Transition-Metal-Mediated Activation of Sulfur toward C–S Bond Formation

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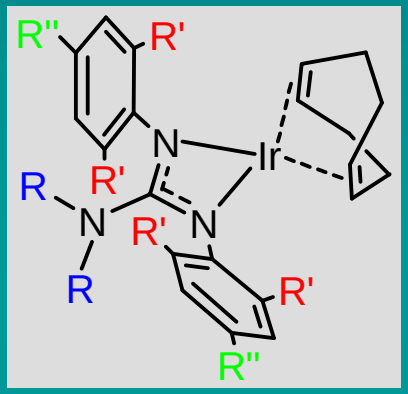
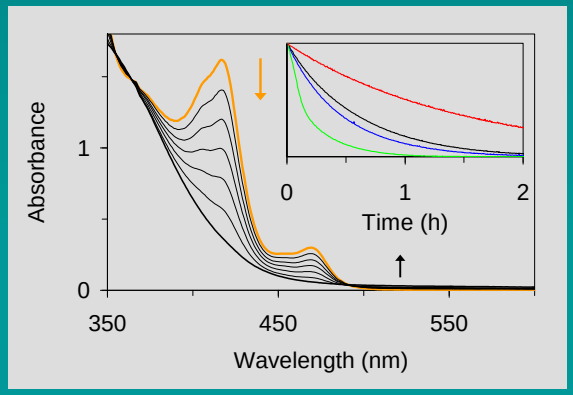
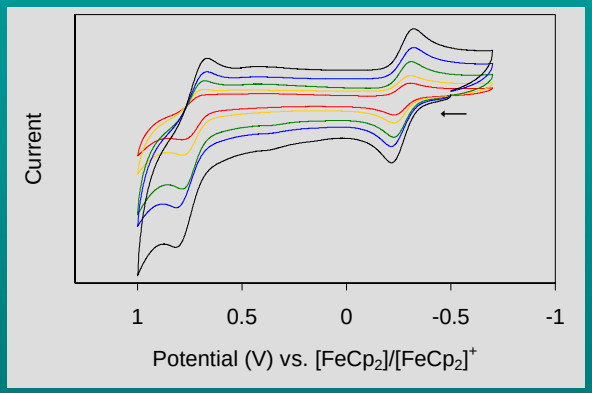
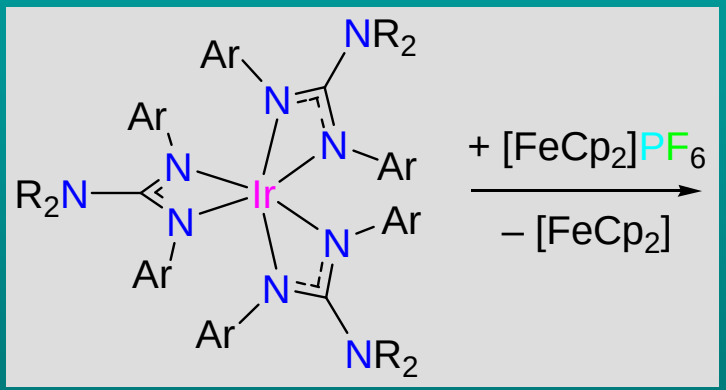
Tunable N,N-dialkyl-N',N''-diarylguanidinates provide access to low- and high-valent iridium, ranging from Ir^{I} to Ir^{IV}:

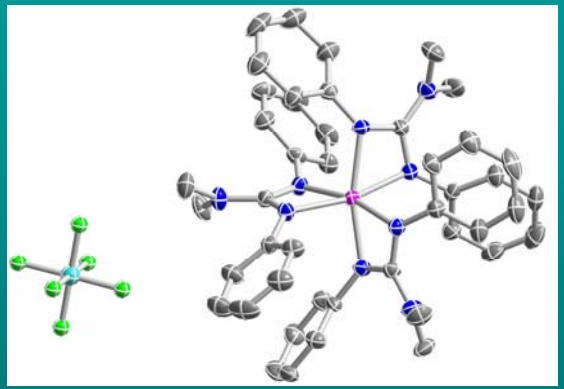
1. Ir^{I} complexes react with O_2 and S_8 under ambient conditions, and the reactivity can be modulated through substituent effects (right).











2. Ir^{III} complexes can be oxidized at unusually low redox potentials.

3. Ir^{IV} can be stabilized in a nitrogen-donor ligand environment.