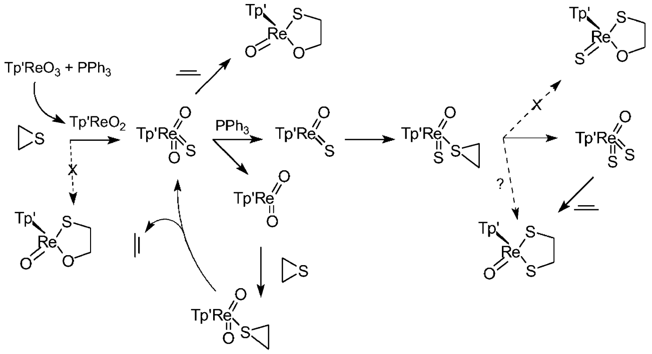
The more remarkable feature is incorporation of two sulfurs in the rhenium product. If we propose the simplest extension of eq 1 to episulfides, the mechanism requires two aspects of selectivity be satisfied (Scheme 2). First, the initial interaction of episulfide with Tp′ReO$_2$ must be highly selective for atom transfer. The preference for direct atom transfer is seen by the high alkene:diolate ratios seen. If ring expansion were competitive here, then formation of thermally inert monothiodiolate would be observed. None is seen under catalytic conditions, although stoichiometric reaction of Tp′ReO(OH)(OEt) shows significant amounts. Since Scheme 2 proposes Tp′ReO$_2$ as a common branch point intermediate under all conditions, the monothiodiolate formation should not be concentration dependent. (We initially presume that, based on the high stereoselectivity observed, the mechanisms involved in both atom transfer and ring expansion will be concerted, though there remains the possibility that oxidative addition of the C−S bond might lead to an unobserved metallacyclic intermediate.)

Second, the putative Tp′ReO$_2$S that forms must selectively react with PPh$_3$ to transfer oxygen rather than sulfur. Triphenylphosphine is a potent thiophile, but the thermodynamic selectivity will be determined by the Re═S versus Re═O bond strengths in addition to the inherent propensity of phosphine to abstract one or the other. Experimentally, ^{31}P NMR spectra show formation of both phosphine oxide and phosphine sulfide. The former is a necessary initiation of the reaction process, but amounts produced appear to be in excess of the ca. 5 mol % catalyst present. The predominance of the phosphine sulfide suggests that, as expected, S atom transfer from rhenium is preferred during catalysis. Kinetic facility of either transfer could be wholly unrelated to thermodynamics, though this seems unlikely for such a straightforward reaction.

Scheme 2. Initial Proposal for the Mechanism by Which Dithiolate Is Generated



Scheme 3. Modified Mechanism for Episulfide Desulfurization



An alternative mechanism is seen in Scheme 3. Here, initiation of the cycle again requires reduction of Tp′ReO$_3$ to Tp′ReO$_2$; preferential direct atom transfer again leads to predominant alkene formation. Phosphine reduction of the terminal sulfide regenerates the dioxo intermediate, completing a catalytic cycle.

However, S atom transfer from rhenium need not be completely selective; O atom transfer will generate Tp′ReOS, which ought to be similar to the dioxo complex in terms of reactivity toward substrate. Selective S atom

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transfer will now generate $Tp'ReOS_2$. This also can be reduced and engage in a separate but indistinguishable catalytic cycle. Thermodynamically, cycloaddition of the alkene (generated in the earlier catalytic cycle) will terminate the processes by formation of the inert dithiolate. Of course, under conditions where no further reduction is likely, $Tp'ReO_2S$ can also cycloadd to the alkene, leading to the monothiodiolate observed in the absence of triphenylphosphine. We did observe formation of a precipitate as the reactants were consumed; careful decantation and addition of a solution of *trans*-cyclooctene led to predominant formation of monothiodiolate. Because the precipitate could not be clearly characterized as the dioxomonosulfide, this experiment is not rigorously conclusive, but it suggests cycloaddition of alkene is a reasonable process[24] for generating the observed products.

One may question whether the ring expansions seen in epoxide chemistry can similarly be explained by readdition of fragmented alkene to $Tp'ReO_3$. The answer is clearly no in the case of unstrained alkenes, in that experimentally these fail to effect this reaction. Even in the case of strained alkenes, the bimolecular cycloaddition process (which does in fact alter the diolate/alkene ratio) is much slower than the initial formation of the diolate.

Conclusion

Reactions of cyclooctene oxides with the reduction product from $Tp'ReO_3$ rigorously demonstrates the retention of stereochemistry in both ring expansion and in direct atom transfer reactions. Reaction of cyclooctene episulfides under the same conditions is more complex. Desulfidation of the *cis*-episulfide by rhenium is faster than the uncatalyzed reaction; the latter is uncompetitive for the *trans*-episulfide. Catalytic desulfidation of both isomers results in predominant formation of dithiolates, but can be accompanied by formation of monothiodiolates. These observations are best explained by a combination of direct atom transfer and readdition of alkene, suggesting that ring expansion of episulfides is not as competitive as for epoxides.

Experimental Section

General Procedures. All reactions were performed using either standard benchtop or inert atmosphere techniques on a double-manifold Schlenk line or in a nitrogen-filled glovebox (Vacuum-Atmospheres Co. HE 493). All deuterated solvents were used as purchased from Cambridge Isotope Labs. Benzene, dichloromethane, and THF were dried, degassed, and distilled under vacuum prior to use. Benzene was predried with CaH_2 overnight, then dried with Na/K alloy. Dichloromethane was distilled from CaH_2. THF was distilled from Na/benzophenone. Chemical reagents were used as purchased from Aldrich or Acros (Fisher), unless otherwise noted. Triphenylphosphine was recrystallized from hexane. Silica gel (Scientific, catalog number: 162544, particle size: 32–63, lot number 322303201 and 322044201) was used for flash column chromatography. Molecular sieves (4 Å, Fisher) were activated by heating at 150 °C overnight prior to use. Hydrido-tris(3,5-dimethyl-1-pyrazolyl)borato(trioxo)rhenium(VII), $Tp'ReO_3$, and hydrido-tris(3,5-dimethyl-1-pyrazolyl)borato(ethoxy)(hydroxyl)(oxo)rhenium, $Tp'ReO(OH)(OEt)$, were prepared according to the procedure described previously.[5] *trans*-Cyclooctene,[10] its epoxide,[9] *cis*-cyclooctene episulfide,[12] *trans*-cyclooctene episulfide,[13] and *trans*-mercaptocyclooctanol[25] were prepared according to literature procedures.

GC-MS spectra were collected on an HP 5890 II GC/5971A MSD under 99.999% helium using an RTX-20 column, 0.25 mm diameter, 30 m long with a 5 m guard column, coated with a 1 μm film of 20% diphenyl and 80% dimethyl polysiloxane.

Fast atom bombardment/mass spectroscopy (FAB/MS) was performed on a Kratos MS-50TC double-focusing instrument operated at unit resolution. The analyte of interest was mixed on the probe tip with a 3-nitrobenzyl alcohol (98%, Sigma-Aldrich) matrix. Xenon gas was used to generate the primary ionizing beam from an Ion-Tech gun operated at 7–8 kV. For high mass accuracy measurements with the FAB/MS, poly(ethylene glycol) (PEG) was used as a reference compound. The mixture consisted of PEG compounds in three masses: 600, 800, and 1000. The ratio of PEGs was 4:2:1, respectively.

Infrared spectra (KBR pellet) were run on a Nicolet Magna-IR560.

All NMR spectra were collected on either a Brüker DP300 (operating at 300.13 MHz for ^1H, 75.409 MHz for ^{13}C, or 121.50 MHz for ^{31}P) or a Brüker DPX400 (operating at 400.134 MHz for ^1H or 100.614 MHz for ^{13}C). All chemical shifts were referenced to residual protons or carbons in deuterated solvents and are reported in ppm downfield from tetramethylsilane. Due to the large quadrupole of boron, the B–H signal appears as an extremely broadened doublet at 3–5 ppm in the ^1H spectrum and is typically not reported. T_1 measurements were done by the inversion–recovery method. Baseline correction was performed on all FIDs and Fourier transformed spectra. For quantitative NMR work, relaxation delays of 70 s ($>5T_1$, $T_1 = 12.829$ s) per pulse for the sample using tetramethylsilane as an internal standard or 30 s ($>5T_1$) for the sample using anisole as an internal standard were collected on the Brüker DPX400 at 16 scans.

Hydrido-tris(3,5-dimethylpyrazolyl)boratorhenium(oxo)(1,2-cyclooctanediolate) (3, 4). The cis and trans isomers were prepared as reported before from the corresponding cyclooctanediolates by reductive cyclocondensation with $Tp'ReO_3$ and PPh_3. The trans isomer **4** is a new compound. ^1H NMR (C_6D_6): 1.4–1.6 m, 4H; 1.6–1.9 m, 4H; 1.90 s, 3H; 2.00 m, 1H; 2.19 s, 3H; 2.20 s, 3H; 2.40 m, 1H; 2.48 s, 3H; 2.60 m, 1H; 2.79 s, 3H; 2.81 s, 3H; 3.00 m, 1H; 4.95 m, 1H; 5.20 s, 1H; 5.59 s, 1H; 5.60 s, 1H; 5.61 m, 1H. ^{13}C NMR (C_6D_6): 12.3, 12.4, 12.5, 14.0, 14.6, 15.4, 23.4, 24.9, 27.9, 28.7, 38.0, 38.6, 98.1, 102.6, 106.9, 107.7, 107.8, 142.5, 146.4, 146.9, 153.7, 157.6. IR (solution, CH_2Cl_2): 3054, 2986, 2926, 2854, 2685, 2546 (ν_{B-H}), 1722, 1602, 1543, 1452, 1422, 1384, 1265, 1204, 1073, 948 ($\nu_{Re=O}$), 899, 739 cm^{-1}.

Hydrido-tris(3,5-dimethylpyrazolyl)boratorhenium(oxo)(*trans*-2-thiocyclooctanediolate) (9). Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed $Tp'ReO_3$ (0.144 g, 0.27 mmol), triphenylphosphine (0.0822 g, 0.31 mmol), *p*-toluenesulfonic acid monohydrate (0.0507 mg, 0.27 mmol), ground molecular sieves (1.0 g), and *trans*-2-mercaptocyclooctanol (0.043 g, 0.27 mmol) in 5.0 mL of dry THF. The solution was then freeze–pump–thaw degassed. The vessel was stirred at room temperature for 24 h. The blue-green solution was filtered, and the volatiles were removed under reduced pressure. The product was purified by flash column chromatography on silica gel. A 1:1 mixture of dichloromethane and hexane was used to elute the blue-green product. Removal of solvent left a light blue solid. Yield: 0.0109 g (0.0166 mmol, 6.1%). The stereochemistry of this compound was determined by the NOESY and NOE experiments. ^1H NMR (C_6D_6): δ 1.38 (m, 1H), 1.53 (m, 2H),

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1.68 (m, 2H), 1.77 (m, 1H), 1.82 (m, 1H), 1.88 (s, 3H), 1.99 (m, 1H), 2.02 (m, 1H), 2.22 (s, 3H), 2.35 (s, 3H), 2.55 (m, 1H), 2.82 (m, 1H), 3.95 (ddd, $J = 4.85, 9.15, 13.90$, 1H), 4.89 (ddd, $J = 4.76, 10.70, 13.90$, 1H), 5.16 (s, 3H), 5.56 (s, 1H), 5.56 (s, 1H). ^{13}C NMR (C_6D_6): δ 12.13, 12.13, 12.13, 12.52, 15.84, 17.02, 24.95, 26.70, 27.15, 27.56, 38.90, 40.26, 62.69, 106.47, 107.17, 107.95, 108.29. IR (KBr): 2921, 2852, 2538 (ν_{BH}), 1545, 1452, 1416, 1383, 1206, 1066,1044, 950 (ν_{ReO}), 920, 816, 657 cm^{-1}. MS (FAB): (^{187}Re) 658.6 [M$^+$]. HRMS: 656.22440 (calc for $C_{23}H_{36}BN_6O_2S^{185}Re$ 656.22433).

Reaction of *cis*-Cyclooctene Oxide with Tp′ReO$_3$/PPh$_3$. Tp′ReO$_3$ (3.4 mg, 0.006 mmol) and PPh$_3$ (5.0 mg, 0.019 mmol) were placed under 0.5 mL of C_6D_6. To this was added *cis*-cyclooctene oxide (2.8 mg, 0.020 mmol). The tube was degassed with three freeze−pump−thaw cycles and sealed under vacuum, then heated to 75 °C for 15 h. NMR of the mixture showed characteristic peaks for *cis*-cyclooctene (5.64 ppm) and hydrido-tris(3,5-dimethylpyrazolyl)boratorhenium-(oxo)(*cis*-1,2-diolate) (**3**) (5.59 ppm) in a 24.5:1 ratio. GC-MS of the solution confirmed the production of *cis*-cyclooctene compared to a known standard.

Reaction of *trans*-Cyclooctene Oxide with Tp′ReO$_3$/PPh$_3$. Tp′ReO$_3$ (10.0 mg, 0.019 mmol) and PPh$_3$ (6.1 mg, 0.023 mmol) were placed under 0.5 mL of C_6D_6. To this was added *trans*-cyclooctene oxide (5.3 mg, 0.039 mmol). The tube was degassed with three freeze−pump−thaw cycles and sealed under vacuum, then heated to 75 °C for 45 h. NMR of the mixture showed characteristic peaks for *trans*-cyclooctene (5.43 ppm) and hydrido-tris(3,5-dimethylpyrazolyl)boratorhenium-(oxo)(*trans*-1,2-diolate) (**4**) (4.95 ppm) in a 1.07:1 ratio. GC-MS of the solution confirmed the production of *trans*-cyclooctene compared to a known standard.

Reaction of Ethylene Sulfide with Tp′ReO$_3$/PPh$_3$. Tp′ReO$_3$ (100 mg, 0.188 mmol), PPh$_3$ (60.9 mg, 0.236 mmol), and ethylene sulfide (22.6 mg, 0.376 mmol) were mixed with 25 mL of THF and stirred under argon for 15 h. The solvent was removed in vacuo, and the residue chromatographed on silica with 1:1 hexane/dichloromethane. The dark brown band was collected; after removal of solvent 29.6 mg (0.05 mmol, 26.7%) was obtained, identical by NMR to the ethanedithiolate **5** prepared by reductive condensation of Tp′ReO$_3$ with ethane-1,2-dithiol and reported previously.[8]

Reaction of *cis*-Cyclooctene Episulfide with Tp′ReO$_3$/PPh$_3$. Tp′ReO$_3$ (3.4 mg, 0.006 mmol) and PPh$_3$ (5.0 mg, 0.019 mmol) were placed under 0.5 mL of C_6D_6. To this was added *cis*-cyclooctene episulfide (3.2 mg, 0.021 mmol). The tube was degassed with three freeze−pump−thaw cycles and sealed under vacuum, then heated to 75 °C for 45 h. NMR of the mixture showed predominantly the characteristic peak for *cis*-cyclooctene (5.73 ppm). Very weak signals were observed for rhenium-containing compounds.

Scale-up of this reaction was performed to isolate and identify rhenium-containing compounds. Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed Tp′ReO$_3$ (0.136 g, 0.256 mmol), triphenylphosphine (0.236 g, 0.90 mmol), and *cis*-cyclooctene episulfide (0.128 g, 0.901 mmol) in 3 mL of dry C_6D_6. The solution was then freeze−pump−thaw degassed. The vessel was stirred at room temperature for 24 h. The dark brown solution was filtered, and the volatiles were removed under reduced pressure. The product was purified by flash column chromatography on silica gel. A 1:1 mixture of dichloromethane and hexane was used to elute the dark brown product. Removal of solvent left **7** as a dark brown solid. Yield: 0.0123 g (0.018 mmol, 7.03%). By NMR analysis, it was confirmed products are in a 10:7 ratio of anti and syn isomers. The stereochemistry of this compound was determined by the NOESY and NOE experiments. IR (KBr): 2924, 2850, 2548, 2360 (ν_{BH}), 1525, 1452, 1416, 1367, 1213, 1066, 1041, 941 (ν_{ReO}), 861, 818, 778, 648 cm^{-1}. MS (FAB): (^{187}Re) 674.6 [M$^+$]. HRMS: 674.20652 (calc for $C_{23}H_{36}BN_6OS_2{}^{187}Re$ 674.20427).

Anti isomer: ^{1}H NMR (C_6D_6): δ 1.43 (m, 1H), 1.60 (m, 1H), 1.88 (s, 3H), 2.18 (s, 6H), 2.20 (m, 1H), 2.29 (m, 1H), 2.43 (s, 3H), 3.07 (s, 6H), 4.63 (m, 1H), 5.20 (m, 1H), 5.59 (s, 2H) ^{13}C NMR (C_6D_6): δ 12.18, 12.62, 16.48, 17.07, 26.27, 33.98, 65.32, 107.62, 108.68.

Syn isomer: ^{1}H NMR (C_6D_6): δ 1.60 (m, 1H), 1.71 (m, 1H), 1.89 (s, 3H), 2.19 (s, 6H), 2.46 (m, 3H), 2.64 (m, 1H), 3.03 (m, 1H), 3.10 (s, 6H), 4.19 (m, 1H), 5.21 (m, 1H), 5.61 (s, 2H) ^{13}C NMR (C_6D_6): δ 12.19, 12.65, 16.48, 17.84, 30.39, 34.83, 67.20, 107.95, 108.80.

Reaction of *trans*-Cyclooctene Episulfide with Tp′ReO$_3$/PPh$_3$. Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed Tp′ReO$_3$ (0.5752 g, 1.08 mmol), triphenylphosphine (0.9935 g, 3.79 mmol), and *trans*-cyclooctene episulfide (0.5006 g, 3.52 mmol) in 4 mL of dry C_6D_6. The solution was then freeze−pump−thaw degassed. The vessel was stirred at 75 °C for 24 h. The dark brown solution was filtered, and the volatiles were removed under reduced pressure. The product was purified by flash column chromatography on silica gel. A 1:1 mixture of dichloromethane and hexane was used to elute the dark brown product. Removal of solvent left **8** as a dark brown solid. Yield: 0.1748 g (0.259 mmol, 23.59%). The stereochemistry of this compound was determined by the NOESY and NOE experiments. ^{1}H NMR (C_6D_6): δ 1.54 (m, 2H), 1.63 (m, 1H), 1.73 (m, 2H), 1.74 (m, 1H), 1.86 (m, 1H), 1.89 (s, 3H), 1.92 (m, 1H), 2.01 (m, 1H), 2.17 (s, 3H), 2.17 (s, 3H), 2.43 (s, 3H), 2.52 (m, 1H), 2.86 (m, 1H), 3.06 (s, 3H), 3.20 (m, 1H), 3.58 (ddd, $J = 3.38, 9.70, 13.45$, 1H), 4.13 (ddd, $J = 3.48, 9.61, 13.45$, 1H), 5.20 (s, 1H), 5.58 (s, 1H), 5.59 (s, 1H). ^{13}C NMR (C_6D_6): δ 12.17, 12.37, 12.37, 15.95, 16.10, 17.47, 26.39, 26.96, 27.17, 27.20, 38.02, 39.57, 63.88, 71.77, 107.84, 108.58, 108.60. IR (KBr): 2923, 2549 (ν_{BH}), 1545, 1452, 1417, 1384, 1213, 1067,1041, 941 (ν_{ReO}), 669, 649 cm^{-1}. MS (FAB): (^{187}Re) 674.1 [M$^+$]. HRMS: 674.20475 (calc for $C_{23}H_{36}BN_6OS_2{}^{187}Re$ 674.20427).

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Supporting Information Available: 1-D and 2-D spectra for compounds **4** and **7**−**9**; computational results for strain in cyclooctenes, epoxides, episulfides, and related compounds. This information is available free of charge via the Internet at http://pubs.acs.org.

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