EXCHANGE-ENHANCED OPEN-SHELL STATES: HUND'S RULE FOR BIOINORGANIC SPECIES APPLIED TO H-ABSTRACTION
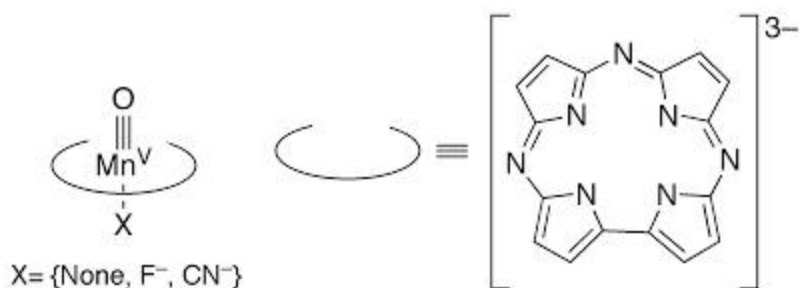
In a Perspective in *Nature Chemistry* last year[1] Sason Shaik and co-workers described bond activation by metal-oxo enzymes and synthetic reagents. In it, they argued that Hund's rule of maximum multiplicity (valid for atoms) has an analogue for reactions and kinetics of (bio)inorganic species: the exchange-enhanced reactivity (EER). Pathways that **increase** the number of unpaired and spin-identical electrons on a metal center will be **favored** by exchange interactions, and hence are favored over pathways that keep the same number (or less) of exchange interactions.

In this recent paper in *Angewandte Chemie International Edition* Shaik and co-workers apply their EER principle on H-abstraction reactions, and show how dramatic axial ligand effects can be explained by it. The systems under study are $[(Cz)(X)Mn^{V}O]$ (Cz: corrolazinato^{3-}, X=None, F^{-}, CN^{-}) complexes (see Figure below), which probably have a singlet ground state (X=None) or a triplet ground state (X=F^{-}, CN^{-}).

X= {None, F⁻, CN⁻}

More important than the ground state of the reactant is however the spin state of the transition states (TSs). The hydrogen abstraction involves a proton-coupled electron transfer (PCET): the migrating H· radical transfers its radical to the d-block of the metal, while at the same time the proton makes the O-H bond. For the singlet state, one obtains at the TS an open-shell singlet with an alpha electron on the metal and a beta electron on the substrate. In the exchange-enhanced triplet state, there are now three alpha electrons on the metal (with favorable exchange interactions) that gives the dramatic decrease in barrier (from 32 kcal·mol^{-1} for the singlet to 23.0 kcal·mol^{-1} for the triplet).

The axial ligand effect has two origins: the exchange interactions become stronger (11.1, 12.4 and 12.9 kcal·mol^{-1} for the three complexes) while at the same time the d-orbitals become closer in energy (smaller excitation energy).