

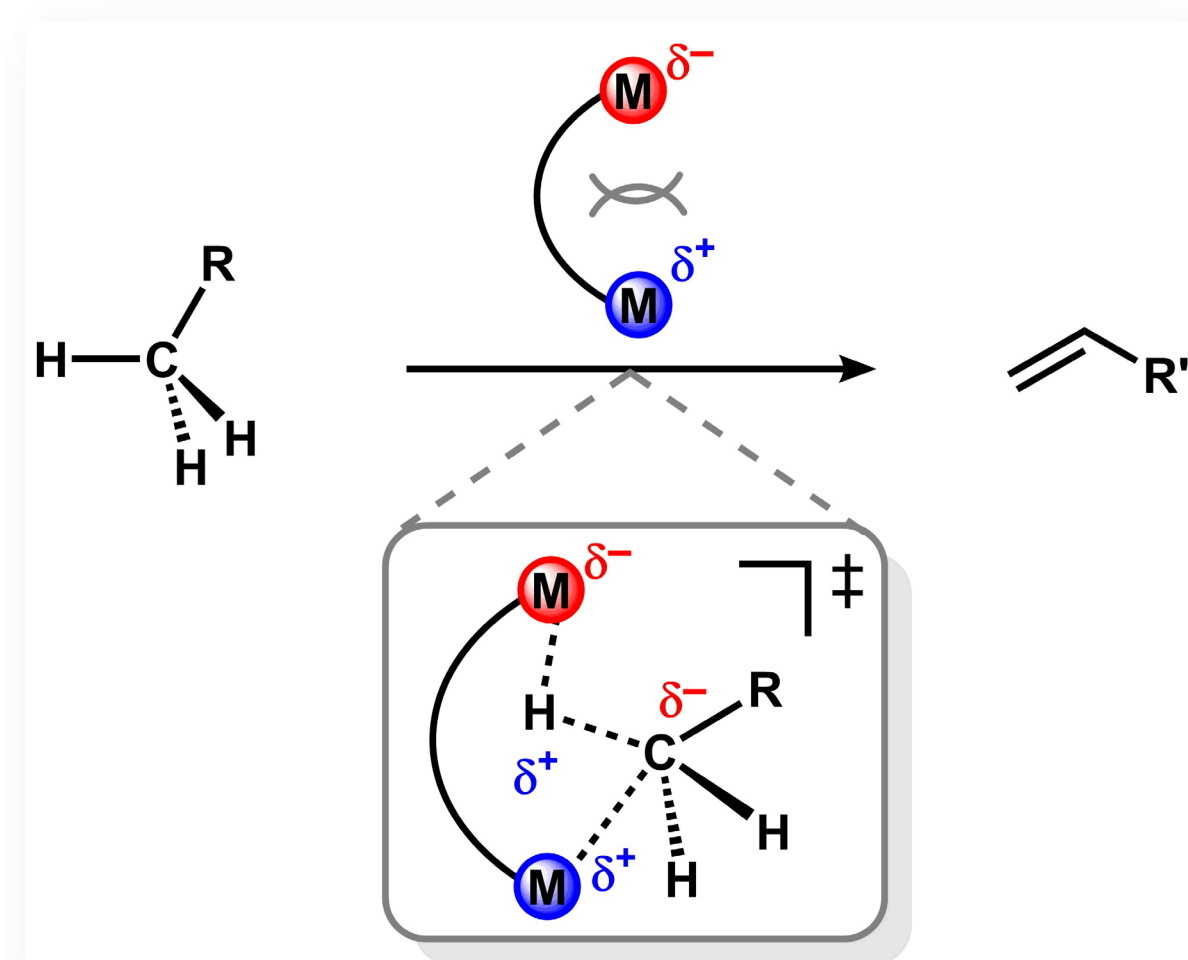


Inorganic Chemistry – Spectroscopy – Bioinorganic Chemistry

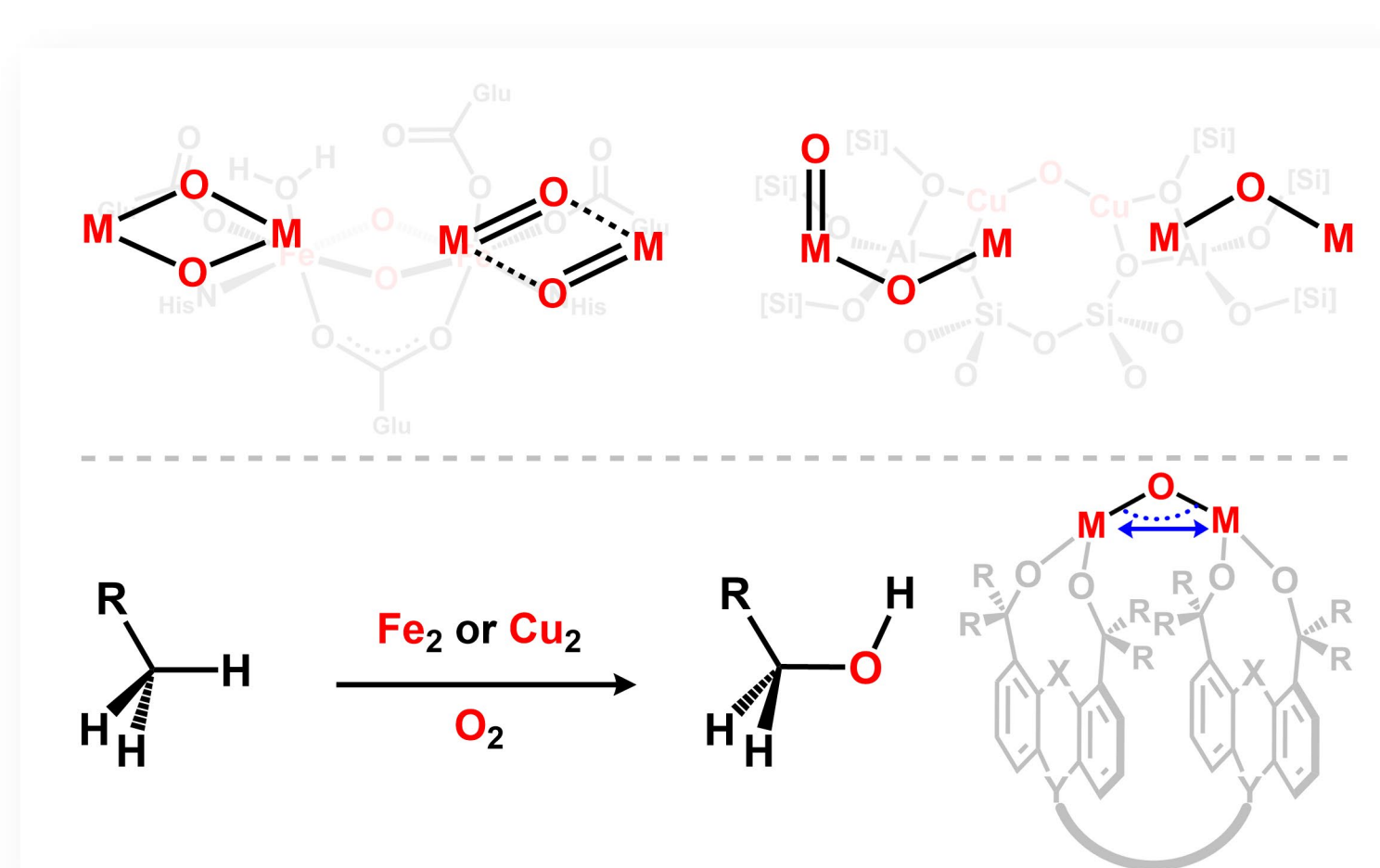
We seek to combine inorganic, organometallic, and bioinorganic tools to enable advancements in energy- and biologically-relevant problems. We aim to leverage metal-metal and metal-ligand cooperativity using synthetic and biological scaffolds to manipulate the electronic structure and reactivity of earth-abundant, first-row transition metals and promote challenging transformations. Spectroscopic, mechanistic, and reactivity studies will help inform the development of efficient catalysts.

titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.6934	copper 29 Cu 63.546
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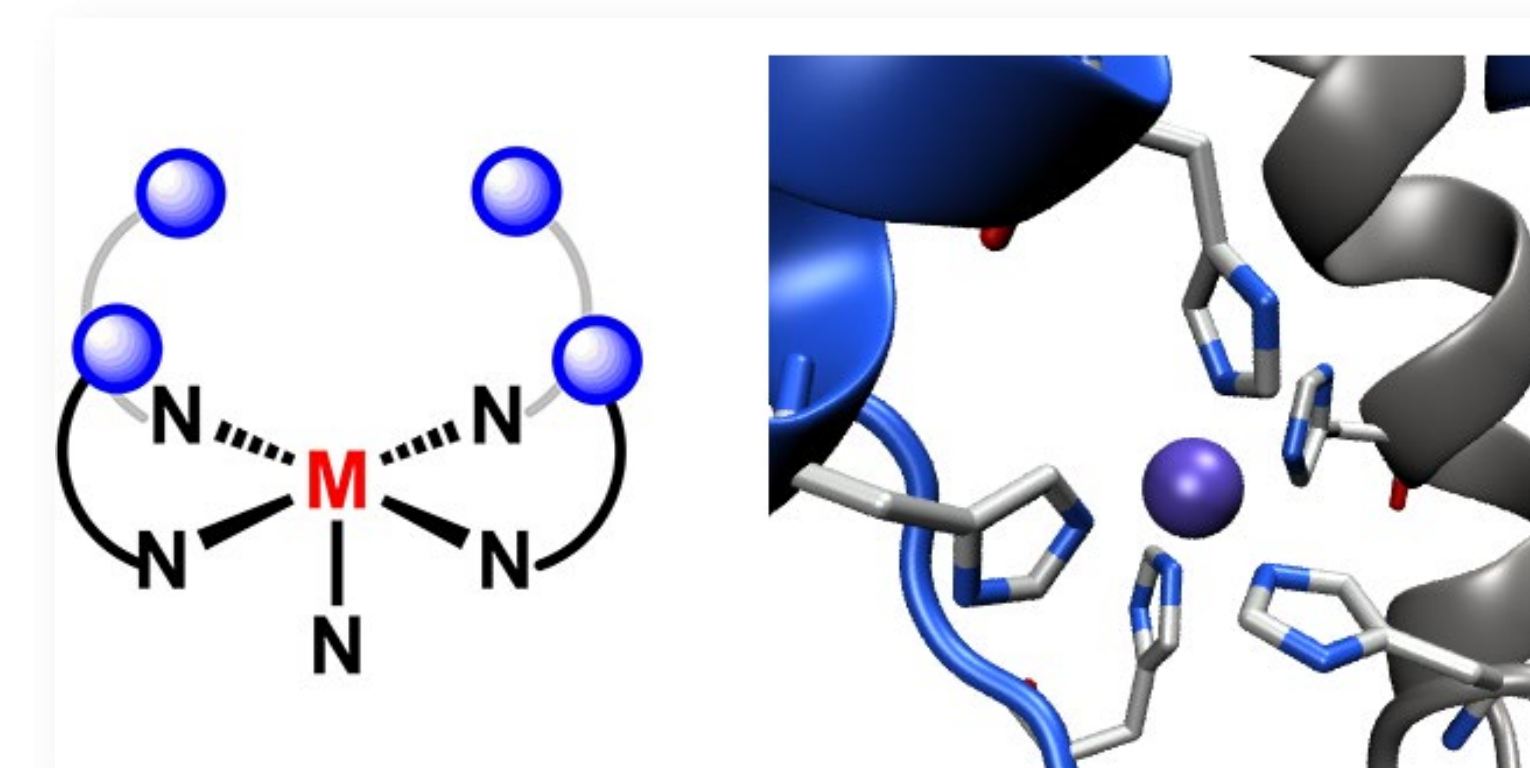
Frustrated transition metal pairs Alkane dehydrogenation



Electronic structure / function correlation Aerobic alkane hydroxylation



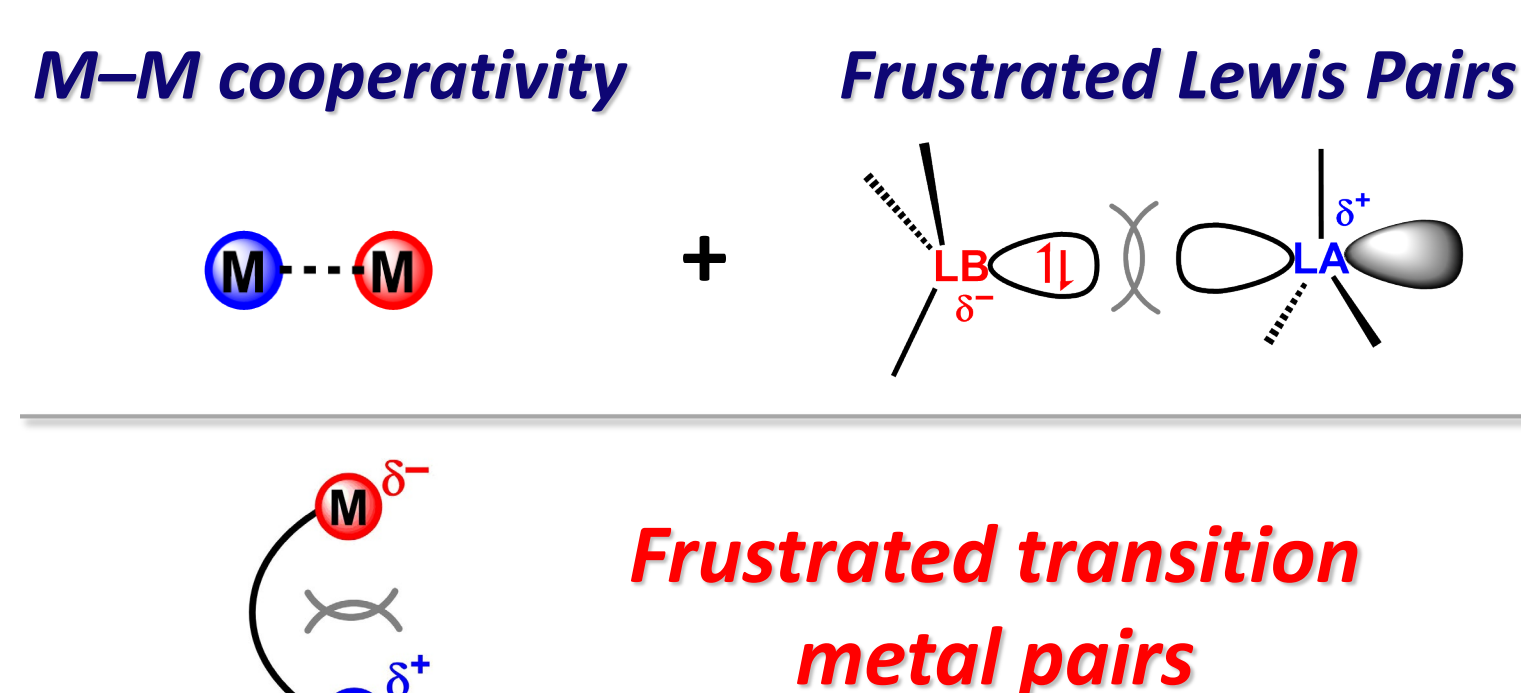
Proteins as ligands for unique metallocofactors Small molecule activation and catalysis



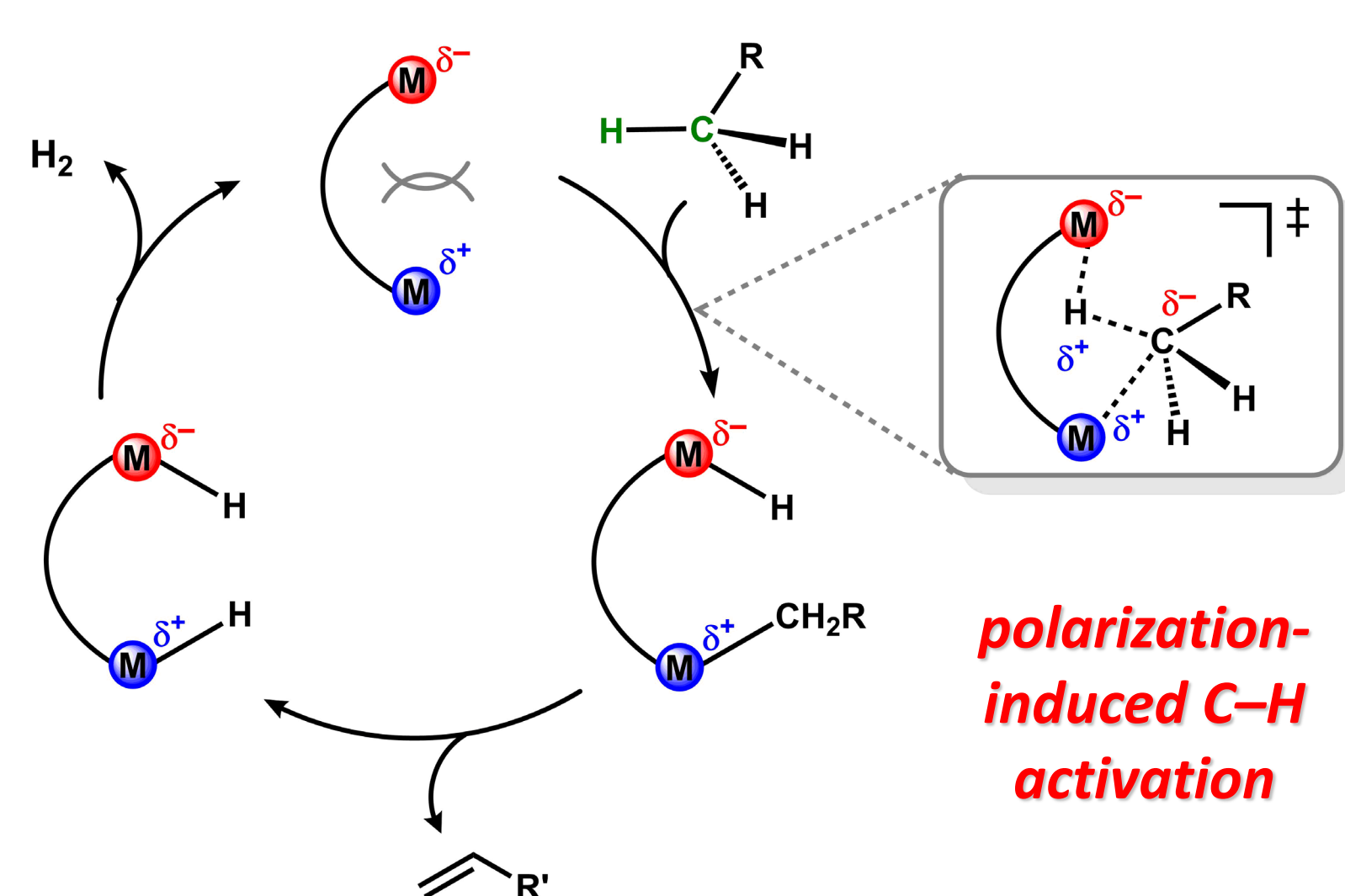
Frustrated Transition Metal Pairs

Frustrated transition metal pairs (FTMPs) for C-H activation

Right. We seek to explore bimetallic cooperativity to induce polarization and promote activation of strong bonds. We are interested in designing and exploring first-row transition metal systems that expand upon the concept of Frustrated Lewis Pairs (FLPs).



Below. We aim to systematically tune these FTMPs to elaborate the extent of polarization and its impact on the reactivity of each metal site. Ultimately, we seek to provide an alternate strategy for activation of strong aliphatic C-H bonds using earth-abundant first-row transition metals.



What is the role of M-M interactions?

What is the reactivity profile of FTMPs?

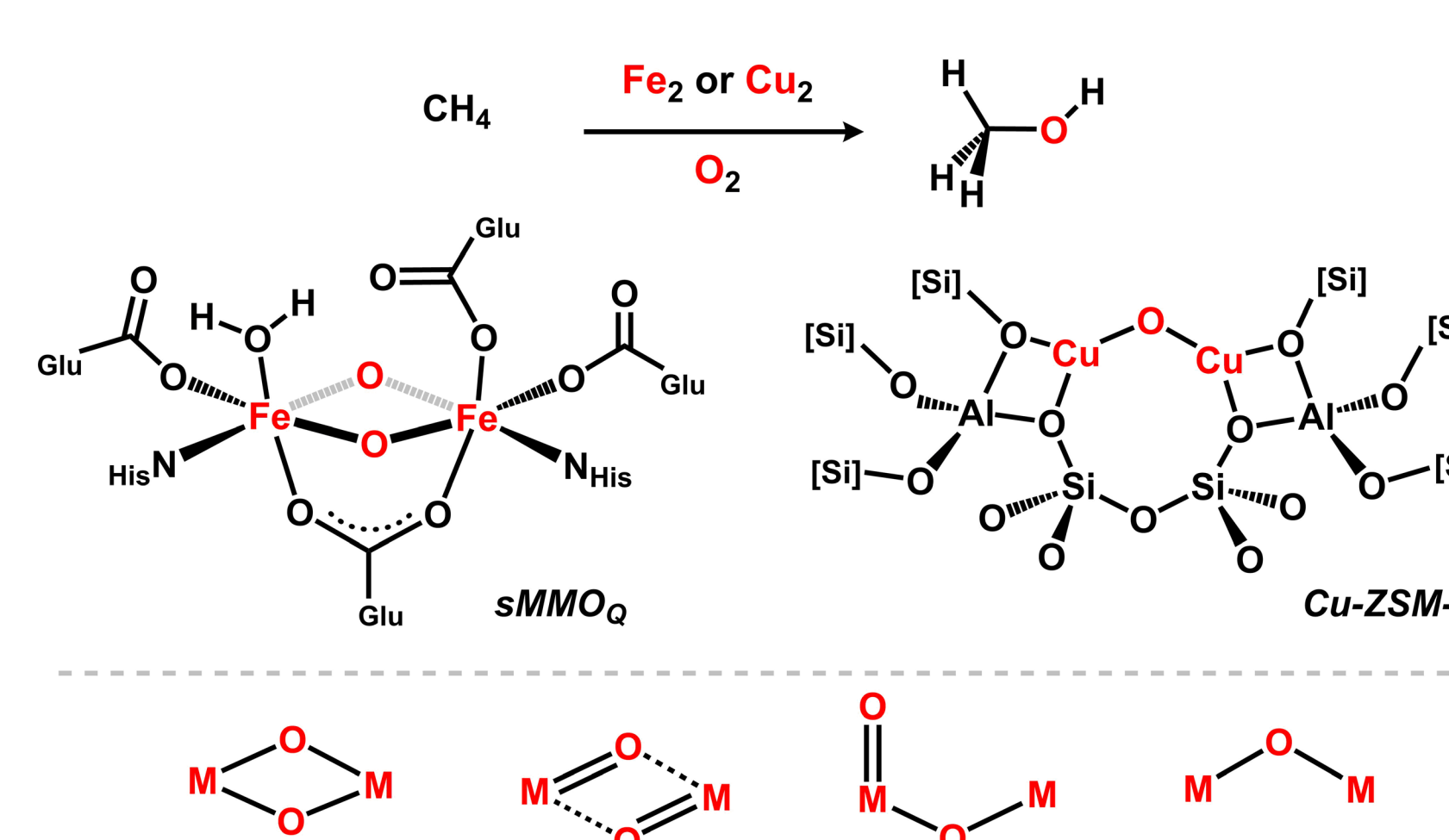
Can we tune the FTMPs to accomplish C-H activation?

polarization-induced C-H activation

Above. We will be targeting both pairs of monometallic complexes as well as design dinuclear platforms to (1) enable synthesis of heterobimetallic complexes; (2) control the M-M separation; and (3) accommodate substrate interactions with the metal sites.

Bioinspired Dinuclear Complexes for Aerobic Hydroxylation

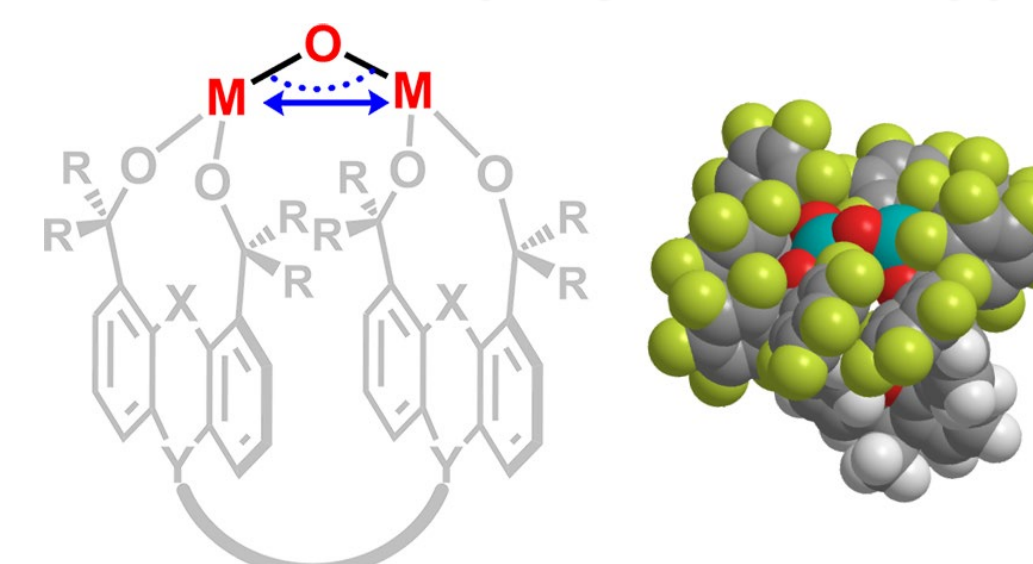
Enzymatic and industrial aerobic methane oxidation – Fe₂ and Cu₂ sites



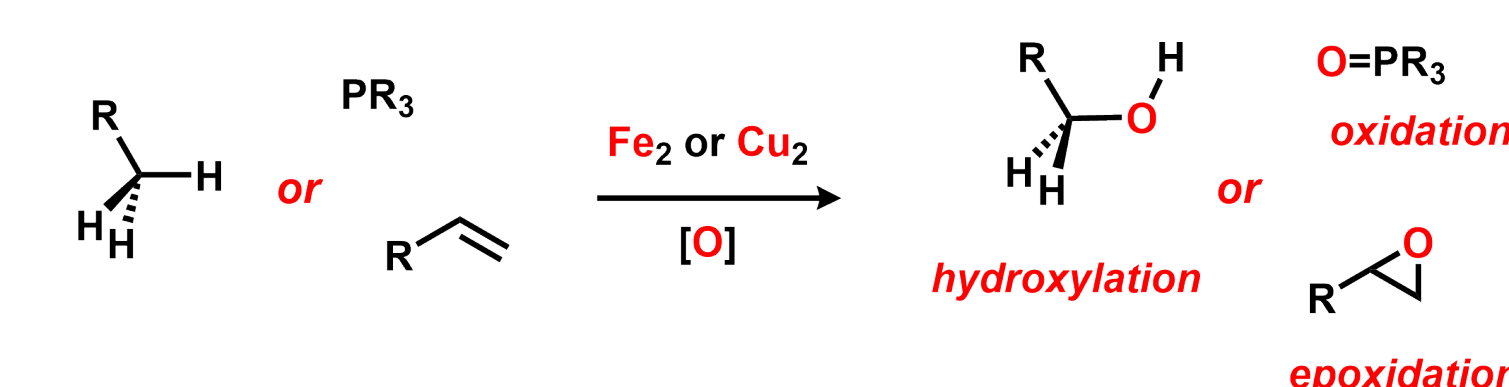
Left. Direct aerobic oxidation of methane to methanol remains a significant target in the synthetic community. Systems such as methane monooxygenase enzymes (e.g., sMMO) and copper zeolites (e.g., Cu-ZSM-5) demonstrate such exquisite reactivity. Studies have proposed bimetallic bridging oxo units as the active species responsible for the challenging C-H cleavage, albeit an understanding of their intrinsic reactivity is still lacking.

What is the correlation between electronic structure and reactivity of dimeric oxo species?

Bis-alkoxide bimetallic platforms to support reactive bimetallic oxo species



Above. Alkoxide based ligands are weak σ -donors with tunable π -donicity and modular steric profile and should afford access to low-coordinate, highly electrophilic metal centers and encourage high-spin configurations. A range of bridging units will be examined to systematically manipulate the core structure of the M-O-M and M₂O₂ units.

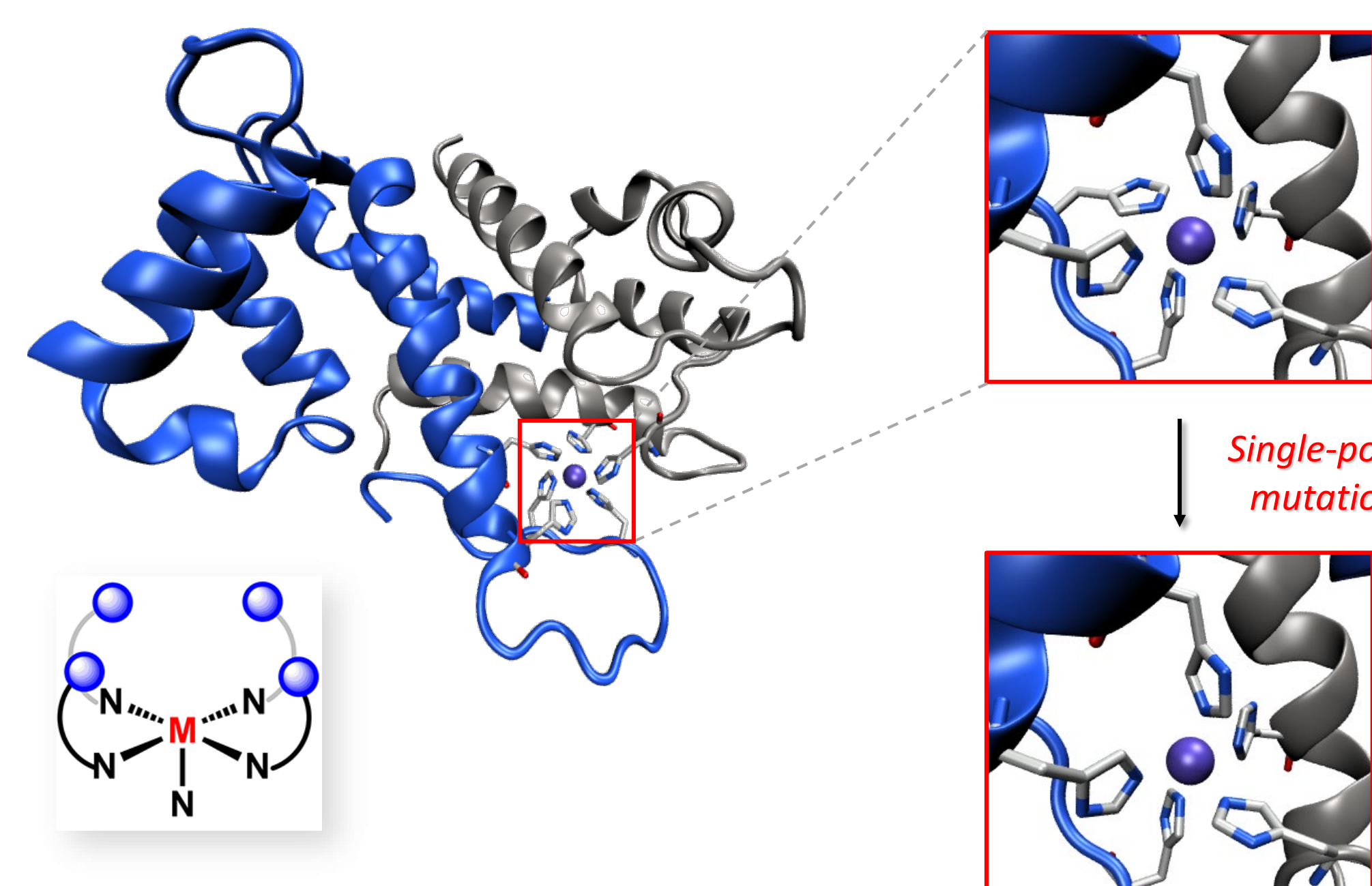


What are the salient electronic features for reactive M₂(μ -O) and M₂(μ -O)₂ units?

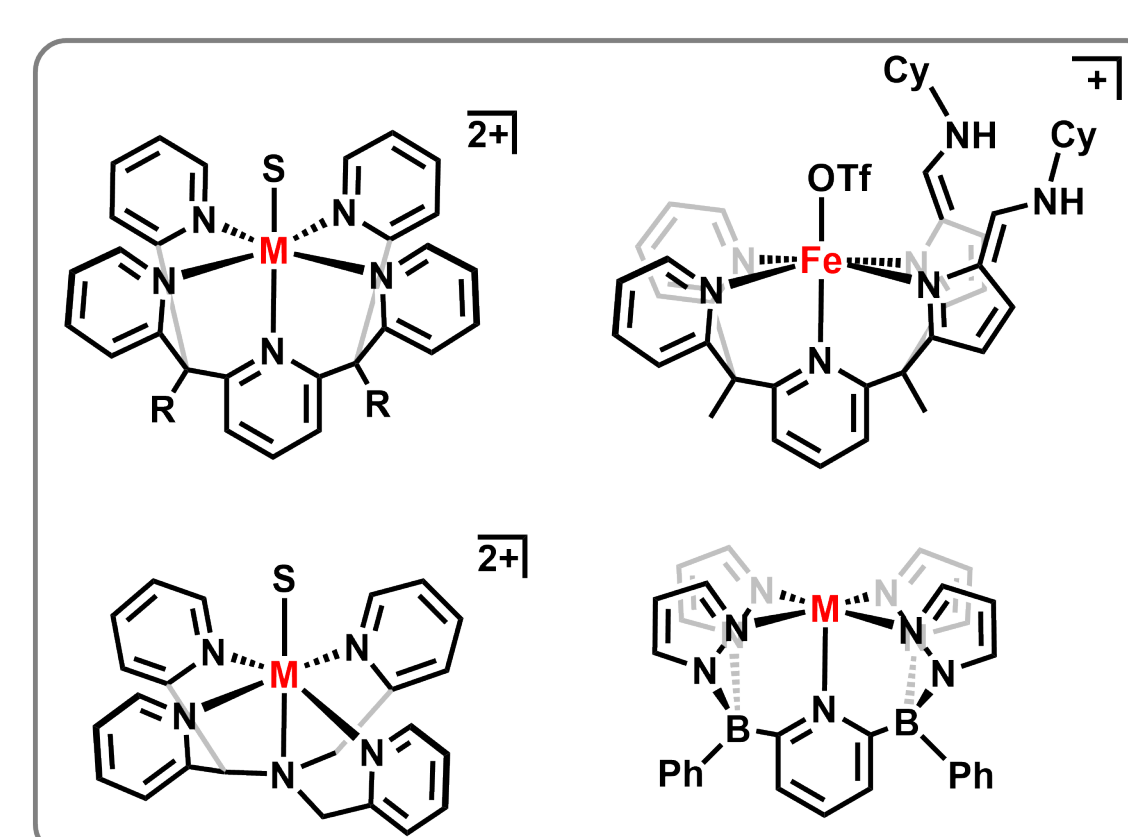
What is the influence of spin state, oxidation state, and geometry?

Proteins as Ligands for Unique Metallocofactors

Reactivity of a His₅ metal binding site

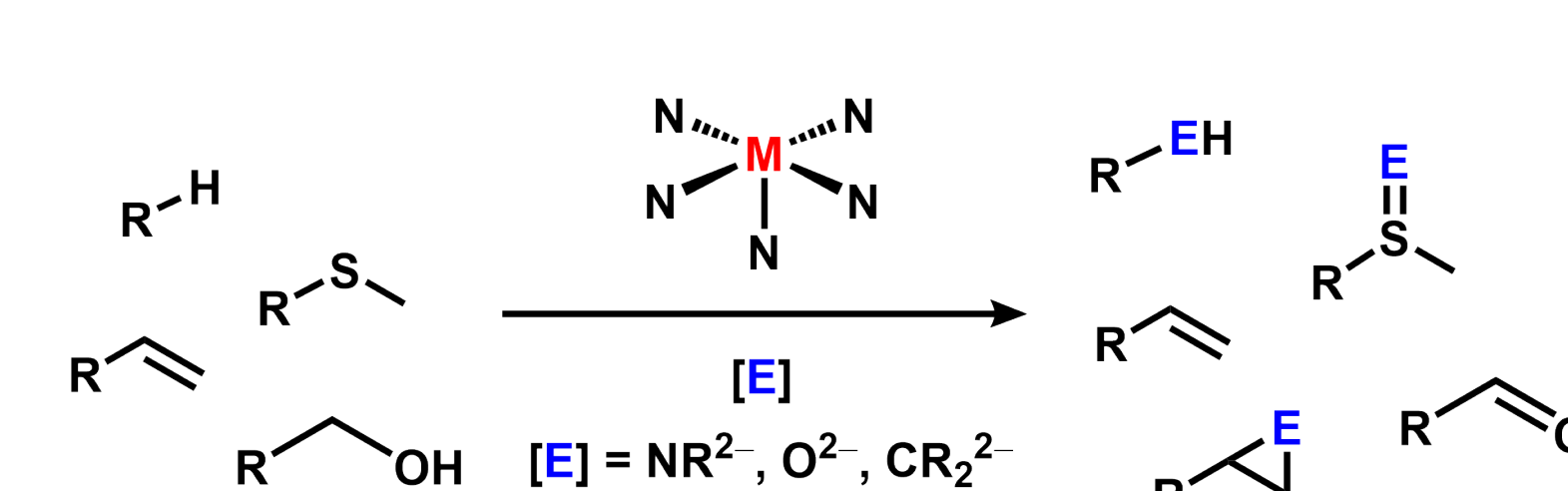


Right. We want to leverage proteins to model organometallic complexes and take advantage of secondary sphere interactions within the protein structure to uncover novel reactivity. **Left.** We are interested in penta-histidine metal scaffolds given the weak-field nature of this residue and the plethora of five-coordinate N-based ligands for transition metal catalysis as benchmarks for reactivity.



How does the secondary coordination sphere influence reactivity and selectivity?

Group transfer and dehydrogenation reactivity



Small molecule activation

