Dioxygen Activation by Synthetic Models of Nonheme Iron Enzymes

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Nonheme iron enzymes activate $O_2$ to carry out a number of metabolically important transformations. The oxygen activation mechanisms proposed for nonheme iron systems generally follow the heme paradigm in invoking the involvement of iron-peroxo and iron-oxo species in their catalytic cycles. However, the nonheme ligand environments allow for end-on and side-on $O_2$ coordination and show greater flexibility in the modes of $O_2$ activation. Thus, the investigation on synthetic functional model complexes that can activate $O_2$ is important to understand the nature of the reactive oxygen intermediates.

In the course of investigating the $O_2$ activation by synthetic model complexes, we report here two different iron(II) complexes of the tetradentate 6-Me$_3$TPA ligand (L). The mononuclear iron(II) complex of mandelate reacts with $O_2$ and undergoes oxidative decarboxylation but the dinuclear complex of phenylpyruvate reacts with $O_2$ to undergo oxidative C2-C3 bond cleavage of phenylpyruvate (Scheme). This difference in reactivity reflects the different $O_2$ activation pathways by the two complexes. Spectroscopic and structural characterization of the complexes, involvement of possible intermediates and in-depth reactivity studies will be discussed.

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\begin{align*}
\text{LFe}^{\text{II}}\text{Fe}^{\text{II}}\text{L} + \cdot_2 & \rightarrow \text{LFe}^{\text{II}}\text{Fe}^{\text{II}}\text{L} + \text{CO}_2 + \text{H}_2\cdot \\
\text{Ph} & \text{O} \quad \text{O} \quad \text{LFe}^{\text{II}}\text{Fe}^{\text{II}}\text{L} + \cdot_2 \rightarrow \text{PhCH}\cdot
\end{align*}
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