

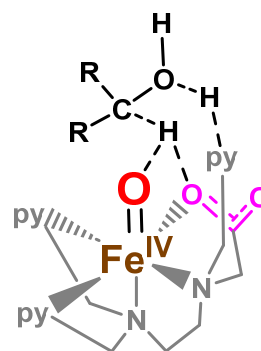
BIOMIMETIC OXIDATION REACTIONS BY IRON COMPLEXES

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A plethora of O₂ activating metalloenzymes provide inspiration for catalyst design for chemical production based on sustainable chemical feedstocks, water and air, and for abating toxic waste.

Towards this goal we have prepared a series of iron complexes which, analogously to the O₂ activating non-heme enzymes, feature a carboxylate donor. In reactive intermediates, this monodentate donor is located *cis* to a coordinated terminal oxidant, or to the oxo ligand in derived high-valent species, proffering steric and electronic influence in the association and reactions with substrates (figure). Significantly these complexes show increased reactivity towards C-H substrates compared to counterparts based on multidentate neutral N-donor ligands. We have characterized several intermediates and demonstrated the oxidation of C-H substrates by a range of terminal chemical oxidants (O₂,^[1] hydro/alkylperoxide,^[2] hypervalent iodine,^[3] hypochlorite^[4], and Ce⁴⁺^[5]). With perspectives for organic substrate oxidation in P2X applications, iron(IV)oxo complexes^[6] can also be electrochemically produced in water.



Proposed enzyme-like supramolecular association of the C-H bond of a substrate with the *cis* oxo and carboxylate groups and a periphery base of an aqueous Fe(IV) complex.

This work has provided valuable lessons for future catalyst, and experiment, design strategies. These will need to take into account competing reactions like the catalysis of terminal oxidant disproportionation,^[7] supporting ligand oxidations,^[1] and light-promoted decarboxylation^[8].

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