

## Heme/Non-heme Diiron Models for the Active Site of Nitric Oxide Reductases

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Nitric oxide reductases (NORs) are anaerobic membrane-bound bacterial enzymes that catalyze the reduction of nitric oxide (NO) to nitrous oxide (N<sub>2</sub>O), using electrons donated from cytochrome *c*. Our first generation model, a heme/non-heme diiron(II) complex [(<sup>6</sup>L)Fe<sup>II</sup>...Fe<sup>II</sup>-(Cl)]<sup>+</sup>, was generated for the reduced active-site form of NORs. [(<sup>6</sup>L)Fe<sup>II</sup>...Fe<sup>II</sup>-(Cl)]<sup>+</sup> was made by reduction of the corresponding μ-oxo diferric compound [(<sup>6</sup>L)Fe<sup>III</sup>-O-Fe<sup>III</sup>-(Cl)]<sup>+</sup>. With O<sub>2</sub> and CO, adducts were formed, [(<sup>6</sup>L)Fe<sup>III</sup>(O<sub>2</sub><sup>-</sup>)(thf)...Fe<sup>II</sup>-(Cl)] {λ<sub>max</sub> 418 (Soret), 536 nm; ν<sub>O-O</sub> = 1176 cm<sup>-1</sup>, ν<sub>Fe-O</sub> = 574 cm<sup>-1</sup>} and [(<sup>6</sup>L)Fe<sup>II</sup>(CO)(thf)Fe<sup>II</sup>-(Cl)]B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> {ν<sub>CO</sub> = 1969 cm<sup>-1</sup>}, respectively. Reaction of purified nitric oxide with [(<sup>6</sup>L)Fe<sup>II</sup>...Fe<sup>II</sup>-(Cl)]<sup>+</sup> led to the dinitrosyl complex [(<sup>6</sup>L)Fe<sup>III</sup>(NO)...Fe<sup>III</sup>(NO)-(Cl)]<sup>+</sup> {ν<sub>NO</sub> = 1798 cm<sup>-1</sup> for non-heme Fe-NO, and 1689 cm<sup>-1</sup> for heme-NO}. With these first generation modeling results in hand (*J. Am. Chem. Soc.* **2005**, *127*, 3310-3320), we are now pursuing other systems, including these mixed-valent Fe(II)...Fe(III) compounds. These or others may lead to functional models, where NO coupling and N<sub>2</sub>O production will occur. Progress in these efforts will be presented.