New reaction channels with nonheme iron oxidation catalysts

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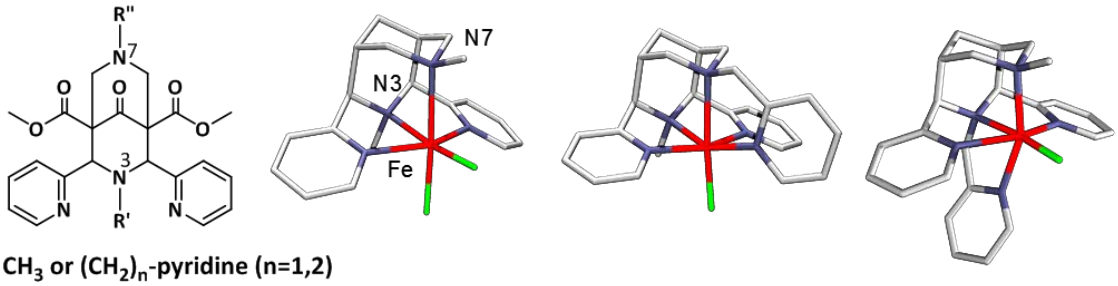
Bispidine ligands are extremely rigid, easy to synthesize and available in a large variety. They enforce coordination geometries derived from *cis*-octahedral, and the two vacant coordination sites with the tetradentate ligand systems are sterically and electronically distinct; with the isomeric pentadentate ligands, the site of the oxo group is enforced by the ligand (see Figure). Co-ligands coordinated *trans* to N3 generally have strong and short bonds, those *trans* to N7 are more labile. Reasons are analyzed on the basis of computational work as well as experimental structural data, thermodynamics, spectroscopy and reactivities. Implications with respect to the mechanism of formation and decay, the structure and spin state of high-valent iron oxidants and possibilities to tune the spin state, structure and reactivity of these high-valent iron complexes are discussed.[1-3]



R', R'' = CH_3 or $(CH_2)_n$-pyridine (n=1,2)

The specific examples that will be discussed are the halogenation of alkanes (the modeling of halogenase activity), the spin state and reactivity of the Fe^{IV}=O species with the tetradentate bispidine and the environmentally important ferryl-assisted natural aerobic methane formation.

[1] Comba, P.; Kerscher, M.; Schiek, W. *Progr. Inorg. Chem.,* **2007**, *55*, 613-704.
[2] Comba, P.; Kerscher, M.; Krause, T.; Schöler, H. F. *Env. Chem.* **2015**, *12*, 381-395.
[3] Comba, P.; Kerscher, M.; Rück, K.; Starke, M. *Dalton (Perspective).* **2018**, *47*, 9202-9220.