



Houk-Jung Organic Colloquium

Bismuth Redox Catalysis

Abstract: The ability of main group element bismuth (Bi) to maneuver between different oxidation states in a catalytic redox cycle, mimicking the canonical organometallic steps of a transition metal, represents a paradigm shift in the field of homogeneous catalysis.^[1] Here, we demonstrate that these catalytic steps are not restricted to the d-block and a series of Bi complexes can certainly undergo catalytic redox transformations akin and beyond transition metals. Catalytic cycles where the Bi revolves between oxidation states Bi(I)/Bi(III) and Bi(III)/Bi(V) have been unlocked and applied in various contexts of catalysis. Capitalizing on the Bi(III)/Bi(V) redox pair, we have developed a catalytic protocol for the fluorination^[2] and triflation^[3] of aryl boronic esters. On the other hand, the low-valent redox manifold based on Bi(I)/Bi(III) enabled the reduction of hydrazines and nitro compounds^[4], the catalytic decomposition of the rather inert nitrous oxide (N₂O),^[5] and the catalytic hydrodefluorination of C(sp²)-F bonds.^[6] In addition, we will show how one-electron pathways are also accessible, thus providing a platform for SET processes for organic synthesis.^[7] Finally, we will also show how redox-neutral catalytic pathways can unlock novel organic transformations via canonical organometallic steps. For all methodologies, a combination of rational ligand design with an in depth analysis of all the catalytic steps proved crucial to unfold the catalytic properties of such an intriguing element of the periodic table.

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Zoom