Understanding and Computing Metalloporphyrin Electronic Structures: From an Alkyl/Aryl/NO Isolobal Analogy to Failures of DFT for High-Valent Iron Porphyrins

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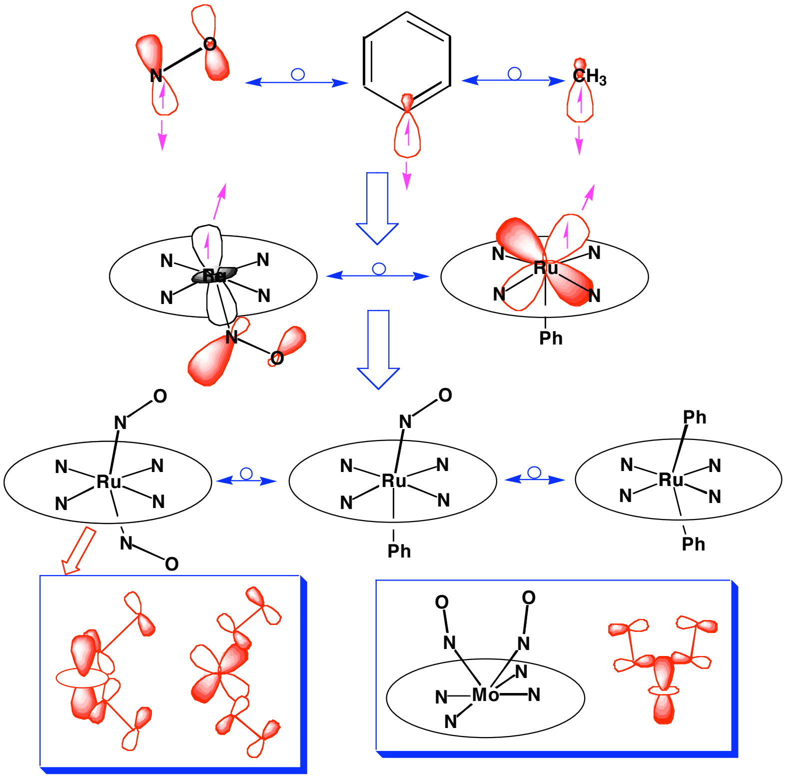
DFT calculations have shown that M(P)$(NO)_2$ and M(P)R_2 (M = Fe, Ru, Os; P = porphyrin; R = alkyl, aryl) complexes exhibit a peculiar *cisoid* tilting of the axial ligands relative to the porphyrin normal. We have attempted to explain this unique structural phenomenon in terms of an (admittedly imperfect) alkyl/aryl/NO isolobal analogy, as depicted below. Thus, M(P)NO and M(P)Ph may also be viewed as isolobal fragments and M(P)$(NO)_2$, M(P)(NO)Ph, and M(P)Ph_2 may be viewed as derived *via* isolobal substitutions of one another. The orbital interactions responsible for the unique structure of M(P)$(NO)_2$ are shown below (bottom left). Also shown is the orbital interaction that accounts for the peculiar *attracto* conformation of the Mo$(NO)_2$ unit of *cis*-Mo(P)$(NO)_2$ (bottom right).



Switching gears from qualitative understanding to quantitative computing, we have identified certain serious failures of DFT in the area of high-valent iron porphyrin complexes. Thus, while B3LYP calculations clearly predict a low-spin Fe(IV) state for Fe(P)F_2, *ab initio* multiconfiguration reference perturbation theory (CASPT2) calculations predict a high-spin Fe(III) a_{2u}-type porphyrin π-cation radical state. These findings may have significant implications for the theoretical modeling of heme protein reaction pathways.