Structural and electronic contributions to redox non-innocent behavior

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Ligands that are capable of accepting or providing electrons during redox reactions of the corresponding complex can be utilized as electron reservoirs to promote multi-electron processes or can be engineered to exhibit ligand based reactivity opening new functionalization pathways. It is known that such a non-innocent behavior depends not only on the ligand but also on the metal center. There are, however, a few ligand frameworks, which exhibit non-innocent behavior quite frequently. Our investigation focuses on the structural and electronic requirements of ligand non-innocent behavior using DFT based techniques. We found that coordination of the metal center makes the ligand-based reduction energetically more favorable. The major component of this stabilization has electronic origin and structural relaxation plays only a minor role. The possible prediction of redox non-innocent behavior is being also addressed.

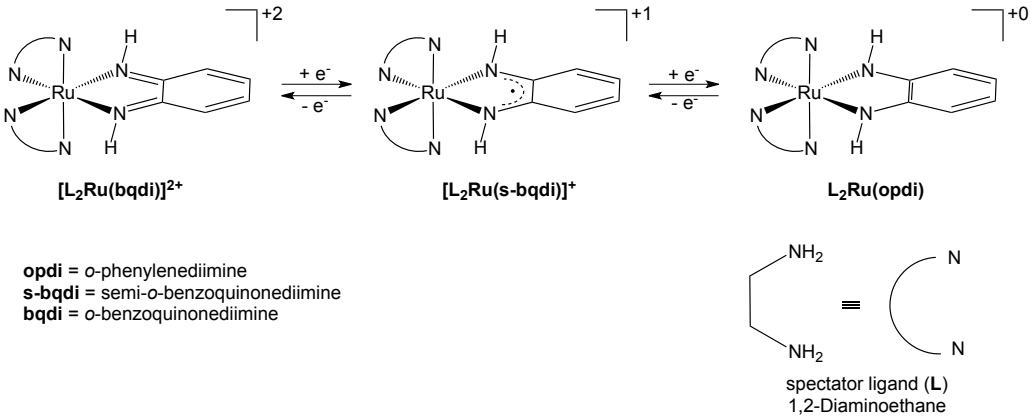

Figure 1. Behavior of a typical redox non-innocent ligand.