The range of electronic structures associated with the versatile ligand btzp with different transition metals

Redox active and redox non-innocent ligands are of great interest to organometallic chemists with applications to a number of fields including homogenous catalysis and non-linear optics. The behavior of one such ligand, bis-tetrazine pyridine (btzp), toward a series of d^6 metals was evaluated by DFT and CASSCF. It was determined that depending on the nature of the metal center the ligand exhibited a wide range of behaviors. In the case of $[Fe(btzp)_2]^{2+}$ and $[Ru(btzp)_2]^{2+}$ the ligand behaved as an unremarkable neutral sigma donor. However, the neutral $Mo(btzp)_2$ analog demonstrated the ability of the ligand to behave as a redox active ligand and a strong oxidant with the ligand withdrawing sufficient electron density from the metal to change its oxidation state; consistent with experimental results obtained from XAS and X-ray crystallography. In contrast to $Mo(btzp)_2$ where the metal ligand interaction occurred through covalent bonds the electronic structure of $Cr(btzp)_2$ was found to exhibit considerable poly-radical character which necessitated the use of the multi-configurational method CASSCF. The calculated absorption spectrum of the Cr complex detected a ligand to ligand intervalence charge transfer band with a large oscillator strength in the near IR region. The predicted existence of a low lying triplet state was consistent with slight paramagnetic broadening of the ^1H NMR signal and EPR results which detected a ligand based radical.