Bismuth Redox Catalysis

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This talk will provide the foundations and the background on the new and emerging field of Bismuth Redox catalysis.[1-8] We will show how Bi challenges current dogmas by emulating canonical organometallic steps of transition metals. A series of Bi complexes capable of revolving between oxidation states have been unlocked and applied in various contexts of organic synthesis. For example, capitalizing on the Bi(III)/Bi(V) redox pair, we have developed a catalytic protocol for the C–F, C–O and C–N bond formation. Additionally, we will show how a low-valent redox manifold based on Bi(I)/Bi(III) has been applied in the reduction of hydrazines and nitro compounds, the decomposition of inert N_2O and SF_6 and the catalytic hydrodefluorination of C(sp^2)–F bonds. In addition to the polar mechanisms, we will show how certain Bi complexes also engage in one-electron pathways, thus providing a platform for SET processes capitalizing on the triad Bi(I)/Bi(II)/Bi(III). Examples using this manifold include C–C, C–N and C–CF_3 bond forming reactions. For all methodologies, an in depth analysis of all the elementary steps and the isolation and characterization of reaction intermediates proved crucial to understand and unlock the catalytic properties of such an intriguing element of the periodic table.

References

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[6] For articles merging red light and Bi: *J. Am. Chem. Soc*. **2023**, *145*, 18742.
[7] For a mono-coordinated bismuthinidene: *Science*, **2023**, *380*, 1043.
[8] For catalytic examples of Bi merging with light: *J. Am. Chem. Soc*. **2023**, *145*, 25538.