# RICHARD A. WALTON
# LECTURE IN INORGANIC CHEMISTRY

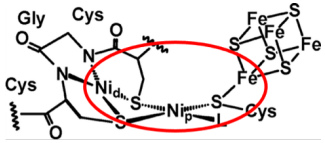


## Professor Marcetta Darensbourg

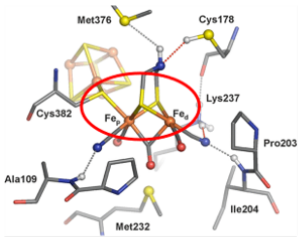
*Distinguished Professor of Chemistry, Texas A&M University*

### *Nature-Inspired Heterobi- and Trimetallics: How Metals Talk to Each Other*

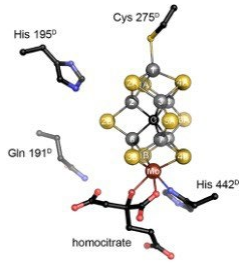
The development of specific-purpose ligands has provided numerous significant scientific advances, particularly in the fields of organometallic chemistry related to catalysis (witness the N-heterocyclic carbenes and the Grubbs catalyst), bioinorganic chemistry, molecular mimics of enzyme active sites; as well as the preparation of novel molecules and new inorganic solid-state materials. These ligands are often evaluated based on their impact on the metals they bind to, with a focus on their steric and electronic properties. By modifications of substituents, the common and extensively useful diphosphines are electronically tunable as sigma donors with variable steric properties. The bipyridine class of ligands offers electron delocalizing properties, photo- and redox activity, and the possibility for synthetic designs wherein the binding motif may be incorporated into numerous π-delocalizing organic platforms.



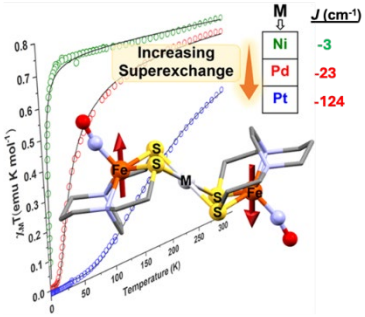

Acetyl-CoA Synthase: CO and



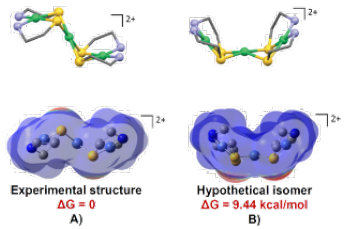

Hydrogenase: Water Splitting/Fuel



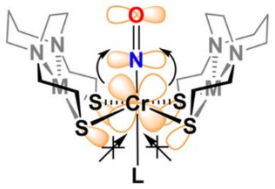

• Nitrogenase: $N_2$ Fixation




We have prepared ligands imbedded with "talkative" metals. An extensive range of heterobi- and polymetallic complexes is thus afforded by this design. Knowledge of the electronic and stereochemical directing properties of both the central metal acceptor and the metallo donors can thus be deconvoluted and developed for understanding multi-metallic cooperativity. Our synthetic program was initially inspired by organometallic natural product catalysts such as the active sites of hydrogenases and, particularly, the AcetylcoA Synthase enzyme. As multimetallic, sulfur bridged catalysts, a useful approach has been to prepare metal-centered ligands in which the metals are engulfed in a largely square planar $N_2S_2$ tetradentate ligand in mimicry of the cys-gly-cys tripeptide, tight nickel-binding site of ACS. In such systems, terminal thiolate sulfurs are well-placed to be capable of snaring a second metal; furthermore the two lone pairs on each sulfur dictate a first coordination sphere stereochemical effect, a feature not possible in phosphine or carbene ligands. As the basis of bi-, tri- and poly-metallics one may track changes in electronic structure through distinctive features at the aggregating metal center(s). The "voices" of the metals within such talkative metallo ligands, particularly the S = ½ radicals of $\{Fe(NO)\}^7$ and $[VO]^{2+}$, are examined by parameters such as redox potential, ν(NO) values, the $\{Fe(NO)\}^{7/8}$ redox couple, $^{57}Fe$ Mössbauer and EPR spectroscopies, and temperature-dependent magnetic susceptibility. Such techniques on designed molecules permit one to ask pertinent questions of structural control of communication through orbitals that define energetic and spin effects. Specifically, the redox-active $Fe(NO)(N_2S_2)$ has proven to be particularly useful tool as a spin probe for studying magnetic coupling interactions, both direct exchange and superexchange.




Structural features of the heterometallic complexes are influenced by extra sulfur lone pairs that are not engaged in σ bonding to the attached metal, leading to unique structural/topological arrangements and electronic properties achievable only with extreme synthetic effort with traditional ligands. Design of basket-like complexes extends the diphosphine derivatives of Molybdenum and Chromium nitrosyls.




PURDUE UNIVERSITY | James Tarpo Jr. and Margaret Tarpo Department of Chemistry

**Thursday, November 12, 2026 | 4:30 PM | WTHR 104**