# Kinetics and mechanism of $O_2$-activation using Zr(IV) with redox-active ancillary ligand

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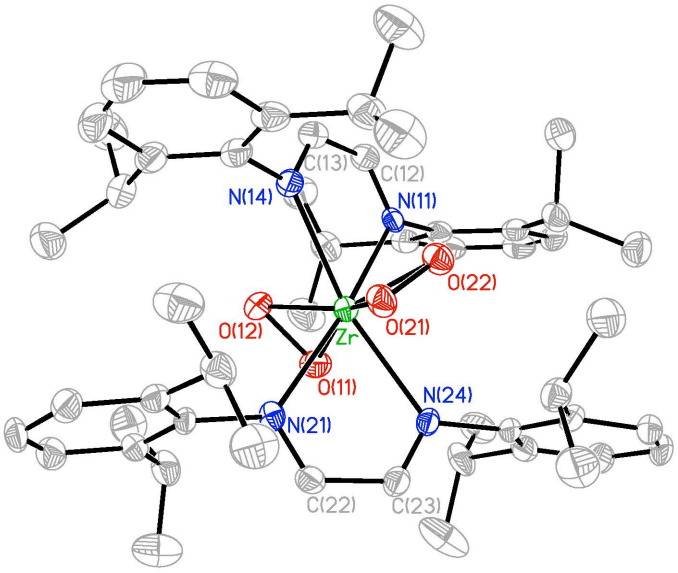
Molecular oxygen is nature's oxidant of choice. Green chemical processes should aim to use dioxygen in oxidation. Non-innocent ligands on zirconium have been shown to facilitate oxidative addition and reductive-elimination processes.[1,2] In one such system, we have shown that non-innocent imine ligands are capable of reducing molecular oxygen to give peroxo ligands on zirconium.[3] See x-ray structure below.

In this presentation, we will describe the synthesis, characterization, and kinetic studies of an $\eta^2$-bisperoxo $Zr^{IV}$ coordination complex supported by two bulky bidentate diimine ligands. The reaction chemistry of Zr versus Ti will be discussed. In the activation of dioxygen, the ligand provides the four electrons ($4e^-$) required for the reduction of two equivalents of dioxygen to form the bis-$\eta^2$-peroxo complex. The kinetics of Zr-peroxo formation takes place over a two step process. The first step is fast and first order in $O_2$ and Zr. The second step is slow, not dependant on $O_2$ and shows solvent dependence. Density Functional Theory (DFT) computations have been employed to shed light on the electronic structure of the Zr starting complex as well as the peroxo product. The peroxo complex shows a degenerate LUMO with large ligand character focused on the backbone.




(1)Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. *Inorganic Chemistry* **2005**, *44*, 5559-5561.
(2)Haneline, M. R.; Heyduk, A. F. *Journal of the American Chemical Society* **2006**, *128*, 8410-8411.

(3)Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *Journal of the American Chemical Society* **2007**, *129*, 12400-+.