REDOX DIALOGUE BETWEEN LIGANDS AND METAL FOR UNCONVENTIONAL REACTIVITIES

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Metalloenzymes are Nature's ultimate catalytic tools. Not only do they display extreme selectivity coupled with efficiency, they also seem to be performing an endless list of chemical reactions. In order to achieve multielectronic transformations with first-row transition metals, which are the basis of the biochemical catalytic toolkit, metalloenzymes often rely on ligand radical species which participate by donating/accepting electrons or by forming and/or breaking substrate bonds. For this redox specificity, these ligands have been classified as **redox** or "**non-innocent ligands**" (**NILs**). Although challenging and elusive, bio-inspired catalysis must still be a goal for today's chemist, especially in the dawn of the foreseen shortage of precious metals resources. While redox non-innocence in biological settings has long been familiar to bioinorganic chemists, the use in a broader context of "synthetic" NILs as surrogates of the original biological radicals is only lately emerging as a catalytic tool of its own.[1]

We are interested in understanding and harnessing alternative mechanisms enabled by the redox-activity of the ligands.[2] This approach led us to study a formal umpolung of CF_3,[2a] copper- and nickel-catalyzed trifluoromethylation[2b,c] and C–N bond formation through redox ligand stabilization of masked high valent metallic oxidation states.[2d]

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