Catalytic deoxygenation of epoxides with $(Cp^*ReO)_2(\mu\text{-}O)_2$ and catalyst deactivation

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***In situ* reduction of Cp^*ReO_3 by PPh_3 to form $(Cp^*ReO)_2(\mu\text{-}O)_2$ allows catalytic deoxygenation of epoxides, however, conproportionation between the Re^{V} and Re^{VII} species to form clusters of $\{(Cp^*Re)_3(\mu\text{-}O)_6\}^{2+}(ReO_4^-)_2$ and new compound $\{(Cp^*Re)_3(\mu^2\text{-}O)_3(\mu^3\text{-}O)_3ReO_3\}^+(ReO_4^-)$ leads to removal of rhenium from the catalytic cycle and loss of activity.**

A primary focus of recent work with metal oxo systems has been formation of new C–O bonds.[1] However, cleavage of C–O bonds with concomitant formation of one or more new M=O bonds is also a useful transformation. One example of this is deoxygenation of epoxides, wherein removal of an oxygen atom generates a new C=C π bond. Given that most methodology for making epoxides begins with the alkene, the combination epoxidation/deoxygenation would provide a useful protection/deprotection sequence for the multiple bond. Few such sequences now exist,[2] and many of these risk loss of stereochemical integrity or remain incompatible with other functional groups in the organic substrate.

We recently observed that $(Cp^*ReO)_2(\mu\text{-}O)_2$ reacted stereospecifically with epoxides to form alkene plus Cp^*ReO_3, presumably *via* the monomeric form Cp^*ReO_2.[3] Cook and Andrews recently reported catalytic deoxygenation of vicinal diols with this rhenium system,[4] so we decided to explore the catalytic deoxygenation of epoxides.

Conditions similar to stoichiometric deoxygenation reactions were used: toluene solvent, sealed under vacuum, heated to 90–120 °C. An initial study of deoxygenation of 1,2-epoxydodecane using 5 mol% Re gave only traces of alkene after extensive reaction times. As seen in Table 1, increasing the porportion of rhenium led to improved yields, but very little turnover. However, catalytic turnover could be achieved if the electronic properties of the epoxide were properly tuned.‡ The optimum turnover was seen in the case of electron-withdrawing substituents (Table 1).

It was evident from these experiments that catalyst turnover was being impeded by an interfering reaction. Further, in cases where poor turnover was observed (Table 1, entries 1, 2, 7), a green solid was seen to precipitate. The rapid reduction of Cp^*ReO_3 to $(Cp^*ReO)_2(\mu\text{-}O)_2$ at room temperature[5a] implied the two compounds did not react with each other, but this might not be true under the fairly severe reaction conditions of the deoxygenation (> 100 °C). Indeed, heating equimolar amounts of the two at 110 °C for 14 h formed a precipitate (sealed tube; isolated yield 5% from $CHCl_3$). This green solid was isolated by filtration and washing with benzene, and was identified as $\{(Cp^*Re)_3(\mu\text{-}O)_6\}^{2+}(ReO_4^-)_2$ **1**, first characterized by Herrmann *et al.*[5] The IR spectrum (908s cm^{-1}, 609, 650w cm^{-1}) and ^{1}H NMR spectrum (δ 2.22, s; CD_3CN) were identical to reported values. As expected, this salt was unreactive toward epoxides at elevated temperatures. Anion exchange with NaI in water gave the iodide salt; the perrhenate band disappeared from the IR spectrum, though the weak μ-O bands remained. Oxidation of the iodide salt with aqueous H_2CrO_4 (Jones' reagent) gave a 37% yield of Cp^*ReO_3 [based on formulating the salt as $\{(Cp^*Re)_3(\mu\text{-}O)_6\}I_2$].

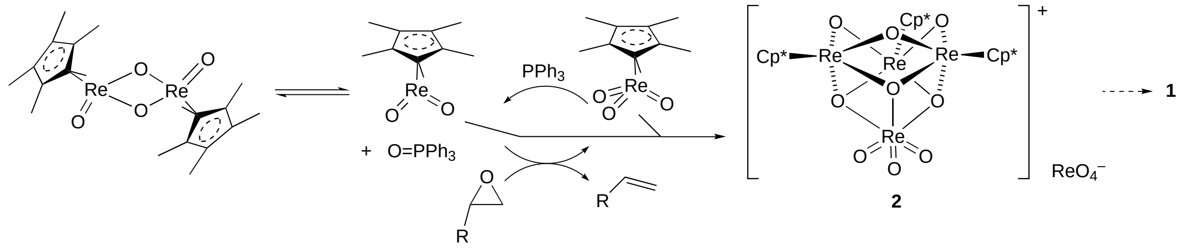
In epoxide reductions and in conproportionation of Cp^*ReO_3 with $(Cp^*ReO)_2(\mu\text{-}O)_2$, this compound was accompanied by formation of an air-stable purple compound **2** that was insoluble in benzene. This second compound became predominant at relatively high rhenium concentrations (Table 1, entries 4, 5); and it was isolated from the conproportionation reaction by precipitation from benzene in 28% yield. Aside from the dramatically different visible spectrum, the only other significant spectroscopic difference from **1** was a new IR peak at 736 cm^{-1} and weak shoulder on the very strong perrhenate Re–O stretch at 908 cm^{-1}. A single sharp peak appeared in the ^{1}H NMR (δ 2.23 in CD_2Cl_2). We obtained high quality crystals of this compound for X-ray diffraction analysis;[6]§ the structure of the cation is shown in Fig. 1.

This compound is formulated as $\{(Cp^*Re)_3(\mu^2\text{-}O)_3(\mu^3\text{-}O)_3ReO_3\}^+(ReO_4^-)$, a monoperrhenate salt of a cluster. Formally, it can be represented by the coordination of ReO_3^- to **1**, although a more useful interpretation is to view it as the neutral $(Cp^*Re)_3(\mu\text{-}O)_6$ coordinated to ReO_3^+. (The latter is consistent with the theoretical prediction that compound **1** should be a ground-state triplet,[7] and similar to other reported structures.[8]) The ReO_3 unit is a slightly distorted octahedral rhenium in a typical $LReO_3$ environment: the terminal oxo bond lengths are normal [1.668(10), 1.685(13), 1.707(12) Å] as are the O–Re–O angles [103.2(6)°, 105.9(6), 104.1(6)°]. The $Re_3(\mu\text{-}O)_6$ core is similar to the trinuclear dication; the Re–Re distances are 2.750(1) and 2.759(1) Å. There is significant distortion of the

Table 1 Reaction of epoxides with catalytic Cp^*ReO_3 + excess PPh_3[a]

	Epoxide	c/M	$[Cp^*ReO_3]$/M	t/h	T/°C	Conversion (%)	Turnover
1	1,2-Epoxydecane	0.16	0.007	20	116	5%	1.1
2	1,2-Epoxydodecane	0.14	0.007	18	112	< 5%	—
3	1,2-Epoxydodecane	0.14	0.029	13	112	20%	0.9
4	1,2-Epoxydodecane	0.14	0.056	13	112	70%	1.6
5	1,2-Epoxydodecane	0.14	0.14	13	112	> 90%	0.9
6	1,2-Epoxydodecane	0.14	0.007†	13	112	50%	10
7	2,3-Epoxynorbornane	0.23	0.009	6	116	< 5%	—
8	*p*-Bromostyrene Oxide	0.12	0.007	16	90	20%	3.4
9	3-Fluoropropylene Oxide	0.28	0.005	3	116	23%	12.9

[a] $[PPh_3]$ = 0.17 M except entry 6, $[PPh_3]$ = 0.35 M.



Scheme 1

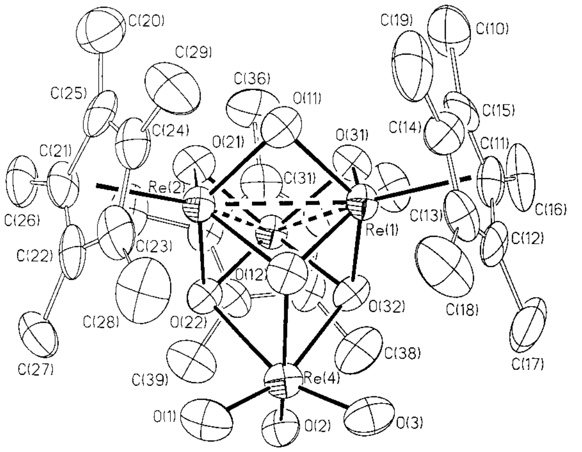


Fig. 1 Crystal structure of the cation for **2**

two sets of bridging oxo ligands compared to compound **1**, with bond lengths averaging to 1.94 Å (μ_2) and 2.02 Å (μ_3). The O–(ReO_3) distances are long at an average of 2.18 Å.

Compound **2** is a precursor to the trinuclear cluster **1**. Heating a Me_2SO solution of **2** in air to 100 °C for 2 h results in quantitative conversion. (Under conditions of the conproportionation or epoxide deoxygenation, Cp^*ReO_3 can play the same chemical role as Me_2SO in converting the ReO_3 unit to perrhenate.)[9] It is still not clear what the origin of the trinuclear core is, nor the fate of the Cp* ligands lost in formation of **1** and **2**. We have seen NMR evidence for monomeric Cp^*ReO_2,[3] but do not see evidence for a trimeric species. It is possible that Cp^*ReO_2 can condense with Cp^*ReO_3, and that this dimeric species initiates a cascade resulting in **2**. Alternatively, if indeed the trinuclear Re^V cluster forms as an equilibrium aggregate of Cp^*ReO_2 units, it may attack Cp^*ReO_3 irreversibly.

Clearly, the success of the catalytic cycle for epoxide deoxygenation (or any other system involving this chemistry) depends on a careful balance of reaction rates (Scheme 1). Cp^*ReO_2 must react with the epoxide substrate rapidly, or else conproportionation will lead to inactivation. The rate of O-atom transfer from epoxide is controlled by the reactivity of the substrate, as seen by the impact of substituent on turnover number. Likewise, Cp^*ReO_3 must be rapidly reduced to Cp^*ReO_2; there is again a competition between reduction and cluster formation. We tested this by increasing the concentration of PPh_3; a 2.4-fold excess led to an increase in conversion from < 5% to 50% (Table 1, Entry 6)! It must be noted that this required an almost saturated solution of PPh_3. Although this modification interferes with the practicality of this catalytic cycle, it shows that the key to an improved system is to design a kinetically more reactive stoichiometric reductant that does not interact with the epoxide.

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Notes and References

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‡ Examination of the stoichiometric O-atom transfer from substituted styrene oxides shows that reaction is accelerated by electron deficient substituents: K. P. Gable and M. A. Gartman, unpublished work.

§ *Crystal data* for $\{(Cp^*Re)_3(\mu^2\text{-}O)_3(\mu^3\text{-}O)_3ReO_3\}ReO_4\cdot NCMe$ (**2**·NCMe). Data were collected on a block shaped (0.5 × 0.3 × 0.2 mm) dark brown crystal of $C_{32}H_{48}NO_{13}Re_5$ (M = 1585.71) on a Siemens P4 equipped with graphite monochromated Cu radiation (μ = 30.002 mm^{-1}) at room temperature. Automated search and indexing routines revealed that the crystals belong to the monoclinic space group $P2_1/c$ (no. 14) with a = 11.180(1), b = 15.631(1), c = 22.612(3) Å, β = 98.614(8)°, U = 3906.8(7) $Å^3$, Z = 4, D_c = 2.696 Mg m^{-3}. Of 10 677 data collected, 5191 were unique (R_{int} = 9.10%), and of these 4997 had $I > 2\sigma(I)$. Data were corrected for the effects of absorption anisotropy by analytical methods (face indexing). The structure was solved using a Patterson map search using SHELXS-90, and expanded by Fourier techniques and refined (full-matrix least-squares refinement on F^2) using SHELXL-93. Refinement of 492 parameters using all data yielded final residuals of R_1 = 0.661, wR_2 = 0.1768. The largest residual electron density peaks (3.28 e^- $Å^{-3}$) were all very close to the Re atoms and are not of chemical significance. CCDC 182/789.

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