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New pathways to gold chemistry: Electronics at Au centers with non-innocent and ambiphilic ligands

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Transition metal driven chemical transformations in organic synthesis offer the promise of new retro-synthetic strategies for generating novel organic compounds. Efforts are continuously being directed at finding unprecedented reactivity for various transition metals in the hopes of developing, new selectivity, catalytic efficiency and sustainability. Recently gold has garnered significant interest as a potential redox switchable catalyst with reversible on-demand control of catalytic activity, as well as applications in photo-redox catalysis. Although significant progress has been made in Au chemistry, the focus has largely been on Au(I) and Au(III) complexes. Au(IV) complexes are unprecedented and single-electron processes involving Au(III) complexes are extremely rare. Therefore, we have begun a comprehensive study to explore Au(III) complexes featuring redox active ligands with the aim to access fake Au(IV) complexes and open a new facet in gold chemistry. In the same line we are exploring ligand architectures that can facilitate milder pathways for Au(I)/Au(III) redox catalysis through transition metal –Lewis acid interactions (TM->LA), which impose geometries that promote the 2-electron oxidation of Au(I) complexes. In both cases a thorough understanding of the electronic and coordination environment at the metal center is essential for future development and fine tuning of catalytic properties. As such, X-ray absorption spectroscopy was employed as a direct probe of the ligand influence on the metal center followed by correlation of *in silico* derived with experimentally determined electronic structure.

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