Towards the synthesis of ligand scaffold for bimetallic systems

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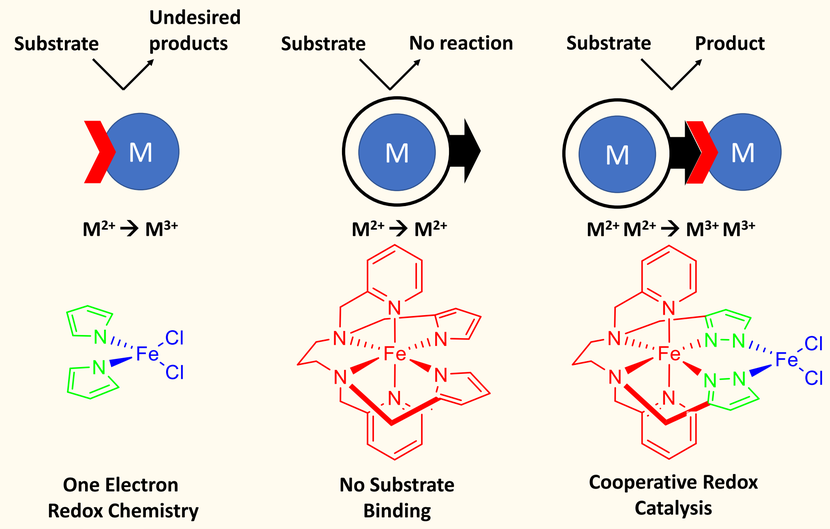
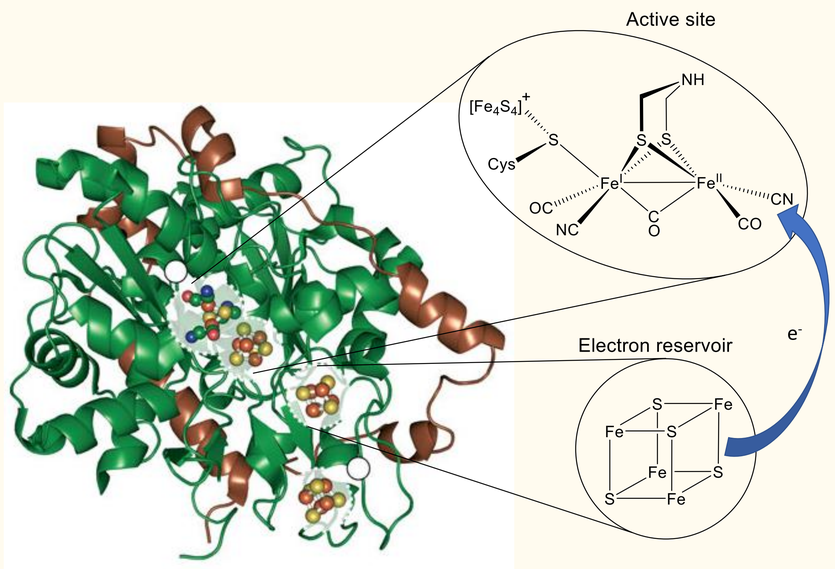
Abstract: Areas ranging from fine chemical synthesis to sustainable energy development rely on highly efficient metal-based catalysts to perform key chemical transformations [1]. Then metals such as Pd, Pt, Rh, Ir or Ru are used because they are proficient at mediating the multi-electron transfer steps required for these applications. In contrast to synthetic chemistry, biological systems do not use noble metals but rather employ cooperative reactivity between multiple redox sites [2]. These sites store and provide additional electrons to avoid unfavorable oxidation states at the reactive centers. Replicating this strategy of redox cooperativity in synthetic complexes could offer a valuable way to enhance the reactivity of base metal catalysts like iron, copper, etc. Such kind of systems have already been developed by Rauchfuss *et al.* to mimic Fe-Fe hydrogenase [3] and Bosnich and co-workers placed the basics for understanding bimetallic systems [4]. However, increase the comprehension of incorporating and controlling the additional redox centers is still a major challenge. Here, we planned to develop new bimetallic complexes where the two metals will be in a close proximity thanks to a ditopic ligand and then, to better understand the cooperativity between the metal centers and highlight the importance of the ligands design.

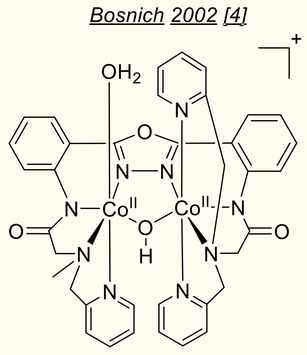


In nature:

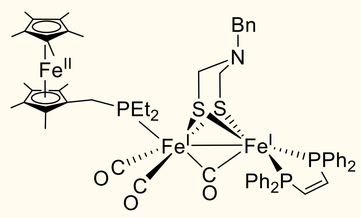


In the lab:

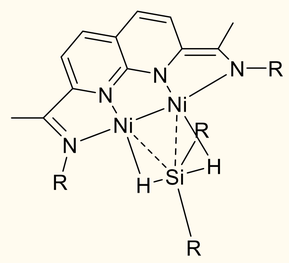
Bosnich 2002 [4]



Rauchfuss 2012 [3]

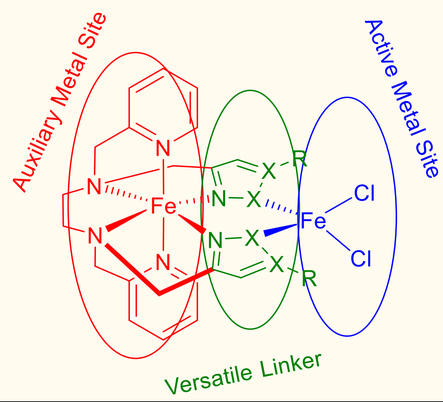


Steiman 2015 [5]

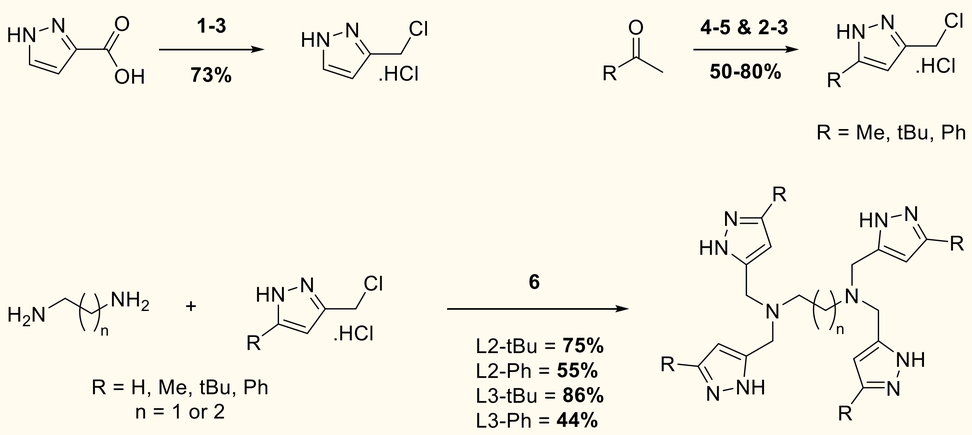


Objectives:

Based on the work of Rauchfuss and Bosnich, we introduce new bimetallic systems with ditopic ligands that are able to complex two metals close to each other. Their proximity will influence their redox behavior and leads to a better understanding of redox cooperativity and possible applications in catalysis.

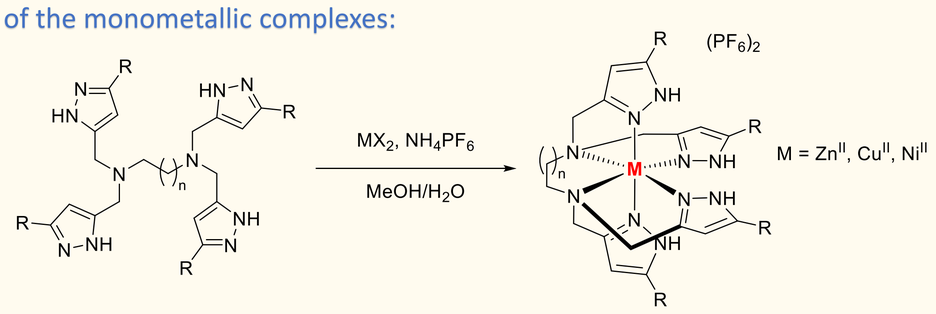


Synthesis of the ligands:

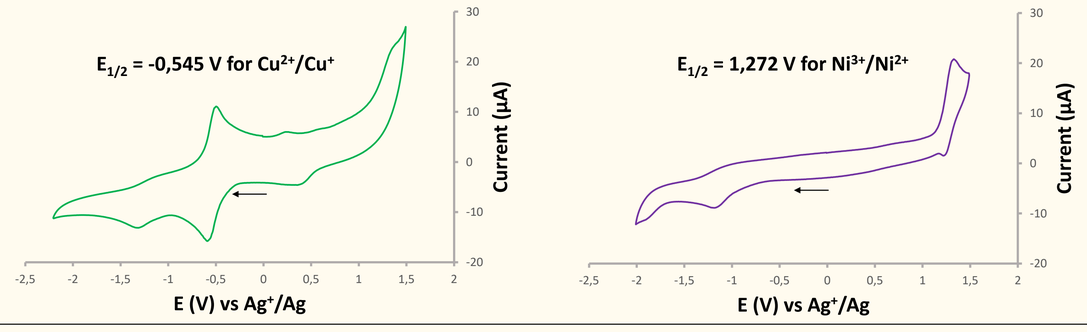


1) H_2SO_4, MeOH, reflux **2)** $LiAlH_4$, THF **3)** $SOCl_2$ **4)** $(CO_2Et)_2$, EtONa, EtOH **5)** NH_2-NH_2, EtOH **6)** K_2CO_3, KBr, CH_3CN

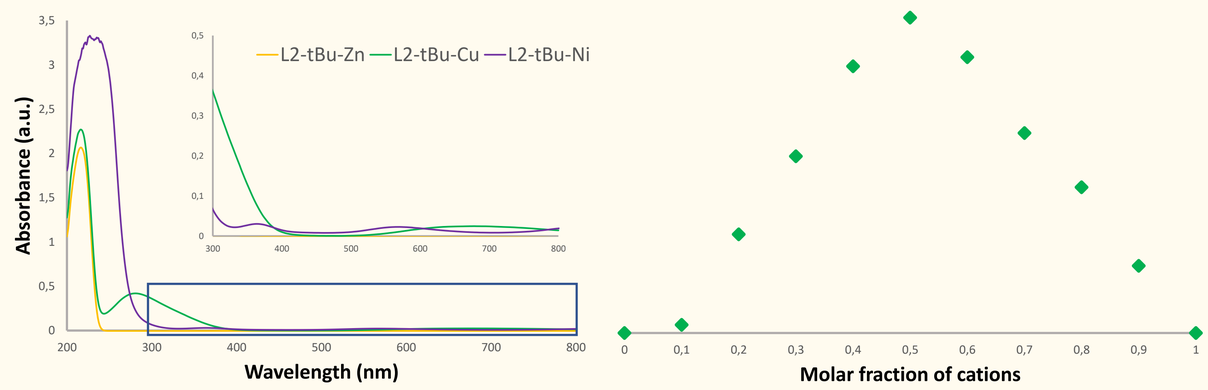
Synthesis of the monometallic complexes:

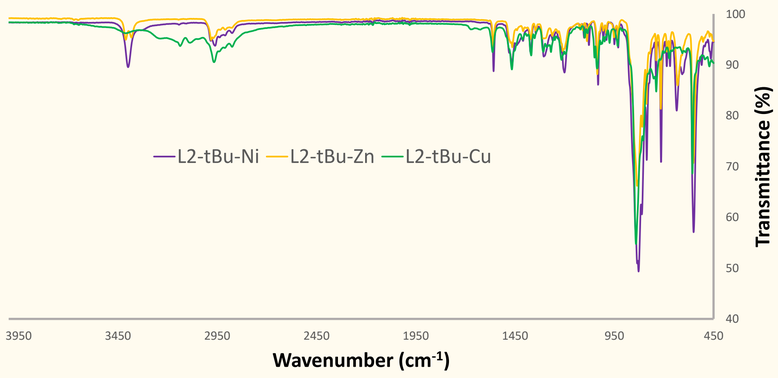


Electrochemistry analysis in CH_3CN:

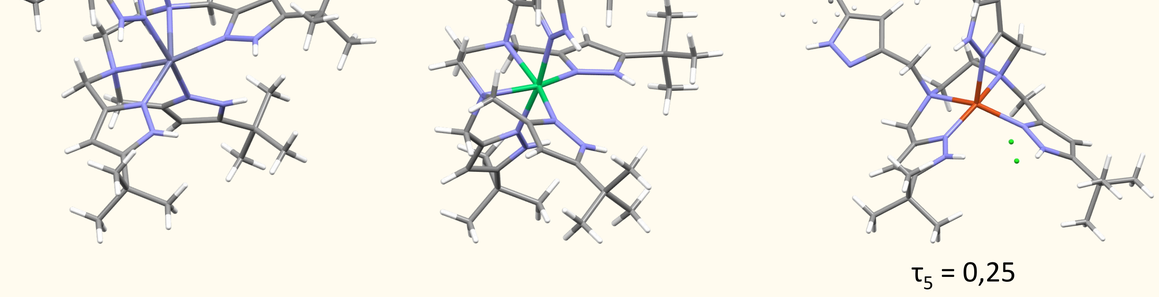


Spectroscopic characterization of L2-tBu complexes:



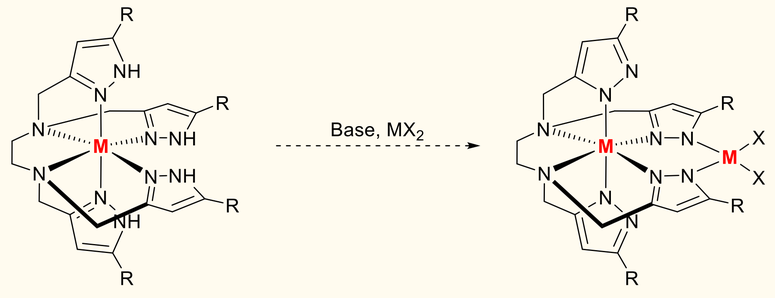


- Charge transfert exhibited by the presence of Cu
- d-d transitions for Ni/Cu
- Ratio 1:1 for complexation
- IR matches for Zn/Ni → Octahedral Geometry (XRD)



Conclusions and perspectives:

By following simple and well-known synthesis pathways in our lab, we achieved the synthesis four new organic molecules **L2-tBu, L2-Ph, L3-tBu** and **L3-Ph**. Unfortunately, other derivatives have only be observed by NMR and for now, we are not able to isolate them. Hopefully, the corresponding mono-metallic complexes of **L2-tBu** have been synthesized and fully characterized. The complexation ratio 1:1 have been measured by Job's method and quasi-reversible electron transfers have been studied by cyclic voltammetry [6]. The formation of the bimetallic system is currently our next goal. However the crystal structures revealed a very small Bite angle that can prevent the insertion of a second metal ion. To avoid this dead end, further investigations must be done on the **L3** complexes with their longer aliphatic linker or we can increase the length of the carbon chain of the pyrazole moiety.



References:

[1] US Geological Survey Fact Sheet 087-02 (pubs.usgs.gov); [2] Gray, H. B.; Winkler, J. R. *Chem Phys Lett.* **2009**, 65, 537 ; [3] Camara, J. M.; Rauchfuss, T. B. *Nat. Chem*. **2012**, 4, 26 ; [4] Gavrilova, A. L.; Qin, C. J.; Sommer, R. D.; Rheingold, A. L. Bosnich, B. *J. Am. Chem. Soc*. **2002**, 124(8) 1714 ; [5] Steiman, T. J.; Uyeda, C. *J. Am. Chem. Soc.* **2015**, 137, 6104 ; [6] de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, 39, 2936