

Efficient Catalytic Deoxygenation of Epoxides Using [Tris(3,5-dimethylpyrazolyl)hydridoborato]rhenium Oxides

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Summary: *In situ* reduction of $\text{Tp}'\text{ReO}_3$ ($\text{Tp}' = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{hydridoborate}$) using triphenylphosphine or triethyl phosphite allows generation of a reduced rhenium species that catalyzes efficient O atom transfer from epoxides to the stoichiometric phosphorus reductant at 75–105 °C. The reaction is stereospecific and proceeds most rapidly with *cis*- vs *trans*-alkenes. The choice of ligand is shown to impart advantages to design of the catalytic cycle.

Metal complexes are known to engage in a variety of O atom transfer processes.¹ Recent studies have shown that rhenium oxo complexes engage in several of these² and that the thermodynamics of the $\text{Re}=\text{O}$ bond are such³ that proper choice of reactants, rhenium complex, and conditions can lead to O atom transfer to or from an organic substrate. The promise of such control of reactivity prompted us to explore catalytic epoxide deoxygenation⁴ using $(\eta\text{-C}_5\text{Me}_5)\text{ReO}_3$. Unfortunately, conproportionation of the oxidized and reduced rhenium intermediates led to irreversible loss of activity.⁵ We report here that judicious modification of the ancillary ligand leads to successful, efficient catalysis.

Polypyrazolylborates have long been known to act as "cyclopentadienyl equivalents"; that is, they are formally anionic, six-electron donors.⁶ Our studies of diolate cycloreversion⁷ suggested minimal perturbation of the reactivity of the metal center on changing from pentamethylcyclopentadienyl to the Tp' ($\text{Tp}' = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{hydridoborate}$) ligand. However, it is well-known⁶ that the steric properties of pyrazolylborate ligands are substantially different from those of cyclopentadienyl ligands. Measured by cone angle, they appear to be much bulkier, but it is also recognized that the interstices between the pyrazolyl rings allow some access to the metal that is not fully accounted for by cone angle alone.

Such a substitution would be advantageous for catalytic O atom transfer for three reasons. First, the electronic comparabilities of Cp and Tp were close enough that we should not see a dramatic change in the $\text{Re}=\text{O}$ bond strength. Second, the ability to increase (and to a degree, tailor) the steric restrictions of the ligand should prevent the clustering reactions that killed catalysis using $(\eta\text{-C}_5\text{Me}_5)\text{ReO}_3$. A third reason stemmed from the chemistry of the reduced Re(V) complexes. Like the $(\eta\text{-C}_5\text{Me}_5)$ analogues, several (pyrazolylborato)rhenium(V) dioxo complexes were known to arise from reduction of LReO_3 with phosphines.⁸ These were presumed to be dimeric by analogy with $[(\eta\text{-C}_5\text{Me}_5)\text{ReO}]_2(\mu\text{-O})_2$; mass spectrometry supported the assignment. Our earlier studies with $[(\eta\text{-C}_5\text{Me}_5)\text{ReO}]_2(\mu\text{-O})_2$ had shown that fragmentation of the dimer was a necessary preequilibrium process for O atom transfer.⁹ Since the steric demands of the Tp' ligand should also disfavor dimerization, we began our studies with this ligand.

Reaction of 1–5 mol % $\text{Tp}'\text{ReO}_3$ with epoxide and PPh_3 (1:1 stoichiometry) in benzene leads to high yields of alkene. Ethereal solvents and acetonitrile are also good solvents for the reaction. Typical reaction conditions are to heat the reaction mixture in a tube sealed under vacuum for 2–100 h at 105 °C. Table 1 shows the results of comparing different epoxides. The reaction is highly stereospecific, giving retention of configuration; none of the stereoisomer is observed by NMR at 75% conversion, leading to a minimum selectivity of 15:1, assuming a 5% detection limit for a minor isomer. Triethyl phosphite was equally effective as the stoichiometric reducing agent.¹⁰ Reactions were performed at 75 and 105 °C; no parameter other than rate appeared to be affected. Triphenylphosphine is known to effect epoxide deoxygenation;¹¹ however, the uncatalyzed reaction requires substantially higher temperatures (200 °C) and proceeds with inversion of configuration. In our hands, the control (excluding rhenium compounds) gives no observable alkene in 24 h.

The reaction is effective on a preparative scale. In one experiment, 750 mg of 1,2-epoxydodecane (4.1 mmol) was dissolved in 60 mL of toluene and dried over CaH_2 .

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(10) Procedure: $\text{Tp}'\text{ReO}_3$ (2.4 mg, 4.5 μmol), *cis*-stilbene oxide (17.7 mg, 90 μmol), and $\text{P}(\text{OEt})_3$ (18.6 μL , 108 μmol) were dissolved in 0.5 mL of C_6D_6 , sealed under vacuum in an NMR tube, and then heated to 75 °C. After 47 h, 62% conversion to stilbene was observed by NMR.

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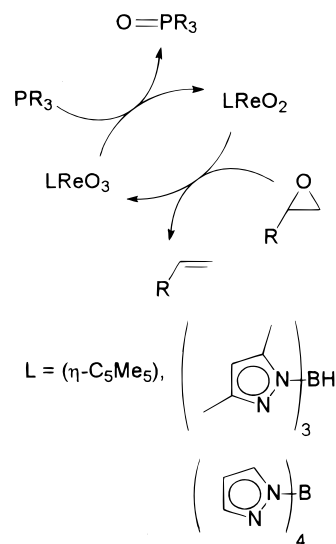
Table 1. Catalytic Deoxygenation of Epoxides with $\text{LReO}_3/\text{PPh}_3$ in Benzene- d_6

Entry	Catalyst, load ^a	Time, hr	Temp., °C	Conversion, %
1	 Tp' , 5%	2	75	33
2	Tp' , 5%	1.5	105	>95
3	Tp' , 1%	5.5	105	>47
4	Tk , 5%	73	105	46
5	 Tp' , 5%	2	75	4
6	Tp' , 5%	1.5	105	18
7	Tp' , 5%	120	105	>95
8	Tk , 5%	73	105	tr
9	 Tp' , 5%	2	75	82
10	Tp' , 5%	1.5	105	93
11	Tp' , 5%	2	75	41
12	Tp' , 5%	1.5	105	63
13	Tk , 5%	120	105	tr
14	 Tp' , 5%	2	75	6
15	Tp' , 5%	1.5	105	12
16	Tk , 5%	120	105	0
17	Tp' , 5%	1.5	105	14
18	 Tp' , 5%	2	75	32
19	Tp' , 5%	1.5	105	45

^a Precatalysts: $\text{Tp}' = (3,5\text{-Me}_2\text{Pz})\text{HReO}_3$; $\text{Tk} = (\text{Pz})_4\text{BReO}_3$. The load is given in mole percent of LReO_3 vs epoxide. All reactant solutions were predried over CaH_2 and sealed under vacuum. Yields were measured by NMR.

$\text{Tp}'\text{ReO}_3$ (110 mg, 0.2 mmol, 0.05 equiv) and 1.18 g of PPh_3 (4.5 mmol, 1.1 equiv) were added. The mixture was stirred in a Carius tube sealed under vacuum and heated to 105 °C for 72 h. An aliquot analyzed by NMR showed no remaining epoxide; distillation gave 440 mg of 1-dodecene (2.6 mmol, 64%).

The experiments summarized in Table 1 show several features. The epoxide's electronic and steric structure has a significant impact on the O atom transfer. *cis*-Alkenes react faster than *trans*-alkenes, and epoxides

Scheme 1

of terminal alkenes proceed faster than those of internal alkenes. Alkyl substituents slow the reaction in comparison with aryl groups, although comparison of epoxytetrafluoropropane with phenyl-substituted epoxides shows that the electronic effects are not at all separable from steric issues. Functional group interference was seen for some substrates; the presence of a nitro group was, as expected, a detriment. Free hydroxyl groups also interfered with catalysis, presumably by forming an inactive bis(alkoxide).⁸ However, even substrates that reacted slowly could be pushed to near completion, given enough time. This is a dramatic change from the Cp^* system, where catalyst degradation interfered significantly with deoxygenation of unreactive epoxides.

The advantage of using the Tp' ligand is seen in entries 4, 8, 13, and 16 in Table 1. Although using tetrakis(pyrazolylborato)rhenium trioxide does allow catalytic turnover, the rate is severely retarded. Further, with this catalyst precursor we see extensive *cis*/*trans* isomerization of stilbene oxide. The decreased steric bulk would be expected to favor dimerization of LReO_2 and remove the catalytically active species from solution. Isomerization may arise from adventitious acidic impurities; whatever its origin, it is exacerbated by the slow catalyst turnover and the low reactivity of the *trans* epoxide. The low reactivity probably stems from the stability of the dimeric form of the dioxorhenium(V) intermediate.⁸

A working hypothesis for the catalytic cycle is shown in Scheme 1. Dissolution of the benzene-insoluble rhenium trioxo complex is evidence for reduction. A brief induction period (<30 min at 105 °C) is also observed for most substrates. The Re(V) species representing the resting state for the catalyst may be either free $\text{Tp}'\text{ReO}_2$ or the dimeric form; in stoichiometric reactions, a dark green color forms, suggesting a Re-Re -bonded species such as the dimer. However, preliminary investigations into the reduction process have suggested the putative dimer and monomer are both quite reactive; reduction in dichloromethane leads to known $\text{Tp}'\text{Re(O)(OH)Cl}$,¹² and attempted purification of the presumed dimer by chromatography on silica leads to a compound we

propose to be the hydrate $\text{Tp}^*\text{ReO}_2(\text{OH}_2)$.¹³ Consistent with this behavior, water does lead to inhibition of catalytic turnover; predrying the epoxide to avoid adventitious water enhances the turnover frequency and provides consistent conversion vs time behavior with each epoxide.

From the evidence we have so far, the mechanism for the O atom transfer is not clear. Concerted O atom transfer is the simplest hypothesis; a minor variant would be association of the epoxide to the metal, followed by concerted C–O cleavage. The intermediate reactivity of styrene oxide (less reactive than *cis*-stilbene oxide; more reactive than *trans*-stilbene oxide) provides some preliminary support for concerted C–O cleavage. Alternatively, oxidative addition of the epoxide followed by a retro-[2 + 2] cycloreversion would also get to trioxo

plus alkene. The dramatic variation of reactivity with substrate stereochemistry is certainly dependent on steric interactions. As we⁷ and others¹⁴ have commented previously, the distinction between the two classes of mechanism is also important to cycloreversion of rhenium(V) diolates, and we are exploring means to distinguish them. It is clear, though, that the epoxide's electronic and steric structure both have a significant impact on the O atom transfer. This efficient catalysis demonstrates how the pyrazolylborate ligand provides a critical tool for tuning this reaction through the use of steric interaction.

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Additions and Corrections

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Mark A. Aubart and Robert G. Bergman*: Tantalum-Mediated Cleavage of an N=N Bond in an Organic Diazene (Azoarene) To Produce an Imidometal ($\text{M}=\text{NR}$) Complex: An η^2 -Diazene Complex Is Not an Intermediate.

Page 811. We wish to add the following two references to the introductory section of this paper: (a) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, 106, 4749. (b) Canich, J. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1986**, 3, 895. We are grateful to Prof. Cotton for calling our attention to these early contributions to the diazene cleavage field.

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Wing-Por Leung,* Wai-Him Kwok, Zhong-Yuan Zhou, and Thomas C. W. Mak: Synthesis and Characterization of Group 14 Dialkylmetal Chalcogenes $\text{R}^{\text{N}}_2\text{M}=\text{E}$ [$\text{R}^{\text{N}} = \text{CH}(\text{SiMe}_3)\text{C}_9\text{H}_6\text{N}-8$ or $\text{CPh}(\text{SiMe}_3)-\text{C}_5\text{H}_4\text{N}-2$; $\text{M} = \text{Ge}$ or Sn ; $\text{E} = \text{S}$, Se , or Te].

Page 303. The following sentence should have appeared in Acknowledgments: We thank Prof. Vivian W. W. Yam and Mr. Eddie C. C. Cheng of the University of Hong Kong for recording the UV–vis spectra of the compounds.

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