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Coordination of a Tethered Epoxide to a Coordinatively Unsaturated Rhenium Oxo Complex

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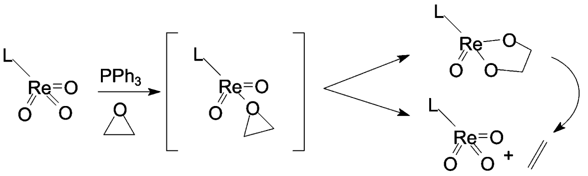
3,4-Epoxy-1-butyltetramethylcyclopentadienyltrioxorhenium(VII) is prepared via a multistep route from bromopentacarbonylrhenium. Reductive deoxygenation with PPh_3 results in a species with NMR characteristics consistent with expectation for a rhenium(V)-epoxide complex.

Oxygen atom transfer chemistry represents an area where transition metal catalysis has played a key role. Many metals catalyze the transfer of oxygen between stoichiometric oxidants and organic functional groups;[1] these reactions are of importance to biologic systems,[2] in industrial processes,[3] and in the synthesis of fine chemicals.[4]

Recent work in our laboratory[5] and elsewhere[6] has shown that high-valent rhenium is a convenient platform from which to explore the fundamental processes involved with O atom transfer. A number of $LReO_3$ complexes can participate (either directly or via related η^2-peroxo complexes) in oxidation of alkenes,[7] alkynes,[8] amines,[9] sulfides,[10] phosphines,[11] halogen anions,[12] C−H bonds,[13] and other functional groups. Variation of the ancillary ligand L can alter the thermochemistry of O atom transfer,[14] where L = Cp*, Tp, or Tp′, and $LReO_3$ is the result of both thermal cycloreversion of rhenium(V) diolate compounds[15] and of reaction between the rhenium(V) dioxo compound and epoxides or sulfoxides.[16] We have recently reported a convenient deoxygenation of epoxides that is catalytic in rhenium.[17]

During our mechanistic exploration of the epoxide deoxygenation,[18] it became evident that the rhenium(V) intermediate was diverging between two reaction pathways (eq 1). In one, there was an apparent direct transfer of oxygen from reactant to rhenium; in the second, the epoxide experienced net insertion of the Re═O bond into a C−O bond to form a metastable diolate, which then underwent thermal fragmentation with loss of alkene. Results of competition experiments and observation of saturation kinetics indicated that coordination of epoxide to the rhenium center was involved in the catalytic cycle. However, this putative epoxide complex was not observed, and ab initio calculations suggested that binding was quite weak.



(1)

Characterized epoxide complexes are rare. A search of the Cambridge Crystallographic Database reveals only 13 examples,[19] contrasted with a much larger number for other cyclic and acyclic ether complexes. Not surprisingly, these tend to consist of moderately electrophilic metals and exhibit fairly long M−O bonds and thus relatively weak interactions; a small number exist for transition metals and have fairly normal M−O single bonds. One can speculate that although epoxides might be expected to be excellent ligands for steric reasons (substituents are as strongly directed away from the metal as possible in an ether), the inherent high reactivity of epoxides to electrophilic ring opening[20] imparts a high degree of kinetic lability to what might

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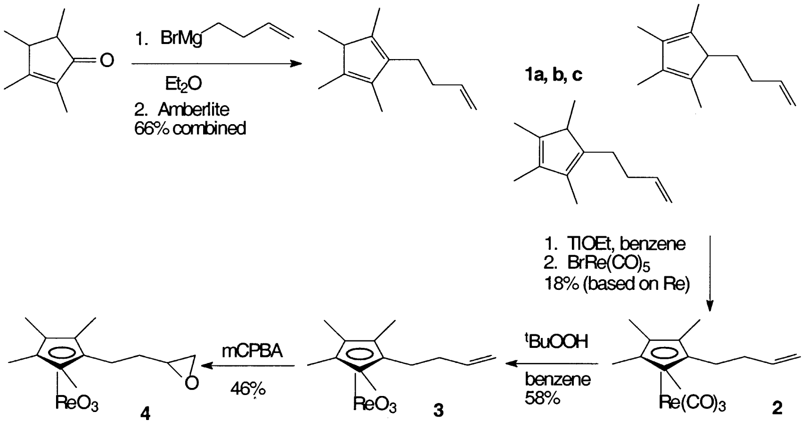
Scheme 1



otherwise be a stable species. Ether−metal interactions are inherently weak, and moderating the electrophilicity of the metal too much will again destabilize the M−O bond. A fine balance of electronic structure is thus necessary to form an observable epoxide complex.

In an effort to bolster the evidence for the participation of a coordinated epoxide in rhenium-mediated O atom transfer, we chose to explore synthesis of a rhenium complex containing a tethered epoxide. Such a species would overcome the significant contribution of entropy to the free energy of binding ($-T\Delta S =$ ca. $+6-10$ kcal/mol for a bimolecular reaction). Successful demonstration of the principle could also open the potential for examining variation in reaction outcome and rate as a function of tether length.

Results

Scheme 1 shows the general approach to the compounds described. Oxidative decarbonylation of an LRe(CO)$_3$ compound was chosen over direct introduction to CF$_3$CO$_2$ReO$_3$ because of reports that the latter method fails for peralkylated cyclopentadienyl groups.

But-3-en-1-yltetramethylcyclopentadiene (1). The ligand was made according to the report by Okuda et al.[21] Addition of but-3-en-1-ylmagnesium bromide (generated in situ from the alkyl halide) to tetramethylcyclopentenone gave the product as a mixture of three regioisomers.

Butenyltetramethylcyclopentadienylrhenium tricarbonyl (2). Two routes have been reported for preparation of Cp*Re(CO)$_3$ complexes. The best current technology is thermolysis of Re$_2$(CO)$_{10}$ in neat pentamethylcyclopentadiene.[22] This method was problematic for this case, in that the pendant olefin of the butenyl group would be subject to polymerization. Attempts to use this method failed to provide more than 9% yield of product. Note that while introduction of the epoxide might have avoided the presumed polymerization difficulties, no feasible means for doing so was obvious. Epoxidation of bromobutene would have been incompatible with formation and reaction of the Grignard reagent, while any attempt to epoxidize **1** would likely have oxidized the ring.

The second method dates from earlier work[23] in which a cyclopentadienide anion effects substitution on BrRe(CO)$_5$. The reported yield of Cp*Re(CO)$_3$ by this route is much lower than for the thermolysis above, but it has the advantage of avoiding conditions that jeopardize the reactive functionality on the tether. Deprotonation of the mixture of isomers of butenyltetramethylcyclopentadiene with TlOEt, followed by addition to BrRe(CO)$_5$ in benzene, led to an 18% yield of the LRe(CO)$_3$ complex. Although this appears to be a marginal improvement over the thermolysis route, it had better reproducibility. This compound exhibited the expected C_s symmetry in the ^{1}H and ^{13}C NMR spectra, and the two IR bands showed a pseudo-C_{3v} system in the carbonyl region (2010, 1918 cm^{-1}). Mass spectrometry (FAB) confirmed the composition, showing a parent ion envelope (M + H$^+$) with the largest peak at $m/z = 445$ (^{185}Re).

Oxidation Reactions. A variety of oxidants are known to convert Cp*Re(CO)$_3$ to Cp*ReO$_3$ via oxidative decarbonylation. One of the best in our hands, ozone,[24] was clearly unsuitable because of the reactive pendant alkene. Our more recent discovery that rhenium catalysis using bis-trimethylsilylperoxide[25] was at least as reproducible and better-yielding opened the intriguing possibility of effecting both oxidative decarbonylation and epoxidation of the alkene.[26] However, in this case the rhenium center in the target complex proved significantly more reactive, and a moderate yield of

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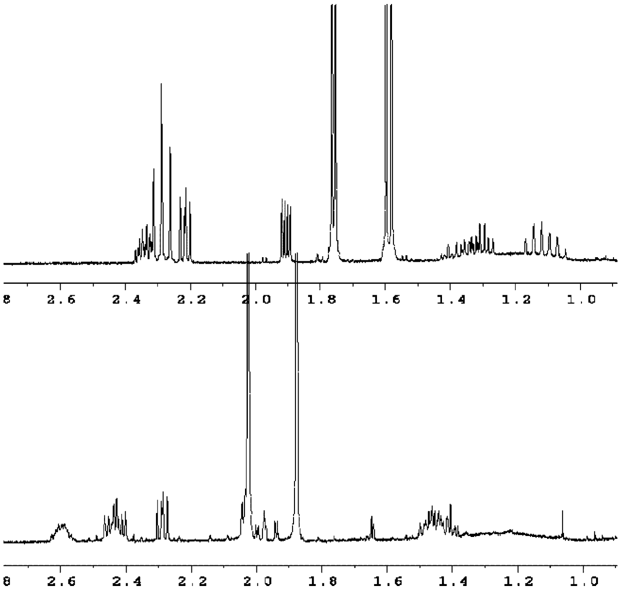


Figure 1. ^{1}H NMR spectra of **4** (top) and **5** (bottom).

butenyltetramethylcyclopentadienyltrioxorhenium (**3**) was obtained as a yellow solid after chromatography on silica. Given the poor material balance, it is possible that some of the epoxy complex was generated, but it was not clearly detected by NMR in the crude reaction mixture nor ever isolated from that mixture. Further, while the trioxo complex was isolated from a small-scale reaction, attempts to scale-up the system failed. Use of ^{t}BuOOH[27] gave modest but reproducible yields of 58% of the trioxide.

The trioxo complex **3** had all spectroscopic behavior expected for this species. The ^{1}H NMR spectrum showed the vinyl system, two coupled methylene units, and two different methyl signals (1.76, 1.61 in C_6D_6). The IR spectrum is very similar to that of Cp*ReO_3, with a strong signal at 909 cm^{-1}. Mass spectrometry confirms the composition; the Re isotopic pattern is noted with M^+ at $m/z = 410$ (^{187}Re).

Further oxidation of this compound with mCPBA in benzene produced the epoxide (**4**) in 46% yield. Reaction of the vinyl group was immediately evident from loss of the downfield signals in the ^{1}H NMR spectrum; the epoxide was evident by appropriately coupled signals at 2.35, 2.22, and 1.92 ppm. The introduction of a new stereocenter had the effect of making protons on C2 in the CH_2CH_2 linker diastereotopic, and the four methyl groups now became distinct. Consistent behavior was seen in the ^{13}C NMR. The IR remained almost the same (908 cm^{-1}), but the mass spectrum showed a gain of 16 mass units to $m/z = 426$ (^{187}Re).

Evaluation of nuclear Overhauser enhancements was performed to ascertain the average solution conformation of the tethered epoxide. Irradiation of the two methyl signals at 1.76−7 ppm led to clear enhancement of the Cp-CH_2 signals at 2.29 ppm and of the other methyl signals at 1.61 and 1.59 ppm, but no other detectable enhancement (see Figure 2).

Reductive Deoxygenation with Phosphines. Reduction of Cp*ReO_3[28] (and many other $LReO_3$ compounds)[29] with PPh_3 is known to produce bridged oxo dimers of the form $\{(LReO)_2(\mu\text{-}O)_2\}$, presumably by direct O atom transfer to phosphorus and dimerization of the reactive $LReO_2$ monomer. While Cp*ReO_2 can be detected by NMR in equilibrium with the dimer at high temperatures,[16a] its equilibrium concentration is never high enough to clearly assign other spectroscopic features such as the IR stretch and the electronic spectrum. The dimer itself has a characteristic dark brown color, likely arising from a Re−Re intermetallic bond supplementing the Re−O−Re linkage;[30] the IR spectrum for the trans-oriented Re=O bonds is at a higher frequency than the trioxide, and the ^{1}H NMR shift of the methyl groups is significantly downfield of those of the monomeric compounds.

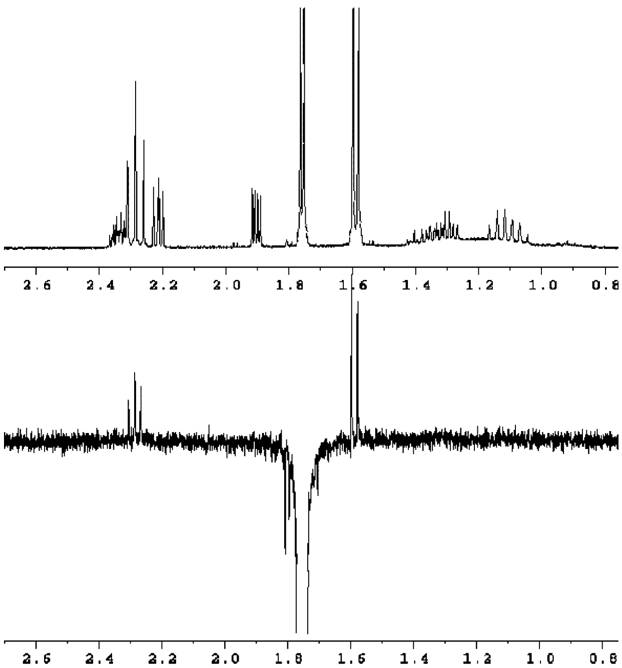
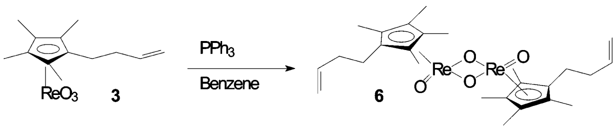


Figure 2. Nuclear Overhauser enhancements seen for **4** upon irradiation at 1.77 ppm.

Compound **3** was reduced with PPh_3 in benzene as a control experiment (eq 2). Production of Ph_3PO was



(2)

observed, as was production of the dark brown color typical of the dimer. Notably, all signals for compound **3** disappeared and new signals attributed to **6** were present. No evidence for coordination of the alkene was seen for **6**; the ^{1}H NMR chemical shift values for the protons on the vinyl group were very similar to those in **3**, and the coupling constants through the tether were almost identical. (See Table 1 for a comparison of chemical shift values.)

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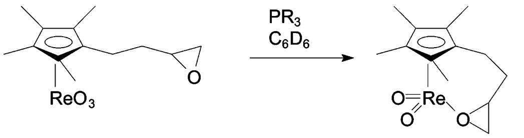
Table 1. Comparison of ^{1}H NMR Chemical Shifts for 3, 4, 5, and 6 (C_6D_6 solvent)

	tether position	3	4	5	6
	C1	2.32	2.29	2.44	2.44
	C2	1.89	1.31	1.46	2.10
			1.14		
	C3	5.52	2.35	2.60	5.72
	C4	4.88	2.22	2.29	4.95
		4.85	1.97	2.04	4.91
$Cp-CH_3$		1.76	1.77, 1.76	2.03	2.03
		1.61	1.61, 1.59	1.88	1.91

When (epoxy)butyltetramethyltrioxorhenium is reacted with either PPh_3 or poly(styryl-PPh_2) in benzene under vacuum, the yellow color of the trioxide turned to a deep red-brown (eq 3). Significant changes in the ^{1}H NMR spectrum occurred for the proton signals from the tether chain (see Figure 1). Most significantly, the Cp-CH_2 signal, a triplet in the trioxide, changed to an overlapping pair of diastereotopic signals for compound **5**. There was also a general downfield shift for all other proton signals in the epoxide and tether. Unexpectedly, the methyl signals in the ^{1}H NMR spectrum exhibited accidental equivalence; only two 6-H signals at 2.03 and 1.88 ppm were seen. In the case where PPh_3 is used as the reductant, characteristic signals for $OPPh_3$ are seen.



5 (3)

The mass spectrum was consistent with loss of a single oxygen: $m/z = 408$ (^{185}Re). The infrared spectrum showed a different signal in the Re═O region at 932 cm^{-1}; while reduction to Re(V) should engender a lower frequency as the metal gains electron density, a compensating factor is loss of competition for π-donation. $LRe(O)X_2$ compounds (L = Cp*, Tp, Tp′) normally have oxo stretches of >950 cm^{-1} and are formally rhenium-oxo triple bonds, whereas the higher oxidation state $LReO_3$ complexes have bands below 920 cm^{-1} and are formally double bonded.

Examination of NOE effects demonstrated that the reaction had caused significant changes in the spatial relationships between the cyclopentadienyl methyl protons and those along the tether and epoxide (see Figure 3). Irradiation of the methyl signal at 1.88 ppm led to enhancement of the second methyl singlet at 2.03 ppm, as well as enhancement of tether protons on C1 and C2 at 1.46 and 2.44 ppm.

Also (and most significantly), the C3 proton at 2.60 ppm was enhanced, demonstrating that the epoxide had moved to within 3 Å of one of the methyl groups.[31] A second epoxide proton at 2.29 ppm was not enhanced; the third proton overlapped the methyl signal at 2.03 ppm (as demonstrated by a 2D COSY experiment), and any enhancement was indistinguishable from the stronger enhancement of the methyl signal.

Unfortunately, the compound formed in solution did not survive attempts to purify it. Chromatography led to formation of an immobile dark band at the top of the column; attempted recrystallization from pentane failed.

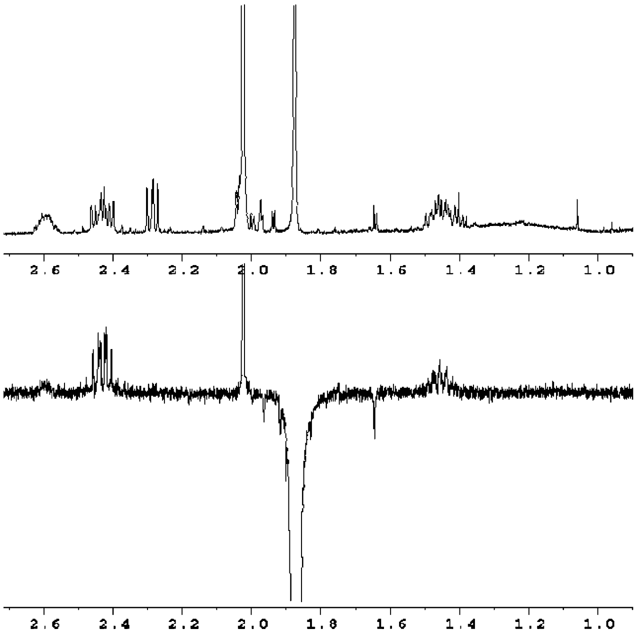


Figure 3. Nuclear Overhauser enhancements seen on irradiating **5** at 1.88 ppm.

Thermolysis of the benzene solution might have led to ring expansion to form a more tractable diolate compound, or formation of compound **3**, but neither was observed (see also modeling results, below). It is somewhat surprising that no **3** was detected as a thermolysis product, although one possible rationale is that the orientation of the epoxide is different from that required in the bimolecular epoxide deoxygenation. The most likely reason is thermal lability of **3** itself; thermolysis at 120 °C in toluene led to decomposition. A final possibility, deoxygenation of the epoxide followed by further reduction, was excluded; neither **3** nor compound **6** was seen in any of the spectra of crude **5**.

Molecular Modeling. The observation of new NOE effects for the C2 protons in **5** suggests a closer interaction with the cyclopentadienyl methyl groups than exists for the freely rotating chain in **4**. We explored molecular modeling for **4** and **5** in an attempt to provide a predictive rationale for the observations that support the claim that the epoxide has coordinated to the metal.

Structures **4**, **5**, and an unligated form of **5** were modeled at the molecular mechanics level using the MMFF94 force field.[32] As expected, the epoxide-terminated butyl chain adopts an extended conformation (Figure 4) in both **4** and unligated **5**. The H−H dihedral angles across C1−C2 are 65° and 180°, consistent with a rotationally averaged observed *J* value of 7.8 Hz. There is no obvious steric barrier to rotation about C2−C3, and the closest methyl-C2−H interaction is 2.62 Å. However, the methyl-C1−H distance in the optimized structure is as short as 2.37 Å, consistent with the observed NOE. Close methyl−methyl interatomic distances are generally in the range of 2.25 Å and again agree with the observation of NOE. The closest approach of a proton on the epoxide ring is well over 3 Å.

A significant change in the tether backbone occurs on coordination of the epoxide in **5**. Now, the backbone

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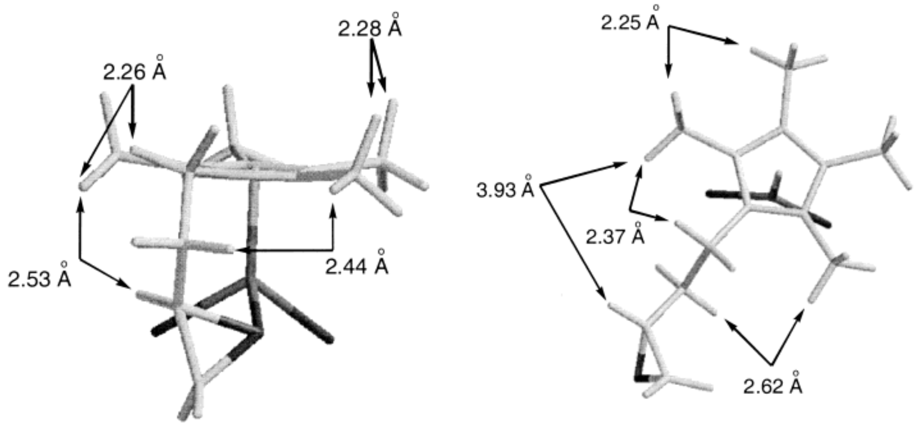

Figure 4. Molecular mechanics-optimized structures of **5** with (left) and without (right) epoxide ligation depicting H−H contacts relevant to NOE experiments described in the text.

curls around to accommodate the Re−O interaction. The Cp−CH_2 methylene group is in a position that provides substantially different dihedral angles with the C2−CH_2 group, consistent with the change in *J* values. Further, the C2−CH_2 group is now in close proximity to one of the methyl groups on the cyclopentadienyl ring: a proton−proton distance of 2.44 Å is noted. The C3 epoxide proton lies 2.53 Å from one of the methyl protons, in perfect accord with the weak enhancement seen. The C4 protons are pointed well away from the cyclopentadienyl substituents. Finally, all protons are in a region of space expected to experience diamagnetic deshielding of some degree from the cyclopentadienyl ring. (An attempt was made to model the diolate that would result from ring expansion of **5**; this would not minimize to a stable species, presumably because of strain along the short tether.)

Discussion

Evidence for ligation of the epoxide to rhenium after reductive deoxygenation with phosphine is circumstantial but strong. Obviously, crystallographic characterization of the product is desirable, but given the extreme lability of the compound (as well as the poor crystallinity of the trioxide precursor) this is not possible.

Three lines of evidence support the claim. The first is that none of the data support formation of the most likely alternative structure: a bridged-oxo dimer. Such a compound is stable (as evidenced by reductive dimerization of **3**), would have a characteristic color different from that observed, and would have an NMR chemical shift for cyclopentadienyl methyl groups that is well downfield of those for either the trioxide precursor or the observed product.

A second line of evidence lies with the changes in coupling behavior among the protons of the tether. While both CH_2 groups are diastereotopic in both the trioxide **4** and the presumed epoxide complex **5**, rotational averaging (and the distance from the stereocenter) leads to a triplet for protons at C1 in **4**. The chemical change at the rhenium (certainly reductive deoxygenation, based on observation of $OPPh_3$) induces a conformational change in the tether that results in distictly nonequivalent protons at C1. Chemical shift changes along the epoxybutyl chain for **5** are consistent with the proposed change in structure but not definitive.

Finally, changes in observed nuclear Overhauser enhancement are precisely in line with those predicted from modeled structures. A noncoordinated epoxide chain has few close spatial interactions (aside from the methyl-C1 proton interactions), as one would expect for a conformationally mobile chain attempting to minimize steric congestion. However, removal of an oxygen atom from rhenium creates a situation in which there is a close enough contact between methyl and C2 protons to observe enhancement upon methyl irradiation. The NOEs clearly arise from creation of close proton−proton contacts in **5**; ligation of the O atom of the epoxide is the only hypothesis that provides a good reason for those contacts to occur.

The primary implication of this observation is to confirm the earlier indirect evidence that an epoxide is a viable ligand for $LReO_2$ compounds, albeit a very weakly coordinating one. There may also be implications for other mechanistically related processes (most importantly, epoxidation) in that the coordinated epoxide represents a viable species with a finite lifetime that can affect reaction kinetics and selectivity.

It is of some note that compound **5**, as postulated, is a d^2 *cis*-dioxo complex. Such compounds are relatively rare as compared to *trans*-dioxo compounds; this has been attributed to electronic instability derived from competition for π acceptor orbitals on the metal.[33] The oxo ligands in **5** (or the nonligated precursor) are precluded from adopting a trans orientation such as is seen in a recent case[34] involving a polypyrazolylborate, where $\kappa^3 \rightarrow \kappa^2$ isomerization allowed rearrangement of the oxos to a trans orientation.

In conclusion, we provide evidence for formation of a tethered epoxide complex on reductive deoxygenation of an $LReO_3$ compound.

Experimental Section

General Procedures. All reactions (unless otherwise specified) were performed under an atmosphere of argon using standard Schlenk vacuum line techniques. Benzene, THF, and ether were dried using Na/benzophenone ketyl; benzene and hexane were dried on Na/K alloy; and dichloromethane was

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[33] (a) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899−3903. (b) Demachy, I.; Jean, Y. *Inorg. Chem.* **1997** *36*, 5956−5958. (c) Demachy, I.; Jean, Y. *Inorg. Chem.* **1996** *35*, 5027−5031.

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dried on CaH_2. All solvents were distilled under vacuum immediately prior to use. ^1H NMR spectra were recorded on either a Bruker DP300 operating at 300.13 MHz or a Bruker DPX400 operating at 400.13 MHz. ^{13}C spectra were recorded on the same instruments; operating frequencies were 75.409 and 100.614 MHz, respectively. Chemical shifts were referenced to solvent lines and measured in ppm downfield from tetramethylsilane ($\delta = 0.00$). IR spectra were recorded on a Nicolet Magna-IR560 spectrometer either as KBr pellets or in NaCl solution cells. Mass spectra were run on a Kratos MS50A in either direct inlet (EI ionization) or FAB mode.

[1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]-rhenium Tricarbonyl (2). A three-necked, 250 mL flask was fitted with a magnetic stirring bar and a Dean−Stark condenser. The flask is filled with argon before dry, deoxygenated benzene (100 mL) is added. Thallium(I) ethoxide (340 μL, 4.8 mmol) is syringed into the solution, followed by the syringe addition of 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene (prepared according to Okuda et al.)[21] (0.97 g, 5.5 mmol). The solution was heated to reflux for 1 h, and 30 mL of benzene was distilled and removed. $Re(CO)_5Br$ (2.0 g, 4.92 mmol) was then added, during which time the solution was heated to reflux under argon for 25 h. Filtration and removal of solvent left a dark orange oil. Purification on a silica column (Scientific Adsorbents Inc, 32-63) eluting with methylene chloride yielded analytically pure product. Yield: 0.37 g (0.84 mmol, 18%). ^1H NMR ($CDCl_3$): δ 5.83 (m, 1H), 5.04 (m, 2H), 2.54 (m, 2H), 2.18 (s, 12H), 2.18(m, 2H). ^1H NMR (C_6D_6): δ 5.57 (m, 1H), 4.90 (m, 2H), 2.24 (dd, 2.24), 1.86 (m, 2H), 1.75 (s, 6H), 1.70 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 198.3, 137.6, 116.0, 101.7, 99.3, 98.9, 36.5, 25.8, 11.14, 11.12. IR (KBr): 2925, 2855, 2010 (ν_{CO}), 1918 (ν_{CO}), 1639, 1452, 1377, 909. MS(FAB): 445 $[M + H]^+$. HRMS: calcd for $C_{16}H_{19}O_3{}^{185}Re$, 444.08640; found, 444.08749.

[1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]-rhenium Trioxide (3). To a solution containing [1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]rhenium tricarbonyl (0.058 g, 0.13 mmol) in 10 mL of C_6H_6 was added dropwise 156 μL of 5.0 M *tert*-butyl hydroperoxide. The solution was stirred at room temperature for 90 min, whereupon the solution was heated to reflux for 20 min. The color of the solution turned to a bright yellow, with a small amount of a brown precipitate. After filtration, volatiles were removed under reduced pressure. The product was then purified by chromatography on silica gel (Scientific Adsorbents Inc, 32-63). CH_2Cl_2 with a trace of acetone was used to elute the product. Yield: 0.031 g (0.08 mmol, 58%). ^1H NMR ($CDCl_3$): δ 5.78 (ddt, 1H, $J = 16.9$, 10.0, 6.8 Hz), 5.06 (ddt, 1H, $J = 17.1$, 3.1, 1.5 Hz), 5.02 (ddt, 1H, $J = 10.2$, 2.7, 1.1 Hz), 2.61 (dd, 2H, $J = 7.8$, 7.6 Hz), 2.28 (m, 2H), 2.24 (s, 6H), 2.17 (s, 6H). ^1H NMR (C_6D_6): δ 5.52 (dddd, 1H $J = 17.9$, 11.1, 8.9, 6.6 Hz), 4.88 (ddt, 1H $J = 11.0$, 2.7, 1.4 Hz), 4.85 (ddt, 1H, $J = 17.8$, 3.5, 1.6 Hz), 2.32 (dd, 2H, $J = 9.3$, 6.8 Hz), 1.89 (m, 2H) 1.76 (s, 6H), 1.61 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 136.7, 121.59, 121.58, 121.2, 116.8, 33.3, 25.4, 10.86, 10.84. IR (KBr): 2927, 2027, 1919, 1637, 1458, 1381, 1364, 909 ($\nu_{Re=O}$), 879 ($\nu_{Re=O}$), cm^{-1}. MS (EI): 410.1 $[M^+]$. HRMS: calcd for $C_{13}H_{19}O_3{}^{187}Re$, 410.08918; found, 410.08812.

[1-(3′,4′-Epoxybutyl)-2,3,4,5-tetramethylcyclopentadienyl]rhenium Trioxide (4). To a solution containing [1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]rhenium trioxide (0.018 g, 0.044 mmol) in 15 mL of C_6H_6 was added 0.02 g of MCPBA (0.1 mmol). After stirring overnight at room temperature, the organic layer was then washed successively with potassium hydroxide and water. The product was then purified by chromatography on silica gel (Scientific Adsorbents Inc, 32-63). One percent acetone in methylene chloride solution was used to elute the product. Yield: 0.009 g (0.02 mmol, 46%). ^1H NMR (C_6D_6): δ 2.35 (m, 1H), 2.29 (t, $J = 7.82$ Hz, 2H), 2.22 (dd, $J = 3.84$, 4.94 Hz, 1H), 1.97 (dd, $J = 2.47$, 4.94 Hz, 1H), 1.77 (s, 3H), 1.76 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H), 1.31 (m, 1H), 1.14 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 121.6, 121.59, 121.3, 121.2, 121.1, 51.8, 47.3, 32.1, 22.5, 10.9, 10.9, 10.74, 10.76. IR (KBr): 2924, 1459, 1364, 908 ($\nu_{Re=O}$), 877 ($\nu_{Re=O}$), cm^{-1}. MS (EI): 426.1 $[M^+]$. HRMS: calcd for $C_{13}H_{19}O_4{}^{187}Re$, 426.08410; found, 426.08420.

[1-(3′,4′-Epoxybutyl)-2,3,4,5-tetramethylcyclopentadienyl]rhenium Dioxide (5). Polymer-supported triphenylphosphine (0.53 g, 0.16 mmol) was added to a 20 mL round-bottom flask containing [1-(3′,4′-epoxybutyl)-2,3,4,5-tetramethylcyclopentadienyl]rhenium trioxide (0.034 g, 0.8 mmol) in 10 mL of benzene at room temperature. The reaction was stirred overnight under a blanket of argon. The solution was filtered, and the solvent was removed under reduced pressure to leave a brown solid. ^1H NMR (C_6D_6): δ 2.60 (m, 1H), 2.44 (m, 2H), 2.29 (dd, $J = 3.84$, 5.21 Hz, 1H), 2.04 (m, 1H), 2.03 (s, 6H), 1.88 (s, 6H), 1.46 (m, 2H). IR (KBr): 2932, 2854, 1459, 932, 643, 538, 419. MS(EI): 408.1 $[M^+ - 2]$. HRMS: calcd for $C_{13}H_{19}O_3{}^{185}Re$, 408.086419; found, 408.08669.

Bis-[1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl(oxo)(μ-oxo)rhenium] (6). Trioxide complex **3** (5 mg) was dissolved in C_6D_6 with PPh_3 (5 mg). The solid reactants dissolved and were allowed to react at room temperature for 1 h. The NMR spectrum showed production of Ph_3PO (7.75, 7.39 ppm), disappearance of **3**, and production of a new compound: ^1H NMR: δ 5.72 (ddt, 1H, $J = 16.8$, 10.3, 6.6 Hz), 4.95 (ddt, 1H, $J = 9.3$, 2.4, 1.1 Hz), 4.91 (ddt, 1H, $J = 17.2$, 2.0, 1.5 Hz), 2.44 (dd, 2H, $J = 10.6$, 6.2 Hz), 2.10 (m, 2H), 2.03 (s, 6H), 1.91 (s, 6H).

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Supporting Information Available: ^1H and ^{13}C spectra for **2**, **3**, and **4**; ^1H spectrum for **5**; 2D COSY spectra for **4** and **5**. The material is available free of charge via the Internet at http://pubs.acs.org.

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