The goal of this project is to develop heterodinuclear homogeneous catalysts for the efficient oxidation of CO, CO + \([O]\) → \(\text{CO}_2\). The design principle used in this research is “bimodal” reactivity, where CO binding (a prerequisite for further reactivity) and oxygen-atom transfer constitute two different types of chemical reactivity, requiring two different types of transition metal sites. Bioinorganic chemistry provides a suitable guideline for possible metal choices for such bimodal catalyst. Mo-Cu CODH is an enzyme that catalyzes efficient oxidation of CO at ambient conditions. The catalytically active form of the enzyme contains a heterodinuclear active site with \([\text{MoO}_2]\) linked via a sulfido bridge to Cu(I) (Figure 1, left). A possible enzyme mechanism involves initial CO binding to the coordinatively unsaturated Cu(I) site followed by an oxo-transfer from a nearby nucleophilic Mo-oxo functionality (Figure 1, right).

**Figure 1.** Left: Active site of Mo-Cu CODH. Right: Possible “bimodal” CO oxidation reactivity.

Binding Mo(VI)-oxo and Cu(I) in close proximity requires prior design of a heterodinucleating ligand. Our initial design of a heterodinucleating ligand (\(L^\text{I}_1H_2\)) given in Figure 2. The ligand contains two different chelating sites: one site (catecholate) for the early (hard) transition metal, Mo(VI), another site for the late (soft) transition metal, Cu(I). \(L^\text{I}_1H_2\) was synthesized via condensation of 2,3-dihydroxybenzaldehyde with 2,7-di-tert-butyl-9,9-dimethyl-xanthene-4,5-diamine, followed by reduction with sodium borohydride, and second condensation with pyridine-2-carboxaldehyde. Treatment of \(L^\text{I}_1H_2\) with either Cu(I) or M(VI) (M = Mo, W) sources led to the anticipated site-selective incorporation of the respective metals. However, the incorporation of both Cu(I) and Mo(VI) into \(L^\text{I}\) triggered intramolecular oxidation reactivity, in which a nucleophilic molybdenum-oxo functionality attacks Cu(I)-bound imine. The reaction was interrogated by NMR spectroscopy and DFT calculations. Molybdenum(VI) complex \([\text{Mo}(L')\text{O}_2](\text{NEt}_4)\), containing a modified ligand “\(L^\text{I}\)’” that contains a new C–O bond in place of the imine functionality, constitutes the major product of the reaction. The complex was characterized by NMR spectroscopy, X-ray crystallography and elemental analysis. The observed hydroxylation reactivity is closely related to the postulated first step of CO oxidation by Mo–Cu CODH, a nucleophilic attack by Mo(VI)–oxo on Cu(I)-bound electrophilic CO.

**Figure 2.** Reactivity of the first-generation heterodinucleating ligand, \(L^\text{I}\).
The intramolecular oxidation enabled by the presence of the electrophilic imino function in the first-generation ligand (L₁) precluded reactivity investigations with CO or other extraneous ligands. To overcome this problem, we have recently introduced a structural modification into L₁ to give a new heterodinucleating ligand precursor, L₂H₂ (Figure 3). L₂H₂ is overall similar to L₁H₂, thus, similar selective coordination of Cu(I) and Mo(VI) can be anticipated. However, L₂H₂ is lacking the imino function, thereby no intermolecular reactivity is expected. The ligand was prepared by the reduction of L₁H₂ with excess sodium borohydride. We have already obtained its Cu(I) complex by the reaction of L₂H₂ precursor with [Cu(NCMe)₄][B(C₆F₄)₄] salt. In the second year of support, our research will focus the reactivity of this new system with molybdate/tungstate. We will attempt to isolate and characterize heterodinuclear complexes, and will investigate their stoichiometric and catalytic reactivity with CO and isocyanides.

**Figure 3.** Synthesis of L₂H₂.