Isomerism of bridging cyanides and dependence on bound metals' oxidation states and spin states: A DFT mechanistic study on Fe^{III}-CN-$Cu^{I/II}$ and Fe^{III}-NC-$Cu^{I/II}$ sequences and conversions.

Shengda Ding, Marcetta Y. Darensbourg and Michael B. Hall*
Texas A & M University, Department of Chemistry

Discoveries of cyanide as a ligand to iron in bio-organometallic enzymes (*e.g.* [NiFe]- and [FeFe]-hydrogenase) and possibilities of linkage isomerism in their formation have inspired us to explore bio-organometallic examples such as Holm's (*J. Am. Chem. Soc.*, **116**, 11357; *Inorg. Chem.*, **37**, 4898) binuclear mimic of the heme-copper oxidase, $[(oep)Fe^{III}(NC)Cu^{I}(MeNpy_2)]^+$(**1**, oep = octaethylporphyrin; $MeNpy_2$ = Methyl-di-(2-picolyl)amine; py = pyridine). During the formation of **1** from $(oep)Fe^{III}(CN)(py)$ (**a**) and $[Cu^{I}(MeNpy_2)]^+$ (**b**), the cyanide isomerism takes place along with the dissociation of the axial pyridine. In contrast, the isomerism was not observed on the oxidized analogue $[(py)(oep)Fe^{III}(CN)Cu^{II}(Npy_3)]^{2+}$ (**2,** Npy_3 = Tri-(2-picolyl)amine).

To investigate the requirements of cyanide isomerism, DFT computational studies were initiated. The experimental spin states of **a**, **1** as well as **2** were used to screen and benchmark DFT functionals. M06L was revealed to be optimal and thus was used to estimate the energetics of the cyanide flipping. Regardless of the presence of the axial pyridine, the cyanide flipping is more prone to happen on the high-spin potential energy surface (PES, Fe^{III}, $S = 2.5$), with the highest barrier of 10.9 (w/ py) or 7.1 (w/o py) kcal/mol while the barriers on the low-spin ($S = 0.5$) or the intermediate-spin ($S = 1.5$) PES are at least two times higher.

The occurrence of the cyanide flipping is rationalized by the synergetic effects of the spin state of Fe, the oxidation state of Cu, and the timely departure of the axial pyridine coordinated to Fe. The immediate product of **a** and **b**, **1*** $[(oep)(py)Fe^{III}(CN)Cu^{I}(MeNpy_2)]^+$ has a low-spin doublet ground state but a sextet excited state is only 1.0 kcal/mol higher. Symmetrically distributed electron densities on **1***'s high-spin Fe^{III} (d^5) and Cu^{I} (d^{10}) weaken C-Fe and N-Cu bonds. The simultaneous ruptures of both bonds are required in the key transition state **TS2** featuring a μ_2-C bridging cyanide, such that the isomerism is kinetically feasible for **1*** on the high-spin PES. Meanwhile **2** contains ferromagnetically coupled low-spin Fe^{III} (d^5) and Cu^{II} (d^9), making the high-spin PES less accessible. The isomerism is exothermic by 6.9 (w/ py) or 7.4 (w/o py) kcal/mol for **1***. Upon the isomerism, if assumed to occur prior to the removal of pyridine, the weaker N end now coordinates to Fe and renders the sextet as the ground state on **1*'**. The successive departure of the axial pyridine (exothermic by 1.1 kcal/mol), further increases the energetic advantage of the high-spin iron and finalizes this thermodynamically irreversible process.

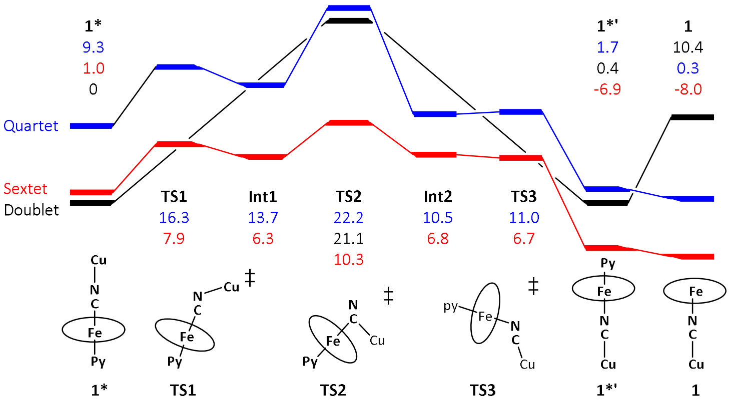

Figure. Gibbs free energies (in kcal/mol) of cyanide isomerism on PES of different spin states