Regiospecific ligand oxygenations in iron complexes

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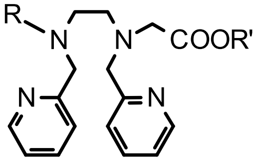
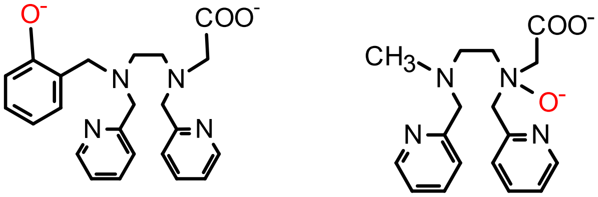
A single oxygen atom can be inserted in two different ways into iron(III) complexes of pentadentate N_4O ligands on their reaction with H_2O_2 or ^tBuOOH. A phenolato arm is produced in the system containing a benzyl substituent $(L^1)^-$ and an *N*-oxide is produced in the related methyl-substituted ligand $(L^2)^-$. The modified ligands, L^1O^{2-} and L^2O^- were characterized by single crystal X-ray diffraction as their mononuclear iron(III) complexes. These iron-promoted oxygenation reactions model substrate activation chemistry of the non-heme iron enzymes, several of which furnish a mononegative endogenous donor set, typically combinations of 2-3 his and an asp or glu. While a few examples of Fe-promoted aromatic C-H activation are known,[1] the formation of an *N*-oxide is unprecedented for this type of biomimetic chemistry.

Ligand precursors:



$(L^1)^-$, R=$CH_2C_6H_5$, R'=H
$(L^2)^-$, R=CH_3, R'=H
L^{me}, R=CH_3, R'= CH_3

The modified ligands L^1O^{2-} and L^2O^- characterized in Fe(III) complexes and produced from iron-promoted oxygen atom insertion reactions:



[1] S. Menage, J. B. Galey, G. Hussler, M. Seité, M. Fontecave, *Angew Chem. Int. Ed*. **1996**, 35, 2353-2355; M. P. Jensen, S. J. Lange, M. P. Mehn, E. L. Que, and L. Que, Jr. *J. Am. Chem. Soc*., **2003**, *125*, 2113-2128; H. Furutachi, M. Murayama, A. Shiohara, S. Yamazaki, S. Fujinami, A. Uehara, M. Suzuki, S. Ogo, Y. Watanabe and Y. Maeda, *Chem. Commun.* **2003** 1900-1901; F. Avenier, L. Dubois, J.-M. Latour, *New J. Chem.*, **2004**, *28*, 782-784.