

The Surprising Nitrogen-Analogue Chemistry of the Methyltrioxorhenium-Catalyzed Olefin Epoxidation

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For three decades, chemists have been searching for four- and five-membered metallacycles as organometallic intermediates in heteroatom-transfer reactions of d^0 metal complexes with olefins.^{1,2} In 1970, Mimoun and co-workers³ reported the epoxidation of olefins with the molybdenum diperoxo complex $[\text{Mo}(\text{O})(\text{O}-\text{O})_2(\text{OPR}_3)]$ ($\text{R} = \text{N}(\text{CH}_3)_2$) and postulated a stepwise reaction mechanism via an "organometallacycle" **III** (metalla-2,3-dioxolane), whereas in 1972 Sharpless and co-workers⁴ suggested a concerted oxygen-transfer mechanism via transition state **V** (Figure 1). The long-standing controversy⁵ was still lasting when Herrmann and co-workers⁶ developed the industrial olefin epoxidation process based on methyltrioxorhenium (MTO) as the catalyst and hydrogen peroxide as the terminal oxidant, with rhenium peroxy complexes, $[\text{Re}(\text{O})(\text{O}-\text{O})_2\text{Me}]$ and $[\text{Re}(\text{O})_2(\text{O}-\text{O})\text{Me}]$, being active species.^{6c} The controversy on the reaction mechanism was solved with the help of the density functional theory (DFT): In 1998, Rösch and co-workers⁷ demonstrated the Sharpless mechanism to be strongly preferred. Recent studies^{8,9} showed the Sharpless mechanism to be favored for other peroxy complexes and substrates as well.

Aiming to design the first d^0 metal complex that follows the Mimoun mechanism, we have performed a DFT study at the B3LYP level on the reaction of $[\text{Re}(\text{O})_2(\text{O}-\text{NH})\text{Me}]$ (**1**) with ethylene.¹⁰ The idea behind the calculations was the fact that the isodesmic reaction, $\text{H}_2\text{O}_2 + \text{NH}_3 \rightarrow \text{NH}_2\text{OH} + \text{H}_2\text{O}$, is -24 kcal/mol exergonic, thus rendering any reaction involving the cleavage of an N–O bond thermodynamically less favorable than the corresponding O–O cleavage reaction. Direct nitrene transfer to the olefin (aziridination) from $[\text{Re}(\text{O})_2(\text{O}-\text{NH})\text{Me}]$ would require N–O cleavage, whereas the competing formation of an organometallic rhenia-2,3- or 3,2-oxazolidine¹¹ retains the N–O bond.

The free enthalpy profile displayed in Figure 2 shows that aziridination ($\Delta G_a = 40.8$ kcal/mol, **3**) is kinetically slightly more favorable than the formation of the rhenia-2,3-oxazolidine via [2+2] addition of ethylene across the Re–N bond of $[\text{Re}(\text{O})_2(\text{O}-\text{NH})\text{Me}]$ ($\Delta G_a = 42.1$ kcal/mol, **9**). Direct oxene transfer (epoxidation, $\Delta G_a = 50.4$ kcal/mol, **4**) and the formation of a rhenia-3,2-oxazolidine upon [2+2] addition of ethylene across the Re–O bond of $[\text{Re}(\text{O})_2(\text{O}-\text{NH})\text{Me}]$ ($\Delta G_a = 48.8$ kcal/mol, **10**) have significantly higher barriers. The rhenia-2,3-oxazolidine (**12**) and rhenia-3,2-oxazolidine (**13**) are less stable than the reactants by only 6.8 and 11.3 kcal/mol, respectively. Figure 2 summarizes the free enthalpy profile of these reactions in red (with Re–O bond cleavage), blue (with Re–N bond cleavage), and green (reactions of $[\text{Re}(\text{O})_2(\text{O}-\text{O})\text{Me}]$ as a reference).

The fragmentation of the rhenia-2,3-oxazolidine ($\Delta G_a = 31.4$ (=38.2 – 6.8) kcal/mol, **15**) is faster than its formation and liberates ethylideneazane via sigmatropic cycloreversion rather than aziridine, indicating that this pathway could be experimentally distinguished from the Sharpless mechanism by a different product. Similarly, the fragmentation of the rhenia-3,2-oxazolidine ($\Delta G_a = 36.1$ (=47.4 – 11.3) kcal/mol, **16**) does not give oxirane but acetaldehyde, which

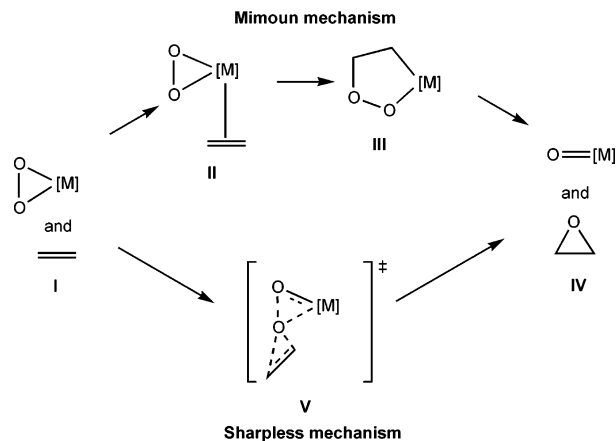


Figure 1. Controversy on the mechanism of the olefin epoxidation with peroxy complexes.

is also the product of the rhenia-2,3-dioxolane fragmentation. Although the fragmentation of the nitrogen-containing metallacycles involves N–O bond cleavage, these reactions are unimolecular and therefore entropically more favorable than the initial bimolecular reactions of $[\text{Re}(\text{O})_2(\text{O}-\text{NH})\text{Me}]$ with the olefin.

The calculations reveal an additional mechanism with a lower activation free enthalpy that also leads to the formation of an organometallic intermediate. Adam and co-workers¹² demonstrated dioxiranes and carbonyl oxides to be different species. Mimoun's^{5a} mechanistic proposals for the olefin epoxidation include 1,3-dipolar metal⁺-O-O⁻ species¹³ as potential precursors of metalla-2,3-dioxolanes. Selke and Valentine¹⁴ reported the formation of a metalla-analogue carbonyl oxide upon ligand-induced opening of a ferric porphyrin η^2 -peroxy complex. However, Mo(VI) and Re(VII) η^2 -peroxy complexes apparently give η^1 -peroxy species only upon protonation at the peroxy ligand.¹⁵ In contrast, we show the rheniaoxaziridine moiety of $[\text{Re}(\text{O})_2(\text{O}-\text{NH})\text{Me}]$ to open with an activation free enthalpy of 16.8 kcal/mol (**21**). The ring-opening product $[\text{Re}(\text{O})_2(\eta^1\text{-O}-\text{NH})\text{Me}]$ (**23**), which is 5.5 kcal/mol less stable than the parent η^2 species, seemed to be a metalla-analogue imine oxide and undergoes a [3+2] cycloaddition with ethylene yielding the rhenia-3,2-oxazolidine. The activation free enthalpy of 30.7 (=36.2 – 5.5) kcal/mol for the [3+2] cycloaddition (**25**) is smaller than those for the reactions of $[\text{Re}(\text{O})_2(\eta^2\text{-O}-\text{NH})\text{Me}]$ with ethylene. Figure 2 summarizes the free enthalpy profile of the reactions via η^1 species in magenta (with Re–O bond cleavage) and cyan (with Re–N bond cleavage).

Analysis of the Wiberg bond index matrix in natural atomic orbital (NAO) basis¹⁶ reveals the unexpected electronic structure of $[\text{Re}(\text{O})_2(\eta^1\text{-O}-\text{NH})\text{Me}]$. The molecule should be considered a metalla-analogue nitrosonium ylide (**23b**) rather than a metalla-analogue imine oxide (**23a**, Figure 2). The Lewis structure **23b** is further supported by a relatively short N–O bond of 1.24 Å (as

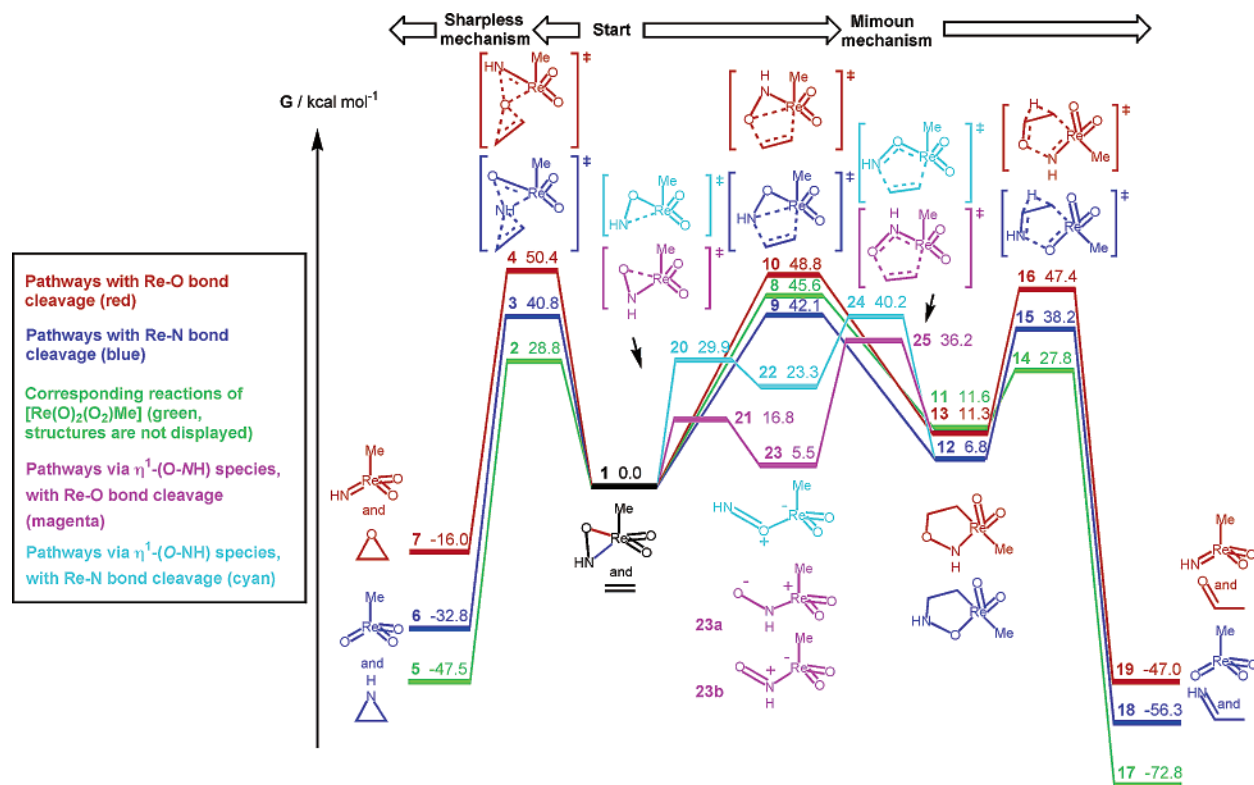


Figure 2. Calculated free enthalpy profile for the reactions of $[\text{Re}(\text{O})_2(\text{O}-\text{NH})\text{Me}]$ with ethylene. The profile for the reactions of $[\text{Re}(\text{O})_2(\text{O}-\text{O})\text{Me}]$ with ethylene is given in green for comparison. **23a** and **23b** are potential Lewis structures of the ring-opening product $[\text{Re}(\text{O})_2(\eta^1-\text{O}-\text{NH})\text{Me}]$. A stable structure of an ethylene complex was not obtained.

compared to 1.41 Å in $[\text{Re}(\text{O})_2(\eta^2-\text{O}-\text{NH})\text{Me}]$, **1**) and by NPA atomic partial charges.¹⁶

In summary, we have predicted a stepwise mechanism for the reaction of $[\text{Re}(\text{O})_2(\eta^2-\text{O}-\text{NH})\text{Me}]$ with ethylene that is more favorable than the concerted nitrene-transfer event. The stepwise mechanism proceeds via a novel $[\text{Re}(\text{O})_2(\eta^1-\text{O}-\text{NH})\text{Me}]$ species and an organometallic rhenia-3,2-oxazolidine. Fragmentation of the organometallacycle gives acetaldehyde. These results stand in sharp contrast to the concerted mechanism of the olefin epoxidation with rhenium peroxo complexes.

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Supporting Information Available: Computational details, calculated structures, and analysis of **1** and **23** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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