

# Bio-Inspired Catalyst Design for Small Molecule Activation

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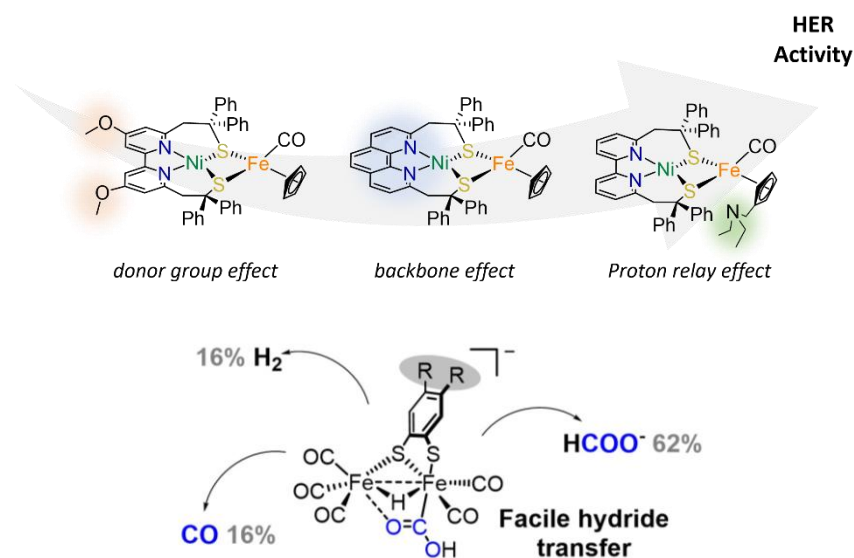
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The activation of small molecules through multi-electron reduction catalysis is a key challenge in the search for sustainable solutions to current energy and environmental issues. These redox processes are generally mediated by metal ions. In our efforts to develop efficient systems for such transformations, we have focused on thiolate-based scaffolds, since metal-thiolate complexes are common in the active sites of enzymes catalyzing similar reactions. Notable examples include hydrogenases, which reversibly reduce protons to generate H<sub>2</sub>, and formate dehydrogenases, which can selectively and reversibly convert CO<sub>2</sub> to formate.

Our goal is to design robust and active catalysts for H<sub>2</sub> production and CO<sub>2</sub> reduction, using thiolate ligands coordinated to earth-abundant, noble-metal-free ions. To this end, we systematically explored series of complexes to assess the influence of the first coordination sphere, highlighting the crucial role of the thiolate and the second coordination sphere, where a proton relay can be introduced. <sup>[1-3]</sup>

Finally, mechanistic investigations involving the generation and spectroscopic characterization of intermediate species provide insight into the key factors governing catalytic activity, guiding the rational design of improved systems.



[1] Tuning Electronic and Molecular Structures of Bio-Inspired Heterodinuclear NiFe Catalysts for Enhanced Catalytic H<sub>2</sub> Evolution, N. Lalaoui, I. Suarez-Antuna, S. Arjunan, M. Curtil, P.C. Ioannou, F. Molton, P. Y. Chavant, C. Philouze, A. Milet, P. Maldivi and C. Duboc, *ACS Organic & Inorganic Au* **2025**, 5(4), 203-237.

[2] Mechanistic tuning of a Bio-Inspired NiFe Catalyst through Proton Relay Introduction for Enhanced H<sub>2</sub> Production, L. Sun, N. Lalaoui, S. Arjunan, I. Suarez-Antuna, C. Philouze, F. Molton, P. Maldivi, V. Artero, A. Milet, C. Duboc, *submitted*

[3] Selective Electrochemical CO<sub>2</sub> Reduction to Formate: Mechanistic Insights into [FeFe]-Hydrogenase Models with Tunable Bridging Ligands, G. L. Tripodi, L. Chatelain, S. Kumar, A. Milet, C. Duboc, N. Lalaoui, *ACS Catalysis* **2025**, accepted.