Understanding the thermodynamic driving force for ligand-based redox-activity; conceptual rules for designing redox active ligands

Ligands that are capable of accepting or providing electrons during redox reactions of transition metal complexes, called redox non-innocent or redox-active ligands, can profoundly modulate the overall redox reactivity of various transition metals. Recent efforts focus on the application of such ligands as electron reservoirs to promote multi-electron processes and to yield reactive ligand radicals to establish ligand-based catalysis. Our approach is distinctively different from the majority of ongoing investigations in that it is governed by chemical concepts that are derived from large-scale first principle computations allowing the full understanding and the development of a unified concept of this behavior. Metal and ligand-based reductions have been modeled in octahedral ruthenium complexes revealing metal-ligand interactions as the profound driving force for the redox-active behaviour of orthoquinoid-type of ligands. Through an extensive investigation of redox-active ligands we revealed the most critical factors that facilitate or suppress redox-activity of ligands in metal complexes, from which basic rules for designing noninnocent/redox-active ligands can be put forward. These rules also allow the rational redox-levelling of ligand-centered electron transfer processes potentially leading to catalysts with low-overpotential in multielectron activation processes.