Redox Cooperativity Analysis with Computational Chemistry:

Electron Fluidity in Platinum Group Metal Complexes

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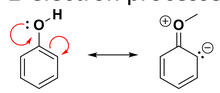
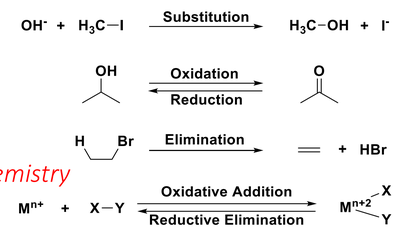
Project Goal

Most chemical processes are 2-electron processes

Resonance



Organic Chemistry



Organometallic Chemistry

- How can cheap first row metals (3d metals – Elements Sc-Zn) which typically undergo radical chemistry ($Fe^{II/III}$, $Co^{I/III}$, or $Cu^{I/II}$) perform 2-electron chemistry?
- Can 4d metals (Elements Y-Cd) and 5d metals (Elements La-Hg) participate in communication when they typically perform isolated 2-electron chemistry?
- What does 4d/5d interactions tell us about 3d cooperativity?

Nature's Solution

Pair multiple 1-electron sites for multi-electron chemistry

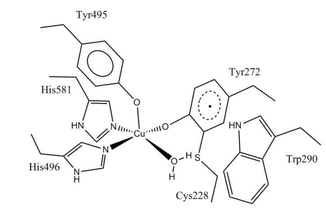
- Tyrosinase (2 Cu centers)
  - Tyrosine oxidation to catechol
- Galactose Oxidase (Cu + tyrosine radical)
  - Alcohol oxidation to aldehyde
- Multicopper Oxidase (4 Cu centers)
  - O_2 reduction to water
- Rieske dioxygenase (Non-heme iron + Rieske Fe_2S_2 cluster)
  - Napthalene to cis-diol

Research Question

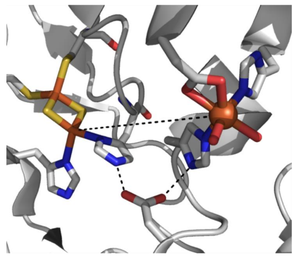
What allows interplay between multiple redox sites?

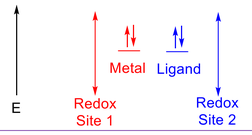
- Proximity (distance)?
- Energy Matching?
- Geometry (angle or dihedral angle)?

Galactose Oxidase



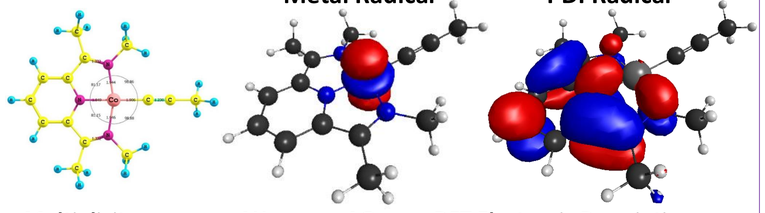
Rieske Dioxygenase





How can one design model systems capable of analogous reactivity?

Unique Example Co-PDI – "Electron Fluidity"

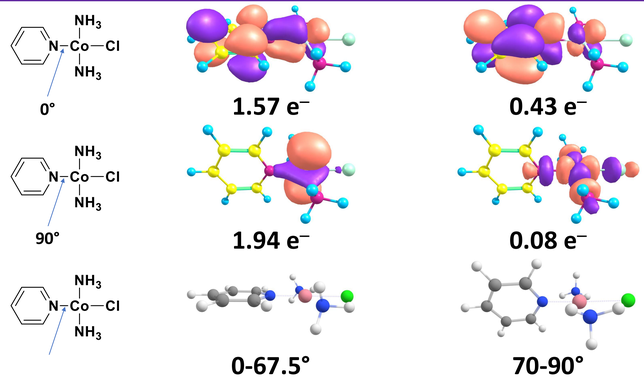


Multiplicity	ΔH_{rel}	ΔG_{rel}	DFT Electronic Description
$^{css}1$	+6.9	+8.3	(PDI)(LS-d^8-Co^{I})(C≡CR^-)
$^{oss}1$	-1.0	+1.1	($PDI^{\bullet-}$)$^{\downarrow}$(LS-d^7-Co^{II})$^{\uparrow}$(C≡CR^-)
3	0.0	0.0	($PDI^{\bullet-}$)$^{\uparrow}$(LS-d^7-Co^{II})$^{\uparrow}$(C≡CR^-)
5	+5.5	+3.3	($PDI^{\bullet-}$)$^{\uparrow}$(HS-d^7-Co^{II})$^{\uparrow\uparrow\uparrow}$(C≡$CR^-$)

- 4 electronic configurations so close in energy is remarkable

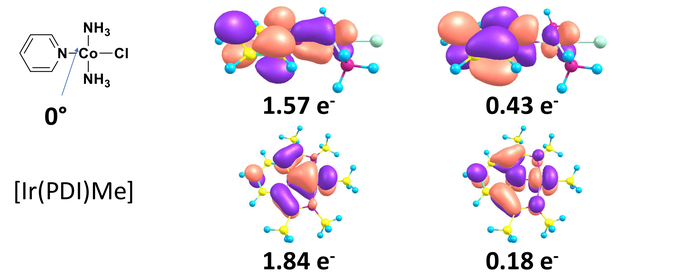
Lopez, K. G.; Cundari, T. R.; Gary, J. B. *Organometallics* **2018**, *37*, 309-313.
Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794-795.

Redox Communication – Redox Switching By Angle

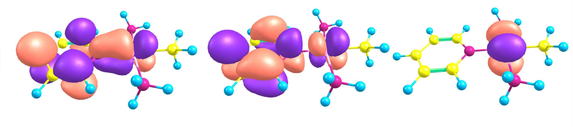


Electron Occupations by MCSCF	**Redox Non-Innocent Communication** Non-Integer Occupations	**Redox Innocent No Communication** Integer Occupations

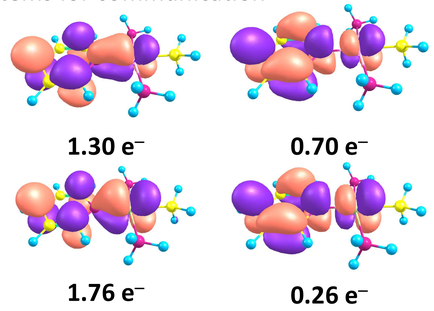
Redox Communication – Geometry vs Electronics



- 4d/5d metals capable of communication.

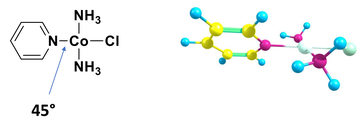


- Not restricted to d^8 systems for communication



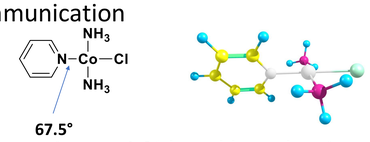
- Occupations much higher than 3d metals.

Redox Communication–Angle vs Distance vs Electronics



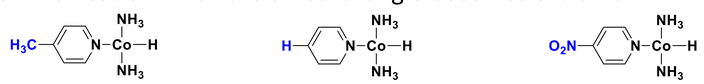
Optimized Distance 1.84 Å
Breaks Communication 2.04 Å

- Approximate 10 % bond lengthening required to break communication



Optimized Distance 1.84 Å
Breaks Communication 1.86 Å

- Approximate 1 % bond lengthening required to break communication when the dihedral angle becomes extreme



Breaks Comm. 8 % extension | **Breaks Comm.** 20 % extension | **Breaks Comm.** 51 % extension

Conclusions and Future Work

- MCSCF is a method to determine non-integer electron occupation and redox communication.
- Distance and dihedral angles are linked properties in redox communication.
- Electronic matching and geometry (distance) are linked in redox communication.
- What can we learn from 4d/5d metals to improve communication at desired 3d metals?

Acknowledgements

- Partial funding for this project was provided by the Summer Undergraduate Research Experience sponsored by the College of Sciences and Mathematics at Stephen F. Austin State University.
- Department of Chemistry and Biochemistry, SFASU
- Robert A. Welch Foundation, Grant AN-0008
- SFA ORSP RCA Grant
- Tom Cundari - UNT CASCaM (NSF Grant CHE-1531468)