$LReO_3$ Epoxidizes, *cis*-Dihydroxylates, and Cleaves Alkenes as Well as Alkenylates Aldehydes: Toward an Understanding of Why[†]

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The relative reaction thermodynamics for the probable pathways leading to alkene epoxidation, *cis*-dihydroxylation, and C−C cleavage as well as alkenylation of aldehydes have been investigated for the reaction of ethylene with $LReO_3$, L = CH_3, Cl, OH, OCH_3, O^-, C_5H_5(Cp), and $C_5(CH_3)_5$ (Cp*). We find the reaction pathway exothermicities to be quite sensitive to the ligand. For $ClReO_3$, CH_3ReO_3, $HOReO_3$, CH_3OReO_3, and O^-ReO_3, reaction with ethylene is endothermic with metallaoxetane preferred over dioxylate formation. For $CpReO_3$ and Cp^*ReO_3, the reaction with ethylene is exothermic but nearly thermoneutral with dioxylate formation preferred. The π-binding attributes of the ligand are found to correlate with thermodyanmic preference.

Concern over the enantiomeric purity of pharmacologically active compounds has made asymmetric synthesis one of the grand challenges of chemical research. Two outstanding examples are the asymmetric *cis*-dihydroxylation of olefins[1] and the asymmetric epoxidation of olefins.[2] Both processes utitilize high-valent transition-metal complexes as the catalytic agent and chiral ligands to induce asymmetry in the product and can use hydroperoxides as oxidizing agents. Complexes of early-transition-metal ions such as titanium, vanadium, and chromium preferentially epoxidize olefins.[3−5] Permanganate,[6] ruthenium tetroxide,[7] and osmium tetroxide[8] preferentially *cis*-dihydroxylate olefins. Why? What is the source of pathway differentiation?

The series $LReO_3$ likely holds the key to unraveling this mystery. When L = CH_3, epoxidation occurs.[9] If L = $C_5(CH_3)_5$ (Cp*), a metalladioxylate is formed.[10] When L = O−M, the alkene C−C bond is cleaved and an olefin metathesis catalyst is generated.[11,12] Further, CH_3ReO_3 is a catalyst for the alkenylation of aldehydes.[13] Finally, $ClReO_3$ reacts with alkenes for form chlorohydrins.[5]

Previous theoretical studies of $LReO_3$[14,15] have focused on the electronic structure of the reactant. Through two-configuration SCF and CI calculations, Bénard and co-workers[14] found the ReO_3 fragment to be roughly as electronegative as chlorine, leading to charge transfer from L to ReO_3 for L = C_5H_5, CH_3, and Cl but charge transfer from ReO_3 to L for L = F and CF_3. Rösch and co-workers,[15] using a LDA density functional method, focused on understanding the photoelectron spectra of a series of $LReO_3$ complexes. The authors did assess the Lewis acidity of the $-ReO_3$ fragment and ascribed the difference in reactivity between $CpReO_3$ and CH_3ReO_3 to differential Lewis acidity.

To gain further insight into the observed reactivity patterns, the thermodynamics of reacting $LReO_3$ with ethylene has been computed as a function of L; the results are provided in the Results and Discussion section. Overall conclusions are provided in the Conclusions section. The present theoretical approach employed and estimates of the errors to be expected are summarized in the Theoretical Details section.

[†] Dedicated to Prof. K. Barry Sharpless on the 21st anniversary of metallaoxetanes.

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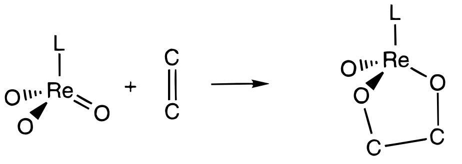
Table 1. Relative Energetics[a] (kcal/mol) of the Dioxylate and Metallaoxetane Intermediate[a]

ligand	dioxylate ΔE	oxetane ΔE	$\Delta\Delta E$
Cp*	−4	+15	+19
Cp	−8 (−3)	+5 (+8)	+13 (+11)
Cl	+16	+10	−6
CH_3	+31	+10	−21
OH	+19	+11	−9
OCH_3	+17	+12	−7
O^-	+33	+27	−6

[a] Obtained from single-point B3LYP calculations in an extended basis at the geometries determined in a more modest basis (see text). The relative energies do not include zero-point corrections, except for L = Cp, where the ZPE-corrected results are given in parentheses.

Results and Discussion

To understand why, for example, Cp^*ReO_3 reacts with alkenes to form dioxylates while CH_3ReO_3 will not, the thermodynamics of the reaction in eq 1 were computed as a function of L; the results are collected in Table 1, column 2. When L = CH_3, the reaction is 31 kcal/mol endothermic. For L = Cp or Cp*, the reaction is slightly exothermic (8 and 4 kcal/mol, respectively). For L = Cl, OH, or OCH_3, the reaction is moderately endothermic (endotheromicities ranging from 16 to 19 kcal/mol). When L = O^-, the reaction is 33 kcal/mol endothermic.



(1)

The source of this more than 40 kcal/mol ligand dependency can be traced to metal−ligand π bonding. A qualitative molecular orbital diagram for tetrahedral ML_4 (see Figure 1a) suggests that there are three ligand π orbitals that are purely nonbonding (the t_1 set), three ligand π orbitals that must compete with σ bonding (the t_2 set), and only two that can form strong π bonds with the metal (the e set). Since the metal center in tetrahedral ML_4 complexes can only form two significant M−L π bonds, there is a strong interplay between the "π-donor" strength of L and the thermodynamics of eq 1. In the reactant, three oxo ligands and possibly L compete for π bonding. This leads to a considerable π-bond "strain" or deficiency. In the product, only a single oxo and possibly L compete for π bonding; π-bond strain is relieved upon dioxylate formation. Cp and Cp* are both stronger π-donor ligands than Cl, OH, OCH_3, or CH_3, hence their reactions with ethylene are more favorable; there is a greater relief of π-bond strain. This π-bond strain effect is geometrically reproduced in the X−O−Re bond angles of $(HO)ReO_3$ and $(CH_3O)ReO_3$, and their corresponding dioxylates. For $(HO)ReO_3$, the angle is 122.5°, whereas for the dioxylate, the angle has opened up to 125.3°. For $(CH_3O)ReO_3$ and its dioxylate, the angles are 131.9° and 143.9°, respectively. The larger angles indicate more XO−Re π-bonding in the dioxylate. As discussed below, these trends and this explanation are consistent with experimental observation.

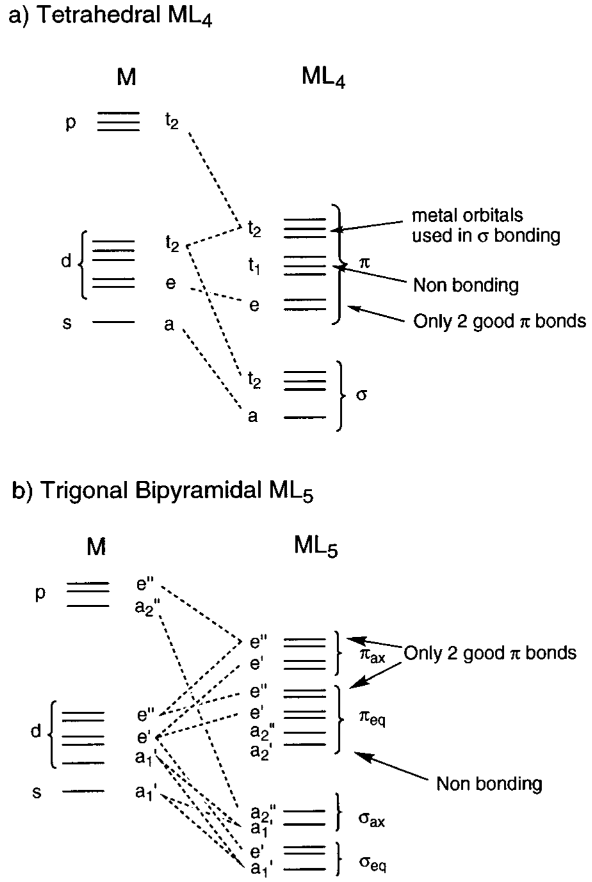
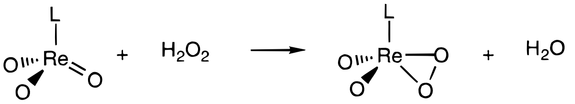
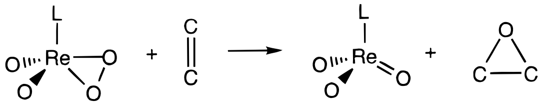


Figure 1. Qualitative molecular orbital diagrams including π bonding for (a) a tetrahedral complex and (b) a trigonal-bipyramidal complex.

Cp^*ReO_3 is observed to react slowly with alkenes as in eq 1.[16] CH_3ReO_3 does *not* directly react with alkenes.[9] Instead, if hydrogen peroxide is present, a peroxo complex is formed, eq 2, which then epoxidizes the olefin, see eq 3. A diperoxo complex is also formed; it also epoxidizes olefins. In the same paper, Cp^*ReO_3 and $CpReO_3$ were observed *not* to epoxide olefins. These observations are consistent with dioxylate formation being thermodynamically favorable for Cp^*ReO_3. For CH_3ReO_3, dioxylate formation is computed to be rather endothermic (more than 30 kcal/mol uphill), opening up the likely slower reaction channel for eqs 2 and 3.



(2)



(3)

It has been suggested[16] that the reaction in eq 1 occurs through the intermediacy of a metallaoxetane, eq 4. We find dioxylate formation is thermodynamically preferred for L = Cp and Cp* but that oxetane formation is favored for L = Cl, CH_3, OH, OCH_3, and O^-, see Table 1, columns 3 and 4. As with the exothermicity of dioxylate formation, the preference for dioxylate or

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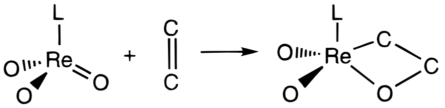
Table 2. Metric Parameters, Distances (Å) and Angles (deg)

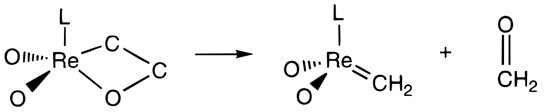
	$LReO_3$		dioxylate			oxetane			
ligand	$R_{Re=O}$	θ_{O-Re-O}	$R_{Re=O}$	R_{Re-O}	θ_{O-Re-O}	$R_{Re=O}$	R_{Re-O}	R_{Re-C}	θ_{O-Re-C}
Cp*	1.72	106.4	1.69	1.94	80.1	1.72	1.95	2.17	66.0
Cp	1.71	105.6	1.69	1.93	80.5	1.69	1.97	2.16	65.8
Cl	1.69	109.9	1.67	1.88	82.1	1.69	1.94	2.18	66.0
CH_3	1.70	113.2	1.68	1.89	81.9	1.69	1.98	2.12	73.0
OH	1.70	108.8	1.68	1.89	81.7	1.70	1.94	2.17	65.9
OCH_3	1.70	109.0	1.68	1.90	81.5	1.70	1.04	2.17	66.0
O^-	1.73	109.5	1.72	1.96	79.2	1.72	2.03	2.18	64.0

oxetane is strongly dictated by L. The computed thermochemistry suggests that dioxylate formation *could* occur through the oxetane intermediate for L = Cp* if the reaction were kinetically permitted. Recent theoretical work on the related OsO_4 *cis*-dihydroxylation reaction suggests that for OsO_4 the oxetane intermediate is kinetically inaccessible.[17] However, as discussed by others[17d] "It should also be noted that a one-step (3 + 2) cycloaddition does not provide an explanation for observations on electronic effects in these reactions or temperature effects on the enantioselectivity that support a complex overall mechanism. Furthermore, Gable's studies on a reversible rhenium analogue seem to require a stepwise mechanism". While not the focus of this paper, as discussed in the Theoretical Details section below, the barriers computed here for the 3 + 2 pathway appear to be in good agreement with Gable's kinetic measurements for $Cp^*ReO_3 + C_2H_4$ and would also tend to support the 3 + 2 pathway mechanism.



(4)

An additional observation is that perrhenate ReO_4^-, moderated by binding to "M", could react with olefins to generate an olefin metathesis precursor. The needed alkylidene complex could be formed by a two-step reaction sequence. In the first step, $MOReO_3$ would react with an olefin, eq 4, to form a metallaoxetane. In the second step, eq 5, the metallaoxetane could cleave to form an alkylidene complex, which then should initiate olefin metathesis. The last entries in Table 1 suggest that perrhenate, ReO_4^-, is not the reactive species, rather perrhenic acid $HOReO_3$ or a metalated perrhenate could be active, if kinetically feasible.



(5)

The metallaoxetane of eqs 4 and 5 has been implicated in aldehyde alkenylation catalyzed by CH_3ReO_3.[13] The reaction pathway proposed is the microscopic reverse of eqs 5 and 4. The alkylidene complex is thought to be formed by reaction with diazoalkane. It subsequently reacts with aldehydes to form a metallaoxetane, the reverse of eq 5, which then cleaves in the alternate manner to form the alkene product, the reverse of eq 4. It is interesting to note that for this reaction sequence where metallaoxetane formation is *the* viable mechanistic possibility, ring expansion to form a dioxylate is not observed. The data in Table 1 suggests that oxetane ring expansion is simply thermodynamically unfavored for L = CH_3.

The observation[5] of chlorohydrin formation and lack of diol formation from the reaction of $ClReO_3$ with alkenes is consistent with initial metallaoxetane formation, ring expansion to form the dioxylate simply being thermodynamically unfavored.

In contrast to dioxylate formation, with the exception of L = O^-, the energetic position of the metallaoxetane, relative to the $LReO_3$ reactant, is nearly constant. A qualitative molecular orbital diagram for trigonal-bipyramidal ML_5 (see Figure 1b) suggests that again there can only be two good π bonds, now of e″ symmetry. Since the number of ligands competing for π bonds has decreased by one in the oxetane, a decrease in π-bond strain would be expected. However, the small O−Re−C bond angle in the oxetane complicates this analysis, see Table 2. As discussed previously for metallacyclobutanes,[18] natural or strain-free angles as small as 60° are not uncommon for transition metals. The optimal angle between d_σ bonds is 54.7°. The bonds in these small natural angle cases are hybrids composed of an equal mixture of $d_\sigma + d_\pi$. Thus, in moving from a tetrahedral reactant to a trigonal-bipyramidal intermediate with a four-membered ring of 60°, there is minimal relief in π-bond strain. The qualitative molecular orbital analysis suggests that the energetic position of the intermediate will be independent of the π-bonding attributes of L. Re, however, is more sterically congested in this trigonal-bipyramidal structure and there is a Re−C σ bond trans to L which must compete with L for a_1' bonding. The complex with L = Cp* is the most sterically congested metallaoxetane and, thus, is the least stable. The oxetane with L = Cp is the most stable; this is consistent with Cp being the weakest σ donor of the set studied and, hence, competing the least effectively with the trans Re−C σ bond. Again, the XORe angle in $(HO)ReO_3$ and $(CH_3O)ReO_3$ provides a geometric diagonistc of π-bonding. For $(HO)ReO_3$, the angle is 122.5°, whereas for the oxetane, the angle has closed down to 112.9°. For $(CH_3O)ReO_3$ and its oxetane, the angles are 131.9° and 119.6°, respectively. The smaller angles perhaps indicating even more π-bond strain in the oxetane.

Conclusions

In summary, competition between Re−L and Re−O π-bonding plays a major role in guiding the thermody-

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namics of reaction pathways observed for alkene oxidation by $LReO_3$. Strong π-bonding ligands such as Cp and Cp* thermodynamically favor dioxylate formation because of π-bond strain relief. Other dominately σ-bonding ligands thermodynamically favor oxetane formation. Future studies will focus on other oxidation substrates and tuning L for more precise pathway control, hopefully leading to the synthesis of stable metallaoxetanes.

Theoretical Details

To characterize the thermodynamics of reaction 1, hybrid density-functional theory B3LYP was employed in conjunction with the Hay−Wadt relativistic effective core potential (ECP) for Re (LANL2)[19] using the G94 suite of programs.[20] In a previous all-electron study[21] of the formally d^0 systems MF_n, where M = Sc, T, V, and Cr, the B3LYP approximation was shown to give excellent heats of formation when used with sufficiently flexible basis sets, the error in the average bond energy in this series being of the order of 2 kcal/mol. The applicability of the Hay−Wadt core potential for use in DFT calculations has also been demonstrated, but it was found that the associated basis sets were sometimes not sufficiently flexible to describe the DFT orbitals.[22] Rather than developing a new contraction of the basis set, a slightly modified LANL2DZ basis (see Table 3) was completely uncontracted and augmented with a single f-function optimized for ReO_4^- ($\zeta = 0.6$). This basis was combined with the 6-31G* basis set for the ligands, and the geometries were optimized using a locally modified version of Gaussian94 which is capable of analytical ECP gradient calculations for the f-orbitals.[23] In the case of L = C_5H_5 (Cp), the second derivatives of the energy at stationary points of interest were also computed in this basis. Table 1 reports the results of single-point calculations at the minima using an extended basis in which the metal f-function was replaced by two ($\zeta = 0.4, 1.14$) and the ligand basis sets expanded to 6-31+G* to account for diffuse (negative ion) character on the ligands. This generally resulted in changes of only 3−4 kcal/mol in the relative energetics, and we believe the results are converged to this degree with respect to the one-electron basis sets. Reaction 1, with L = Cp*, was used for benchmark purposes, since experimental thermochemistry is available. Gable and Phan[16] have determined an exothermicity for dioxylate formation of −5 ± 3 kcal/mol. The theoretical result of −4 kcal/mol in Table 1 does not include zero-point energy (ZPE) corrections. If the reasonable assumption that the differential ZPE computed for L = Cp may be used to correct the L = Cp* numbers, theory gives 0 kcal/mol for the exothermicity, in fair agreement with experiment. In addition, Gable and Phan measure a barrier height of 28.0 kcal/mol for ethylene extrusion (relative to the dioxylate). While this is the same for L = Cp*, our calculations on L = Cp yield a barrier of 27.2 kcal/mol for the [3 + 2] concerted pathway. Furthermore, a per deuterium kinetic isotope effect of 1.06−1.07 was measured for the extrusion, while theory yields 1.09. This work will be reported in more detail elsewhere, but we conclude that our theoretical approach is performing well for this reaction, and the thermochemistries in Table 1 are useful to within a few kcal/mol. Metric parameters for the studied complexes are provided in Table 2.

Table 3. Rhenium s, p, and d Basis

type	ζ	coeficient
s	2.1850	1.0
s	0.8766	1.0
s	0.3517	1.0
s	0.1411	1.0
s	0.0566	1.0
p	3.3580	1.0
p	1.2891	1.0
p	0.4949	1.0
p	0.1900	1.0
p	0.0729	1.0
d	1.1160	1.0
d	0.3922	1.0
d	0.1378	1.0
f	1.1400	1.0
f	0.4000	1.0

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