Dioxygen Activation by Synthetic Models of Nonheme Iron Enzymes

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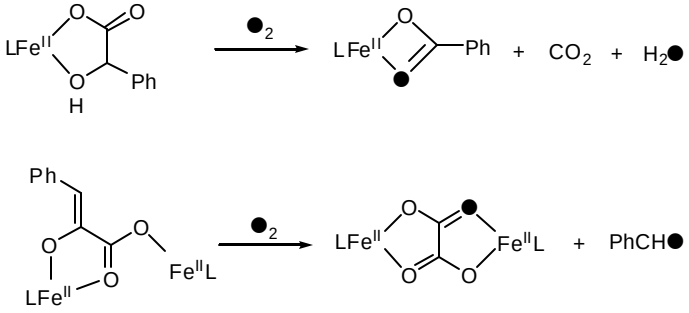
Nonheme iron enzymes activate O_2 to carry out a number of metabolically important transformations.[1] The oxygen activation mechanisms proposed for nonheme iron systems generally follow the heme paradigm in invoking the involvement of iron-peroxo and iron-oxo species in their catalytic cycles. However, 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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1. Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev*. **2004**, *104*, 939-986.