A TALE OF TWO TOPOLOGICAL ISOMERS: REACTIVITY COMPARISON OF *Syn* AND *Anti* OXO-IRON COMPLEXES OF TMC

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Iron oxo complexes of tetramethylcyclam (TMC) are a class of compounds that contain an iron atom bound to a TMC ligand and an oxo (O) group. These complexes are known for their high reactivity towards various oxidants and have been extensively studied for their potential applications in catalytic oxidation reactions. One of the important applications of these complexes is in oxygen atom transfer (OAT) reactions, which are widely used in organic synthesis for the functionalization of organic compounds. In OAT reactions, a functional group is transferred from a donor molecule to an acceptor molecule via an oxygen atom. The use of TMC-based iron oxo complexes as catalysts in OAT reactions has several advantages over other catalysts. For example, these complexes have been shown to exhibit high selectivity and efficiency in a variety of OAT reactions. Moreover, they are relatively stable and easy to handle, making them a practical choice for catalytic applications. Another advantage of TMC-based iron oxo complexes is their low toxicity compared to other metal-based catalysts. This makes them a more sustainable and environmentally friendly option for oxidation catalysis. Additionally, TMC ligands are readily available and relatively inexpensive, which further enhances the practicality of these complexes in catalytic applications. There are different isomers of $[(TMC)Fe^{IV}=O]^{2+}$ depending on the connectivity of oxygen with Fe either on anti or syn face of the complex. As a result, the reactivity and selectivity of OAT towards different substrates might be affected.

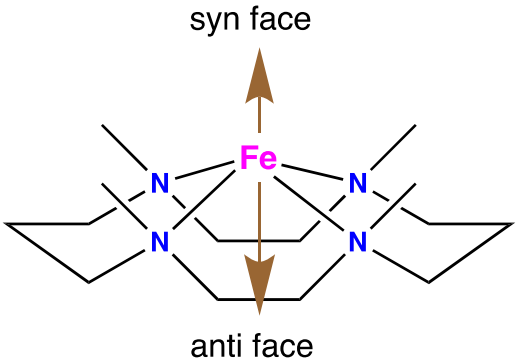

Figure 1. Binding modes of $[(TMC)Fe^{IV}]^{+n}$
(n = 1 or 2 depending on the ligand attached to Fe, on opposite face to oxo in octahederal geometry)

With the help of DFT calculations, we have explored the rates of reactions for OAT when oxygen is either syn or anti to the methyl groups attached to nitrogen atom (Figure 1). It will help us understand the topological effect of the ligands on the reactivity and selectivity of reactions.

[1] Prakash J., et. al. *Inorg. Chem.* 54, (2015): 11055–11057.

[2] Rohde J., et al. *Science* 299 (2003): 1037-1039.