Combining Metal-Metal and Metal-Ligand Cooperativity using 'Expanded Pincer' Ligands

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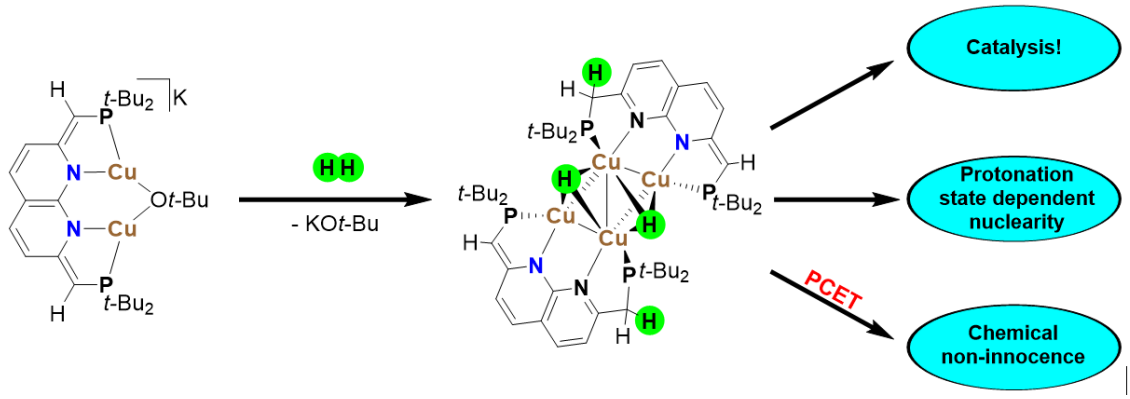
Various metalloenzyme active sites feature complex architectures that enable multiple metals and ligands to work together to facilitate bond activation processes that are essential to enzyme function.[1] Drawing inspiration from nature, various research groups have developed synthetic systems where metals and ligands cooperatively activate chemical bonds.[2] Another avenue in cooperative bond activation involves complexes wherein multiple metal centers are in close proximity and work together to make or break chemical bonds.[3] Our group is currently exploring ligand systems that can both host multiple low-valent 1st-row transition metals, and also contain fragments that enable metal-ligand cooperativity.[4] We have recently reported a new 'expanded pincer' ligand that enables cooperative H_2 activation on a dicopper(I) complex utilizing both metal-metal and metal-ligand cooperativity, and how this led to the formation of a tetranuclear copper complex (Figure, left).[5] In this presentation, we detail how these multinuclear copper complexes can be activated to perform catalytic transformations with significantly enhanced performance compared to mononuclear analogues. In addition, we will show how the ligand protonation state affects the nuclearity. Finally, we will discuss the coordination chemistry and catalytic activity of related complexes, and detail new findings how the PNNP ligand can demonstrate chemical non-innocence through PCET reactivity.



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