Metal Dithiolate Cyanide Complexes for Modeling the Fe-Only Hydrogenases: Why did Nature Choose Iron?

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The Fe-only hydrogenases feature a unique diiron active site containing cyanide and carbonyl ligands. Of topical interest is the mechanism by which this site facilitates the reduction of protons to dihydrogen, as well as the reverse process. In earlier studies, species such as $[Fe_2(SR)_2(CN)_2(CO)_4]^{2-}$ were found to be unstable with respect to protonation thereby precluding studies of the proton reducting properties. Related dimetallic cyanides are however proving to be more tractable. For example, $[Fe_2(SR)_2(CN)(PMe_3)(CO)_4]^-$, is a highly efficient catalyst for production reduction.

This poster will survey the synthesis of metal dithiolate cyanide complexes focusing on comparisons between the reactivity of related Fe vs. Ru species. In most cases, the reactivity is better behaved for the diruthenium compounds but the overpotentials for proton reduction are inferior. These models allow us to address the question - Given a choice, would Nature select a base metal or a platinum metal for proton reduction?