# Towards the synthesis of ligand scaffold for bimetallic systems

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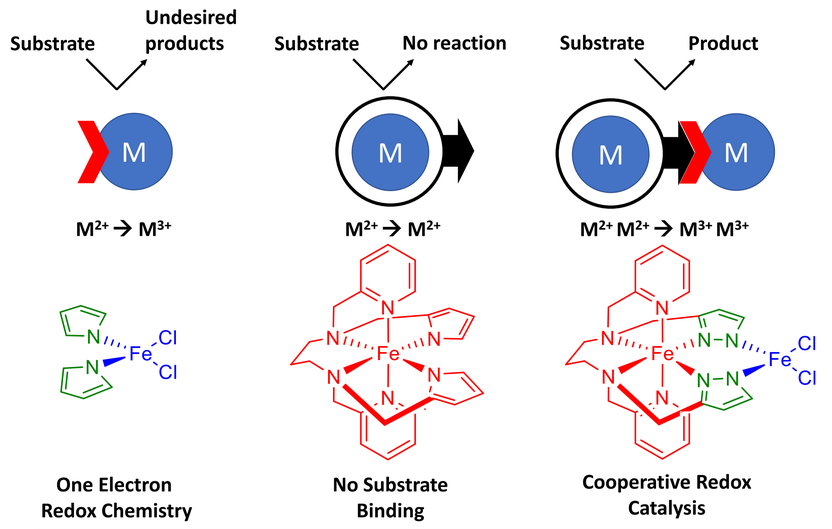
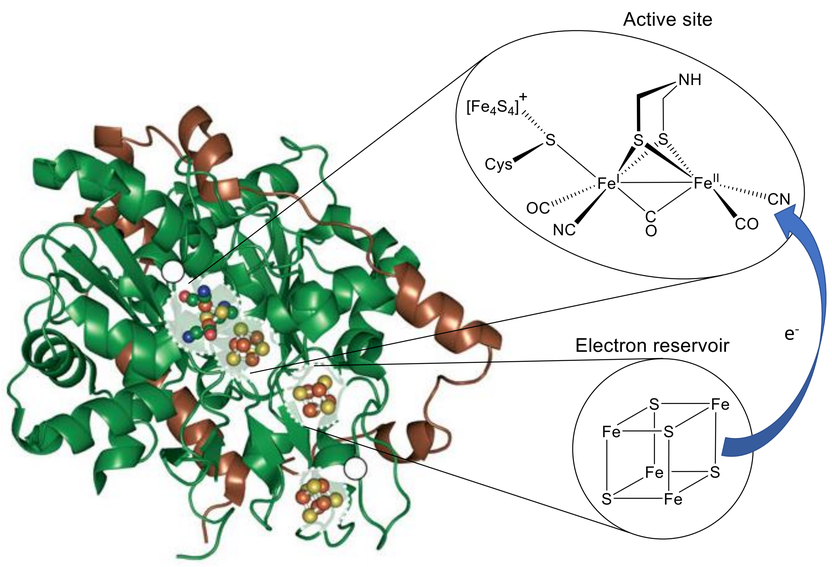
Abstract: Areas ranging from fine chemical synthesis to sustainable energy development rely on highly efficient metal-based catalysts to perform key chemical transformations [1]. Then metals such as Pd, Pt, Rh, Ir or Ru are used because they are proficient at mediating the multi-electron transfer steps 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. However, these cooperative processes remain not well-known, specifically in multi-metallic systems [3]. Then, replicating this strategy of redox cooperativity in synthetic complexes could offer a valuable way to enhance the reactivity of first-row transition metals like iron, copper, etc.
To address this challenge, our project seeks to develop and study the biomimetic strategy of incorporating metal-based electron reservoirs within the periphery of reactive metal centers. Thus, ditopic ligands able to interact with two metallic centers have been developed based on N,N,N',N'-tetra(heterocyclic)propylene- and ethylene-diamines. Modifying the substituents on the heterocycles and the Bite angle may provide interesting properties to our bimetallic systems. For now, their monometallic counterparts have been synthesized and characterized through spectroscopic and electrochemical technics that brought promising results.

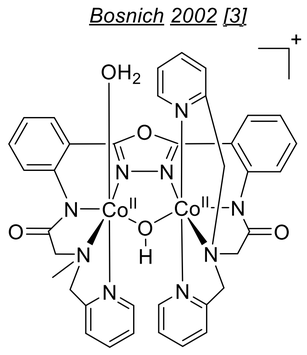



## In nature:

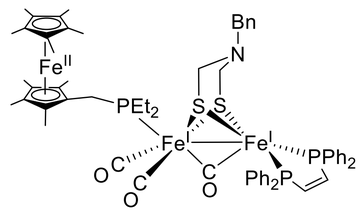



## In the lab:

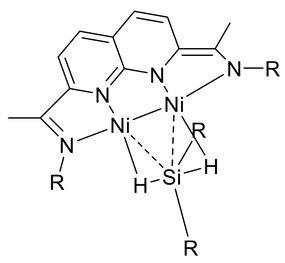
Bosnich 2002 [3]



Rauchfuss 2012 [4]

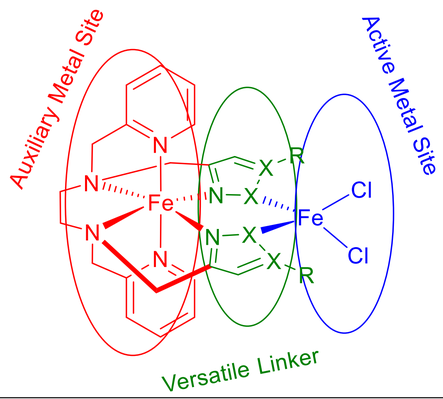


Steiman 2015 [5]



## Objectives:

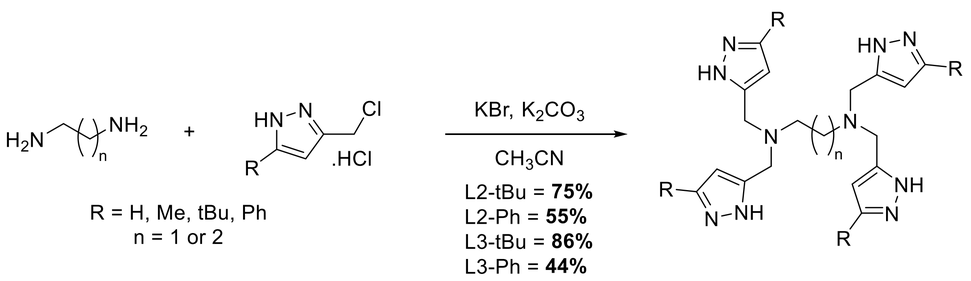
Based on the work of Rauchfuss and Bosnich, we introduce new bimetallic systems based on ditopic ligands able to complex two metals close to each other. Their proximity will influence their redox behavior and leads to a better understanding of redox cooperativity and possible applications in catalysis.

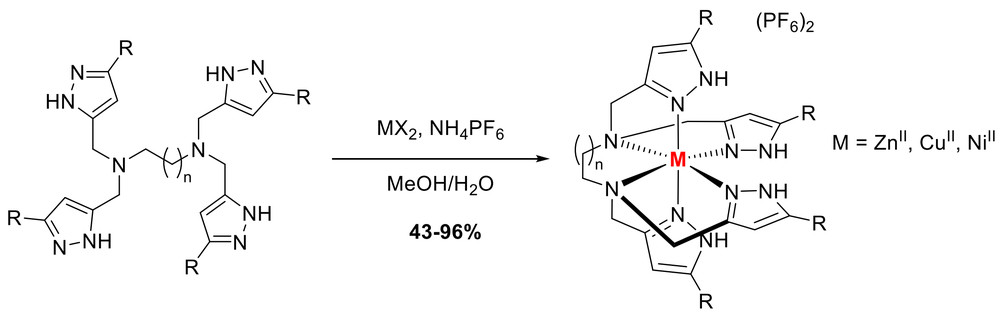



**Challenges to overcome:**
- Electrostatic charge-charge interactions
- Through bond covalent interactions
- Mechanical coupling

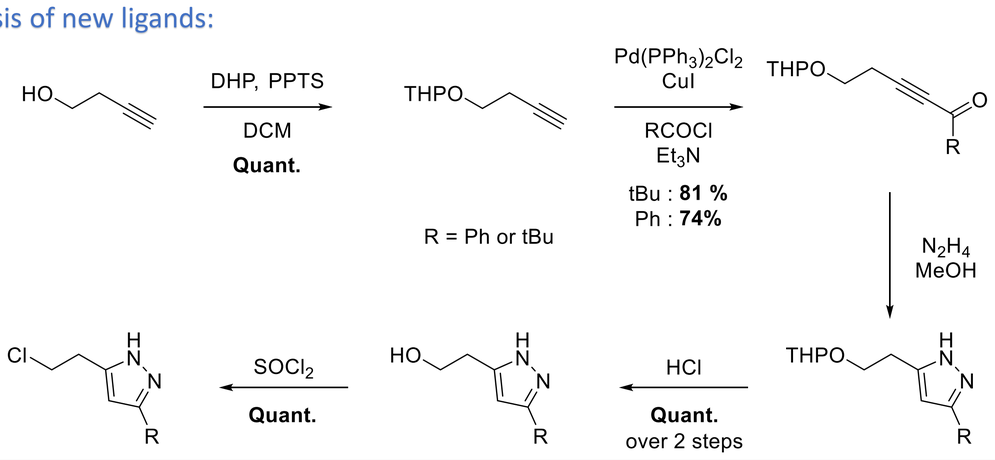
## Synthesis of the first ligands and monometallic complexes:


**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

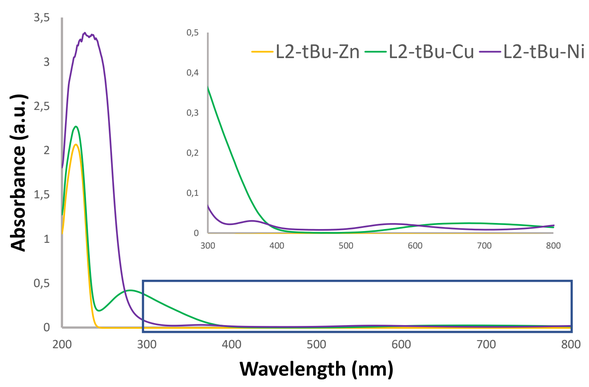


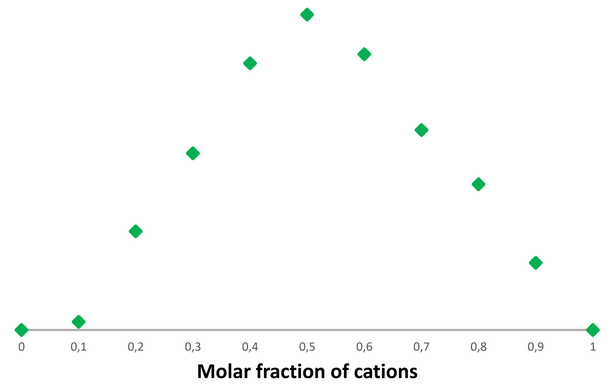




## Synthesis of new ligands:

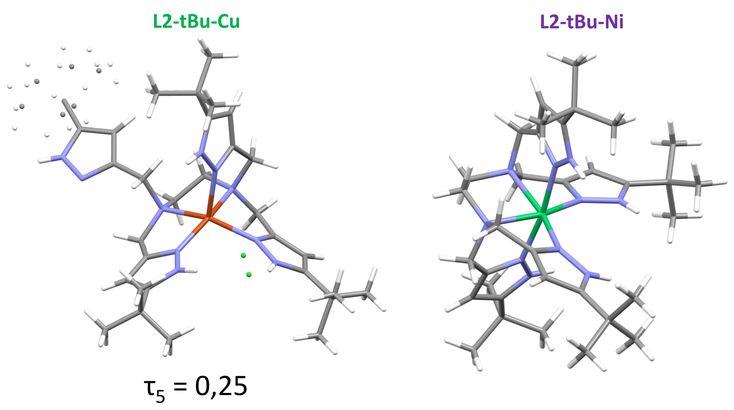



## Spectroscopic characterization of L2-tBu complexes:



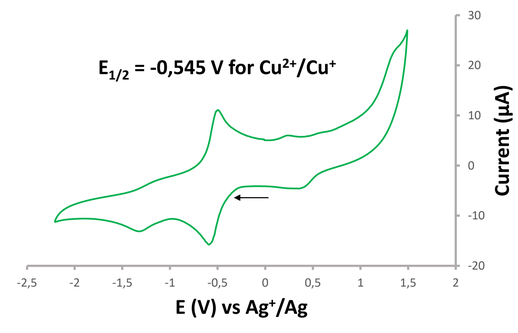



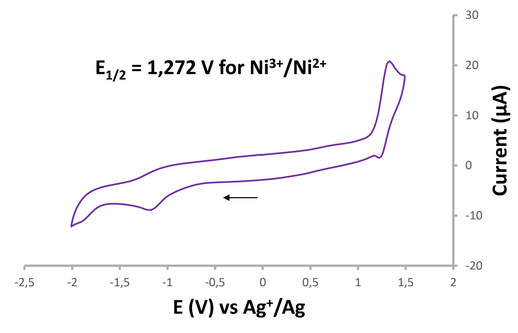

- Charge transfert exhibited by the presence of Cu
- d-d transitions for Ni/Cu
- Ratio 1:1 for complexation
- Small Bite angle and disfavored conformation for 2nd complexation




$\tau_5$ = 0,25

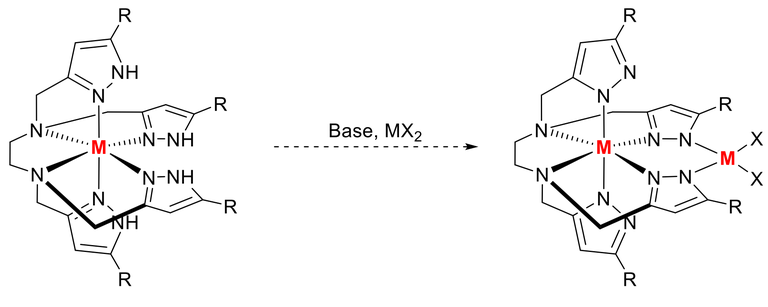
### Electrochemistry analyses in $CH_3CN$:




## 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 (Me and H) have only be observed by NMR and for now, we are not able to isolate them. Hopefully, the corresponding mono-metallic complexes have been synthesized and fully characterized. The complexation ratio 1:1 have been measured by Job's method and electron transfers have been studied by cyclic voltammetry [6]. The crystal structures revealed a very small Bite angle for ethylenediamines based ligands that can prevent the insertion of a second metal ion. To avoid this dead end, increase the length of the carbon chain of the pyrazole moiety have been investigated [7]. The formation of the bimetallic systems through axial and equatorial deprotonation using DBU is currently our next goal and the first attempts brought promising results.




## References:
[1] US Geological Survey Fact Sheet 087-02 (pubs.usgs.gov); [2] H. B. Gray, J. R. Winkler, *Chem Phys Lett.* **2009**, *65*, 537 ; [3] A. L. Gavrilova, C. J. Qin, R. D. Sommer, A. L. Rheingold, B. Bosnich, *J. Am. Chem. Soc.* **2002**, *124*(8) 1714 ; [4] J. M. Camara, T. B. Rauchfuss, *Nat. Chem.* **2012**, *4*, 26 ; [5] T. J. Steiman, C. Uyeda, *J. Am. Chem. Soc.* **2015**, *137*, 6104 ; [6] B. de Bruin, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 2936 ; [7] D. B. Grotjahn, S. Van, D. Combs, D. A. Lev, C. Schneider, M. Rideout, C. Meyer, G. Hernandez, L. Mejorado, *J. Org. Chem.* **2002**, *67*, 9200–9209