

Structural and Electronic Contributions to Redox-noninnocent Behavior

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Ligands that are capable of accepting or providing electrons during redox reactions of transition metal complexes, called redox-noninnocent ligands, can profoundly modulate the overall reactivity of the corresponding complex. Recent efforts focus on the application of such ligands as electron reservoirs to promote multi-electron processes and triggering redox-noninnocence to yield reactive ligand radicals to establish ligand-based catalysis. Our approach is distinctively different in that it is governed and heavily guided by chemical concepts that are derived from first principle computations allowing the full understanding and the development of a unified concept of this behavior. Our most recent investigation focuses on the structural and electronic requirements of ligand noninnocent behavior using DFT based techniques. Octahedral Fe and Co and square planar Co and Ni complexes containing benzoquinonediimine-based noninnocent ligands were selected for this systematic, whereas the analogues Ru and Pd systems serve as references. We analyzed how the coordination of ligand to the metal center makes the ligand-based reduction energetically more favorable to the free ligand. Using square schemes we determined that the major component of this stabilization has electronic origin and structural relaxation – one of the most salient feature of noninnocence – plays only a minor role. We further analyzed the origin of this electrostatic stabilization using various techniques including interaction energy decomposition analysis. A simple measure based on the electron density is introduced to quantify ligand redox-noninnocence.