# Controlling Two Redox Centers to Allow Cooperation for Multi-Electron Redox Chemistry

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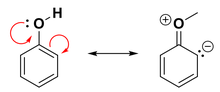
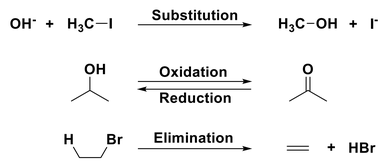
## Project Goal

Most chemical processes are 2-electron processes

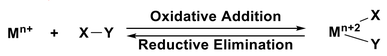
*Resonance*



*Organic Chemistry*




*Organometallic Chemistry*




How can cheap first row metals which typically undergo radical chemistry ($Fe^{II/III}$ or $Cu^{I/II}$) perform 2-electron chemistry?

## Nature's Solution

Pair multiple 1-electron sites for multi-electron chemistry

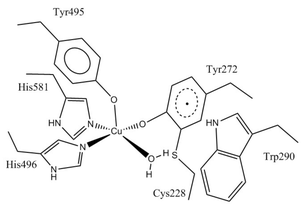
- Tyrosinase (2 Cu centers)
  - Tyrosine oxidation to catechol
- Galactose Oxidase (Cu + tyrosine radical)
  - Alcohol oxidation to aldehyde
- Multicopper Oxidase (4 Cu centers)
  - $O_2$ reduction to water
- Rieske dioxygenase (Non-heme iron + Rieske $Fe_2S_2$ cluster)
  - Napthalene to cis-diol

## Research Question

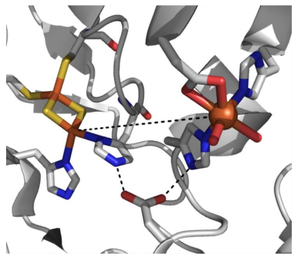
What allows interplay between multiple redox sites?

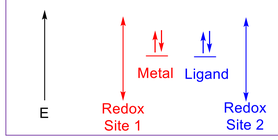
- Proximity?
- Energy Matching?
- Can a metal and ligand be paired for redox reactions?

**Galactose Oxidase**




**Rieske Dioxygenase**

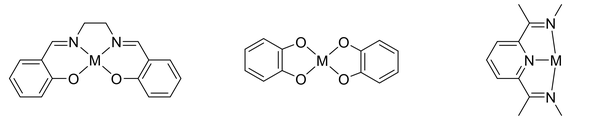





How can one design models systems capable of analogous reactivity?

## Model Systems

**Known Synthetic Systems**




- M(salen) complexes typically perform successive 1-electron chemistry
- Zr(catecholate) complexes pair two ligand redox events
- M(PDI) complexes (Fe/Co)pair metal and ligand (PDI) redox events

Smith, A. L.; Hardcastle, K. I.; Soper, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 14358-14360.
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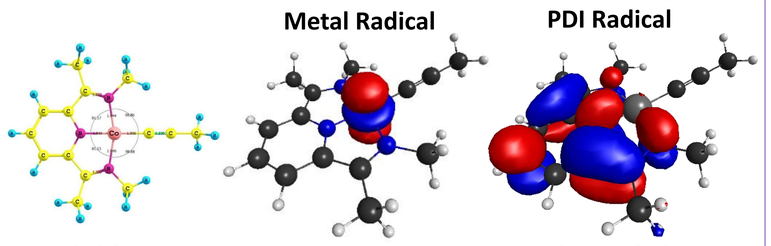
Wong, J. L.; Sanchez, R. H.; Logan, J. G.; Zarkesh, R. A.; Ziller, J. W.; Heyduk, A. F. *Chem. Sci.* **2013**, *4*, 1906-1910.

## Unique Example Co-PDI – "Electron Fluidity"

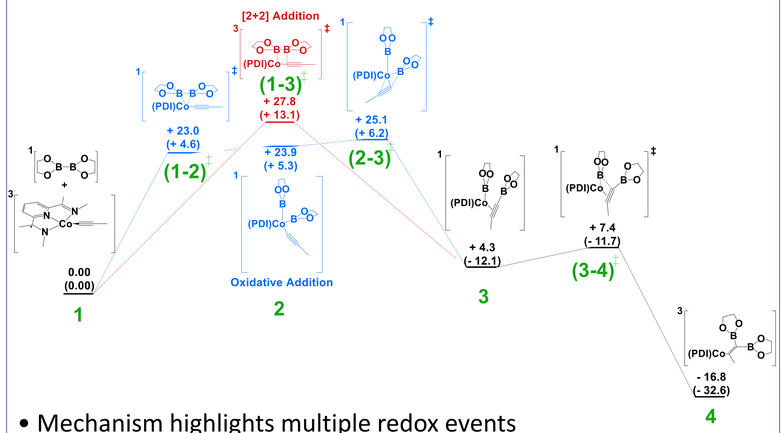



| Multiplicity | $\Delta H_{rel}$ | $\Delta G_{rel}$ | DFT Electronic Description |
|---|---|---|---|
| $^{css}1$ | +6.9 | +8.3 | (PDI)(LS-$d^8$-$Co^I$)(C≡$CR^-$) |
| $^{oss}1$ | -1.0 | +1.1 | ($PDI^{\bullet-}$)$^{\downarrow}$(LS-$d^7$-$Co^{II}$)$^{\uparrow}$(C≡$CR^-$) |
| 3 | 0.0 | 0.0 | ($PDI^{\bullet-}$)$^{\uparrow}$(LS-$d^7$-$Co^{II}$)$^{\uparrow}$(C≡$CR^-$) |
| 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.

## Borylation Mechanism – Redox Switching

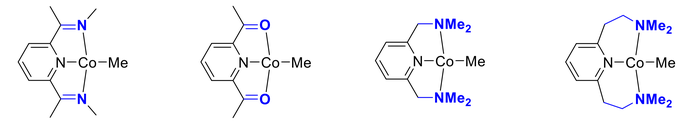



- Mechanism highlights multiple redox events

Lopez, K. G.; Cundari, T. R.; Gary, J. B. *Organometallics* **2018**, *37*, 309-313.

## Why is Co-PDI Special?

**Energy Separation of Four Spin States in PDI Derivatives**

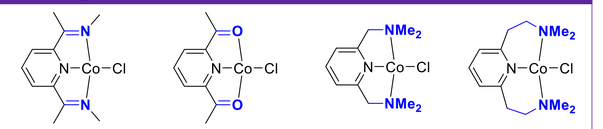


8.3 kcal/mol | 9.3 kcal/mol | 7.9 kcal/mol | 37.6 kcal/mol

*Calculated using Gaussian16 with B3LYP/6-31G(d,p)*

- Atom substitutions cause small changes to spin state gaps
  - This is surprising given the expected large energy perturbation
- Adding additional linker units breaks ligand planarity
  - Ligand planarity may be key to electron fluidity

## Multi-Configurational Electronic Structure



| | | | | |
|---|---|---|---|---|
| HOMO Occupancy | 1.36 e⁻ | 1.38 e⁻ | 1.55 e⁻ | 1.93 e⁻ |
| LUMO Occupancy | 0.65 e⁻ | 0.63 e⁻ | 0.45 e⁻ | 0.09 e⁻ |

*Calculated using CAS(12,12) active space*

- Atom substitutions or hybridization changes cause small changes in orbital occupations
  - Significant bi-radical character indicates redox non-innocence
- Breaking ligand planarity eliminates bi-radical character
  - Eliminates redox non-innocence behavior

## Conclusions and Future Work

- Co-PDI system possesses remarkable electronic structure with multiple electronic configurations in close energy
- Atom changes to PDI cause remarkably little charge to electronic configuration
- Changing ligand planarity appears to have a large effect on electronic structure
- Future work will study the redox reactivity of these PDI derivatives

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