The Career Of Daniel G. Nocera

Jeff Van Humbeck – MacMillan Group Meeting

Daniel G. Nocera

■ From Dead–Head to Whiz–Kid

Dropped out of high school to follow Grateful Dead*

B.A. – Rutgers, 1979

Ph. D. – Caltech, 1984. Supervisor: Harry Gray

Assistant Prof. – Michigant State, 1983

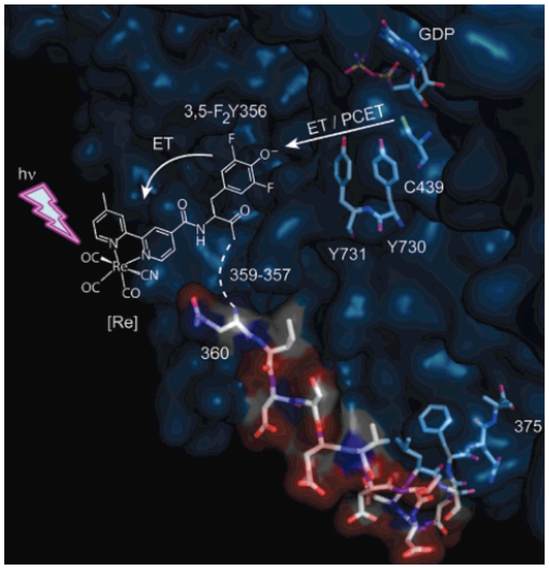
Professor – M.I.T., 1997

W. M. Keck Professor of Energy – M.I.T., 2002

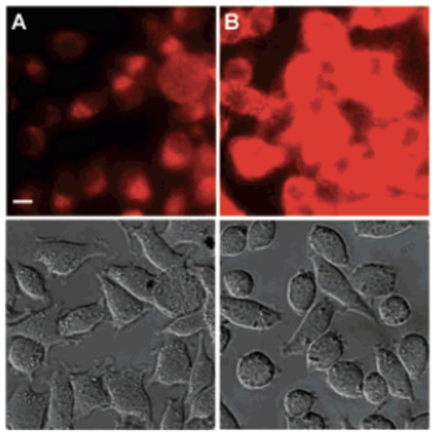
*Confirmed by multiple sources

Scope of Review

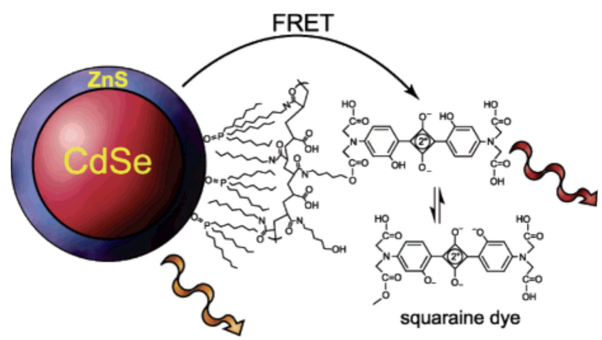
■ Photochemical Probes



Tyrosine Photooxidation



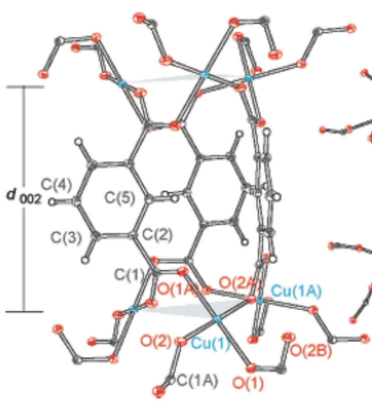
In Vitro Quantum Dots

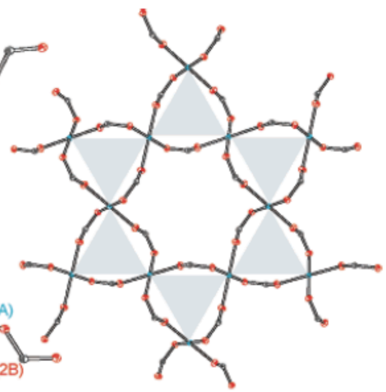


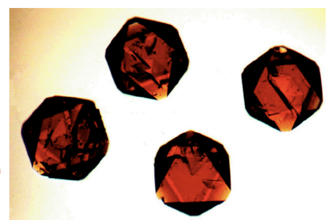
Fluorescence Detection (pH, etc.)

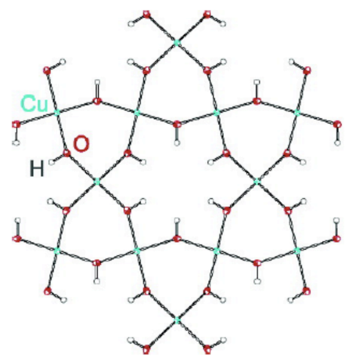
Scope of Review

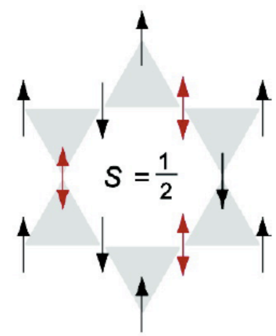
- Chemistry and Magnetism of Spin Frustration









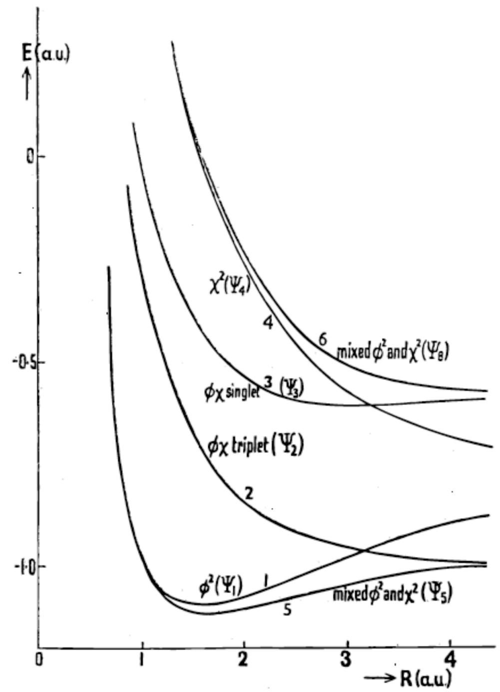


Metal–Organic Frameworks

Purely Inorganic

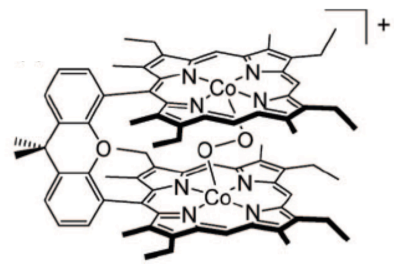
A Wide Career Arc

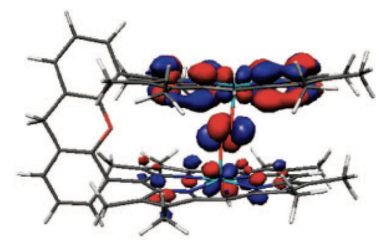
Fundamental MO Theory Leads to Energy



EtOH

20 years



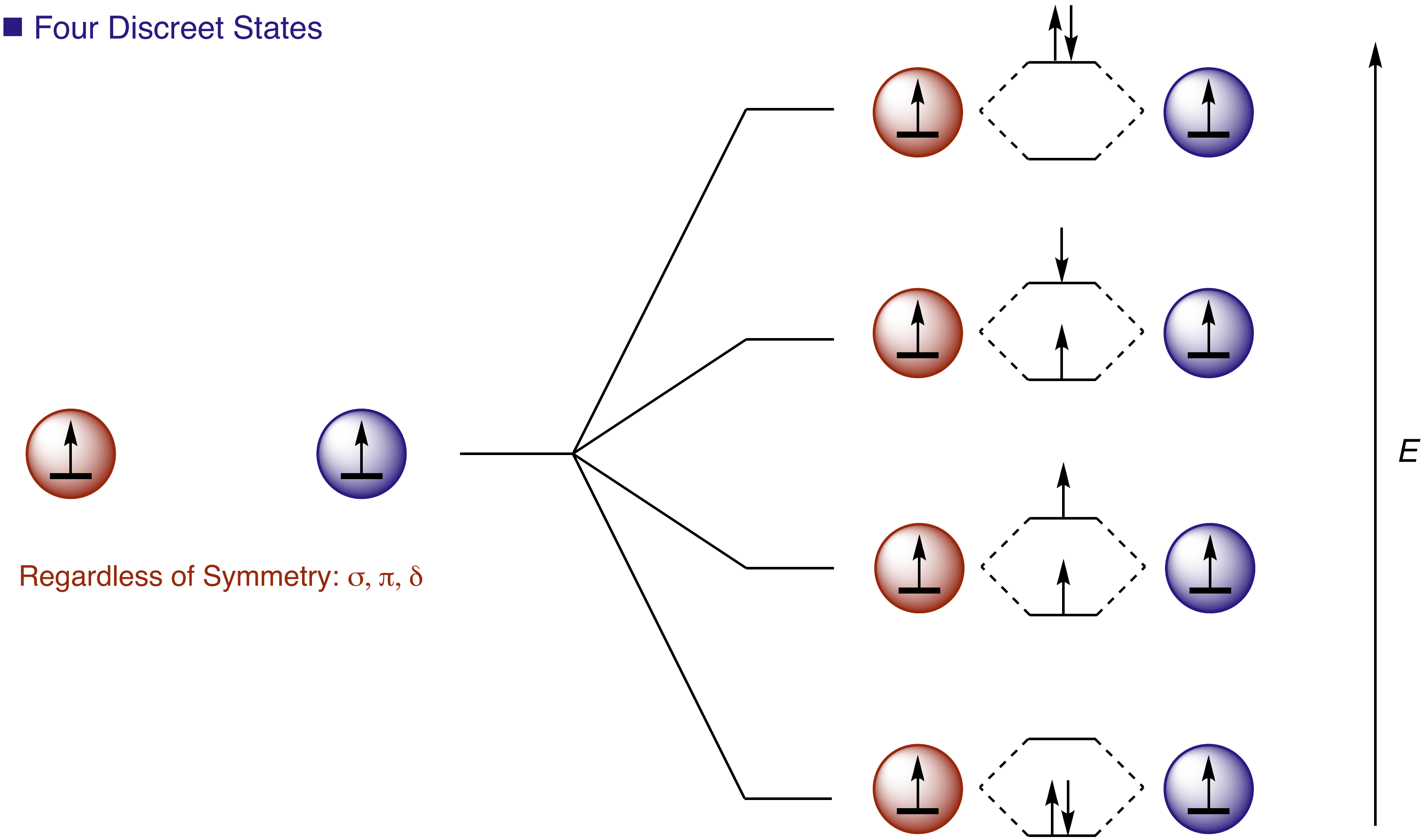


Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

Rosenthal, J.; Nocera, D. G. *Acc. Chem. Res.* **2007**, *40*, 543.

Nature of the Two–Electron Bond

- Four Discreet States

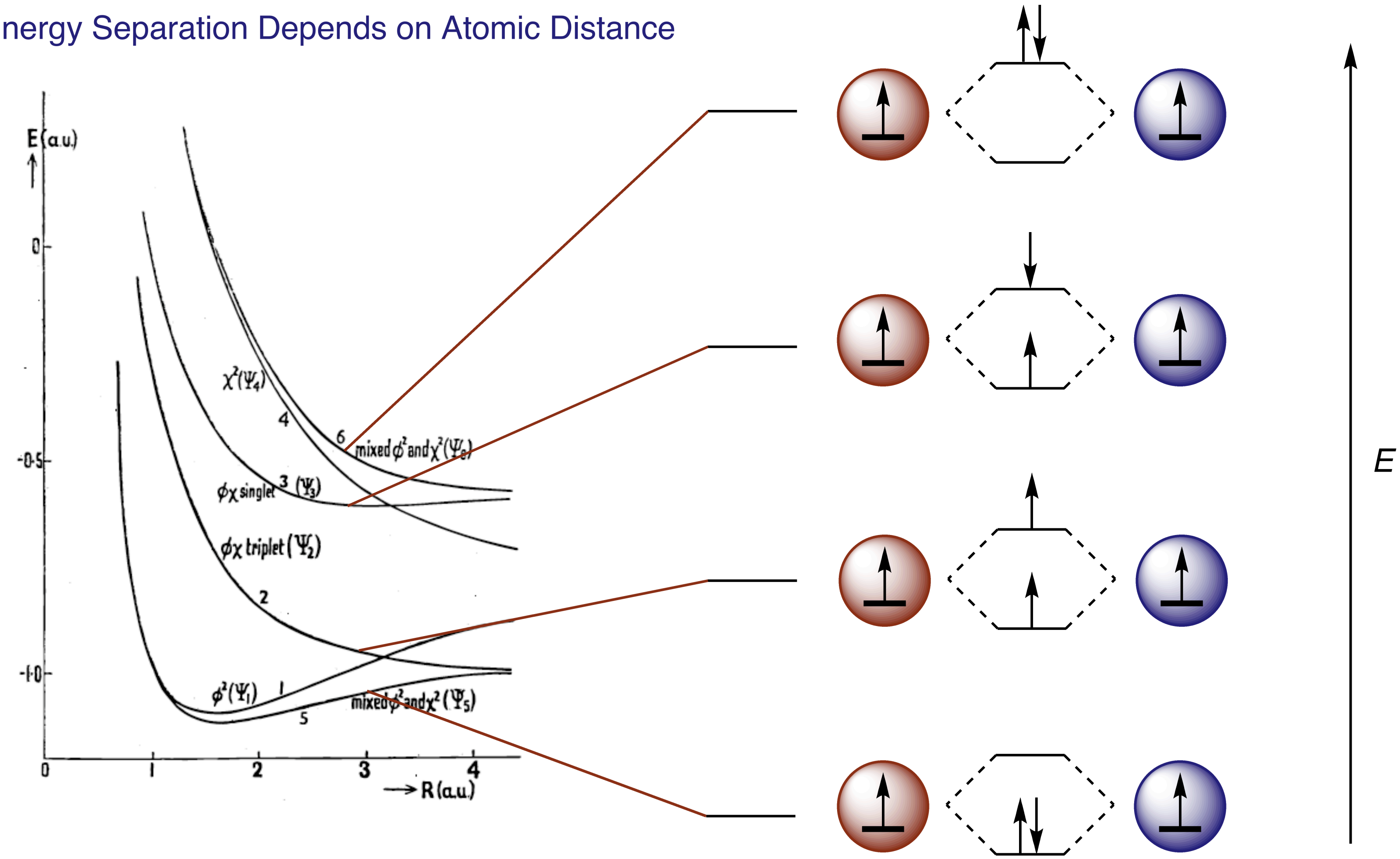


Regardless of Symmetry: σ, π, δ

Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

Relative Energy and Distance

- Energy Separation Depends on Atomic Distance



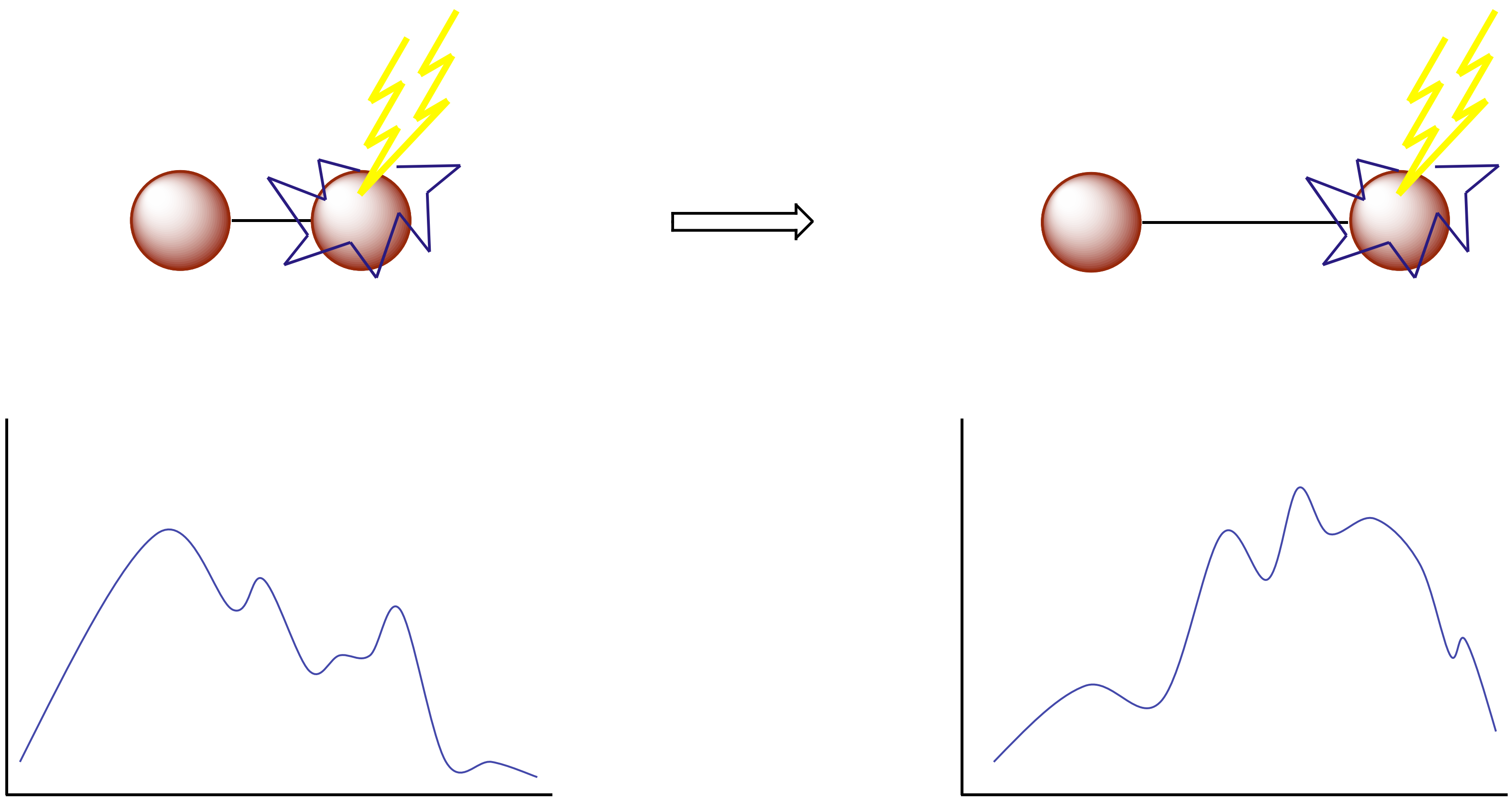
Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

"... it is central to the concept of scientific *research that all theoretical results, however little reason there might be to doubt their correctness, ought to be tested experimentally."*

Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

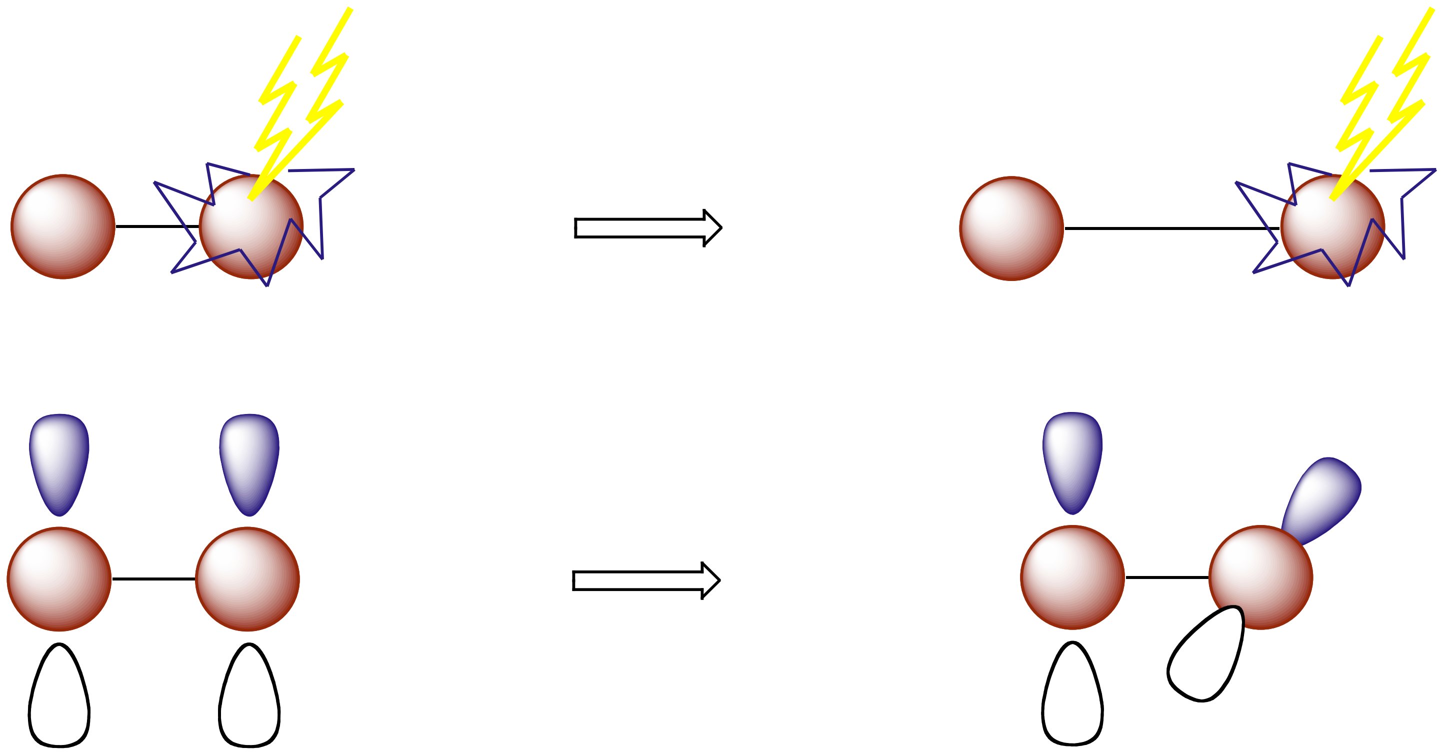
Mission: Impossible

- Molecular Tweezers Do Not Exist



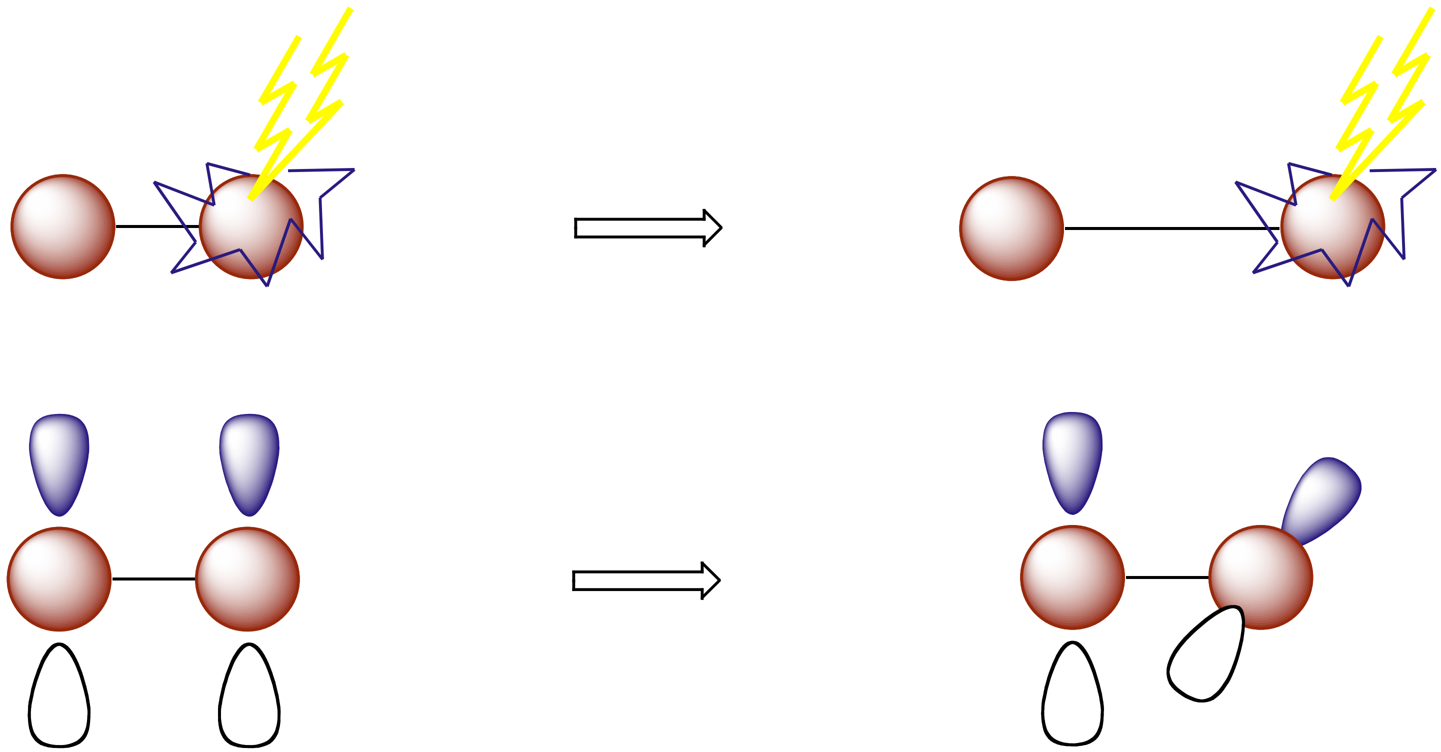
A Crucial Twist

- Rotation of Orbitals Gives Same Effect



A Crucial Twist

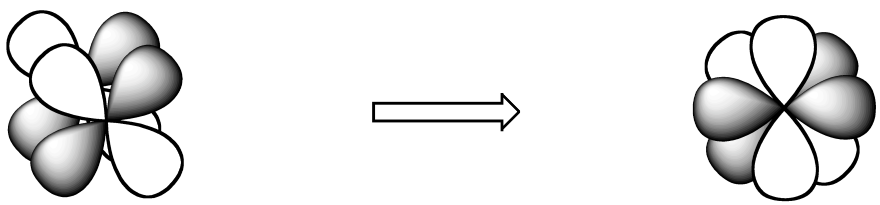
- Rotation of Orbitals Gives Same Effect



- Largest twist of a π–bond only 40°: Leuf, W.; Reese, R. *Top. Stereochem.* **1991**, *20*, 231.

40º: Perfect For Beers and δ–Bonds

- 40º Twist Sufficient to Nullify δ–Bond

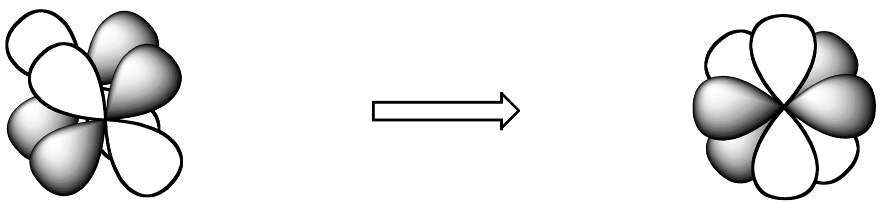


Triple Bond Unaffected

Bond Length Change <3%

40º: Perfect For Beers and δ–Bonds

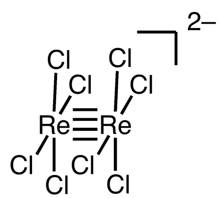
- 40º Twist Sufficient to Nullify δ–Bond

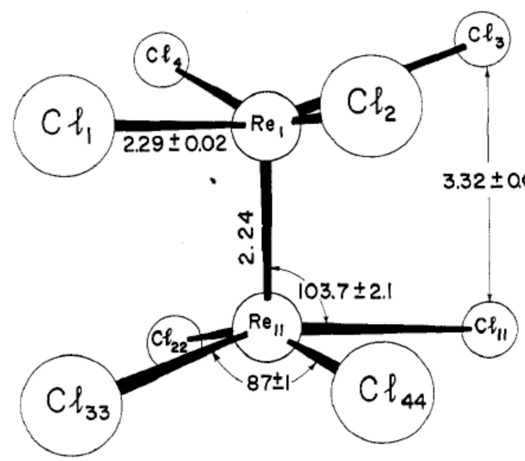


Triple Bond Unaffected

Bond Length Change <3%

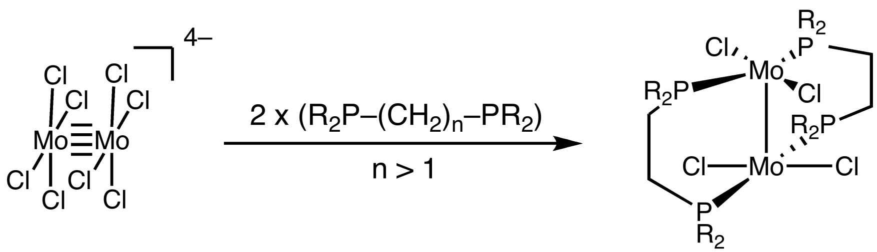
- Simple Metal δ–Bonds are Eclipsed

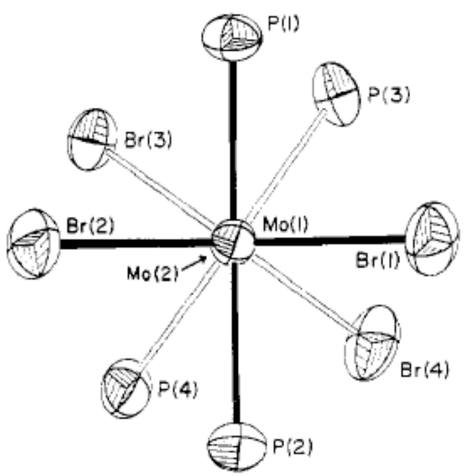




Bidentate Phosphine Torque

■ Varying Chain Length Causes Twist

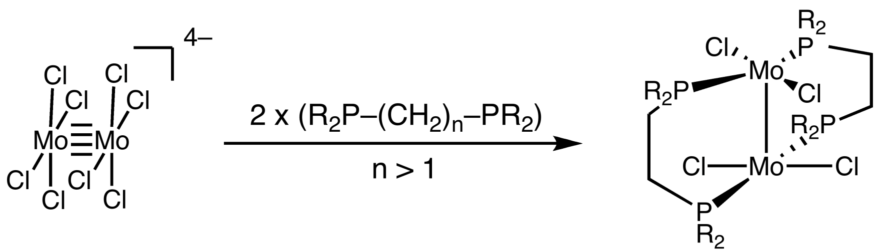


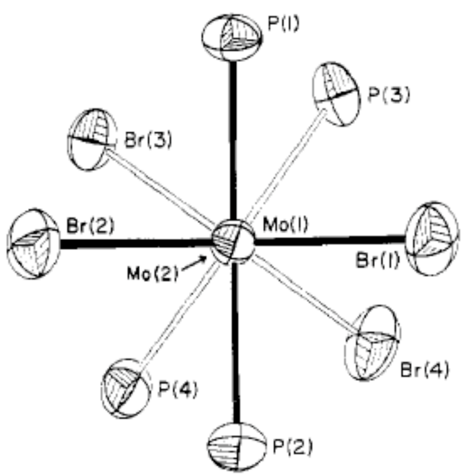


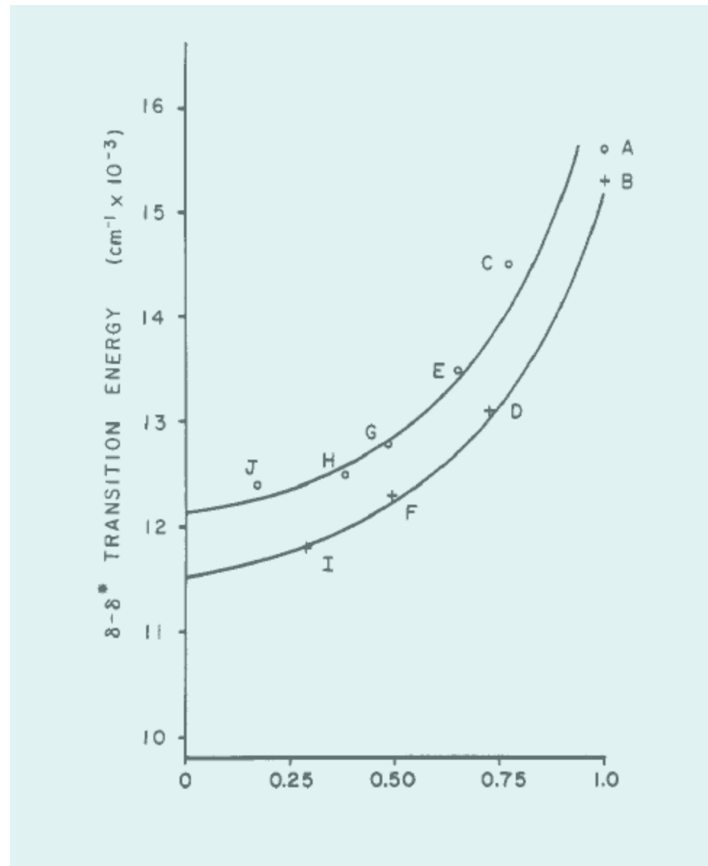
Campbell, F. L.; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1984**, *24*, 177.

Bidentate Phosphine Torque

- Varying Chain Length Causes Twist



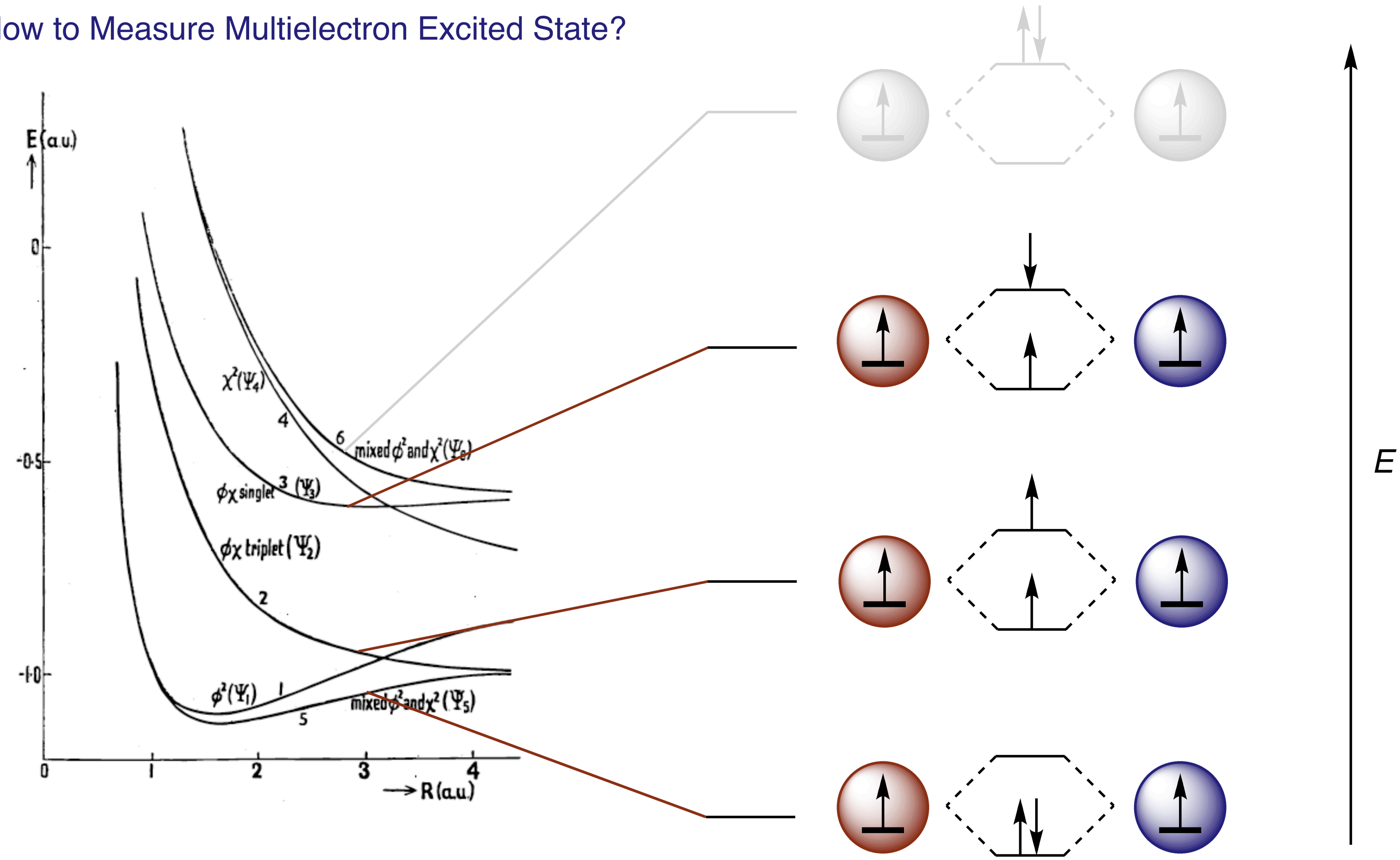




Campbell, F. L.; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1984**, *24*, 177.

Crucial Evidence Lacking

■ How to Measure Multielectron Excited State?



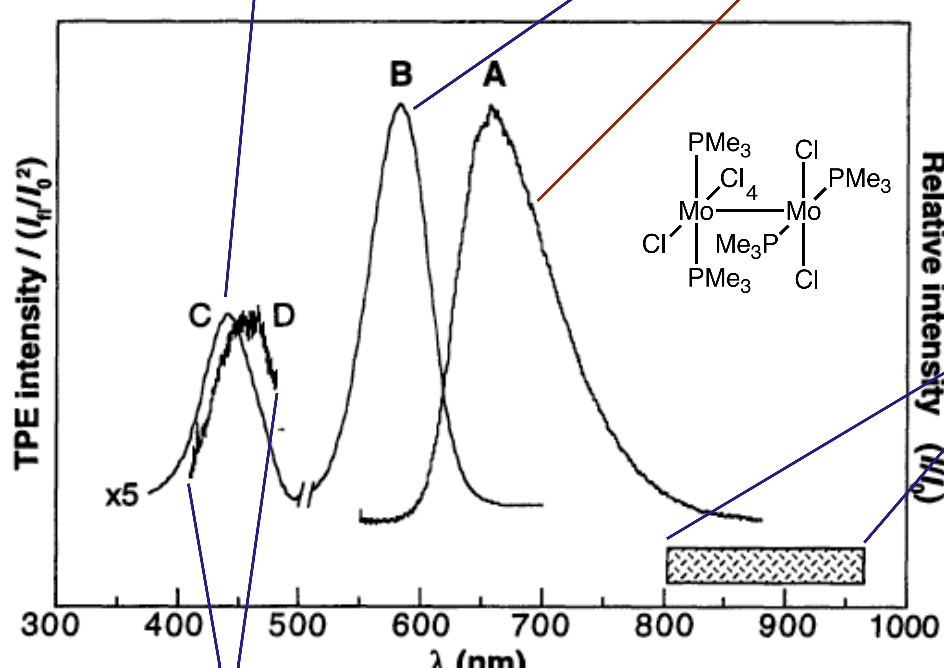
Multielectron Excited States

- Nocera Enters the Mix

Absorption @ 441nm ($^1\pi^3\delta^* \leftarrow {}^1\pi^4$)

Absorption @ 585 nm ($^1\delta\delta^* \leftarrow {}^1\delta^2$)

Red Emission @ 673nm ($^1\delta^2 \leftarrow {}^1\delta\delta^*$)



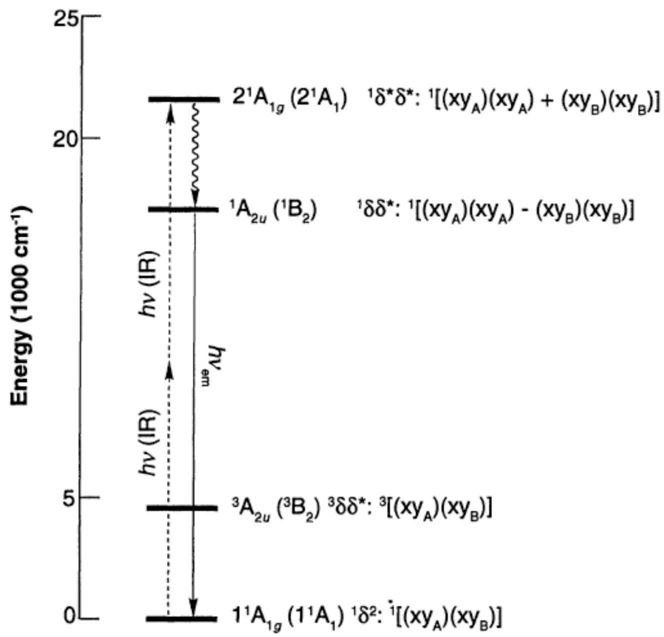
NdYAG Dye Laser Range (800–970 nm)

Laser Absorption (nm/2)

Engebretson, D.S.; Zaleski, J. M.; Lero, G. E.; Nocera, D. G. *Science* **1994**, *265*, 759.

Multielectron Excited States

Observation of Zwitterionic State



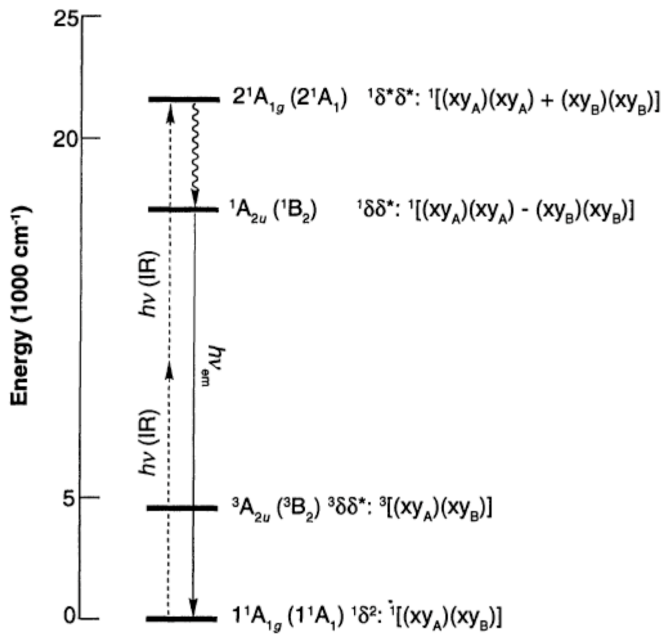
Prove symmetry (A_1) of doubly excited state

Confirms ($2^1A_1 - {}^1B_2$) gap = (${}^3B_2 - {}^1A_1$) gap

Engebretson, D.S.; Zaleski, J. M.; Lero, G. E.; Nocera, D. G. *Science* **1994**, *265*, 759.

Multielectron Excited States

■ Observation of Zwitterionic State



Prove symmetry (A_1) of doubly excited state

Confirms ($2^1A_1 - {}^1B_2$) gap = (${}^3B_2 - {}^1A_1$) gap

Is this what gets you a job at MIT?

Engebretson, D.S.; Zaleski, J. M.; Lero, G. E.; Nocera, D. G. *Science* **1994**, *265*, 759.

“. . .the zwitterionic excited-state manifold has important ramifications on chemical reactivity owing to the pairing of two electrons on one center and two holes on an adjacent one. . . zwitterionic states may prove to be critical intermediates in strategies to effect multielectron transformations”

Engebretson, D.S.; Zaleski, J. M.; Lero, G. E.; Nocera, D. G. *Science* **1994**, *265*, 759.

". . .the zwitterionic excited-state manifold has important ramifications on chemical reactivity owing to the pairing of two electrons on one center and two holes on an adjacent one. . . zwitterionic states may prove to be critical intermediates in strategies to effect multielectron transformations"

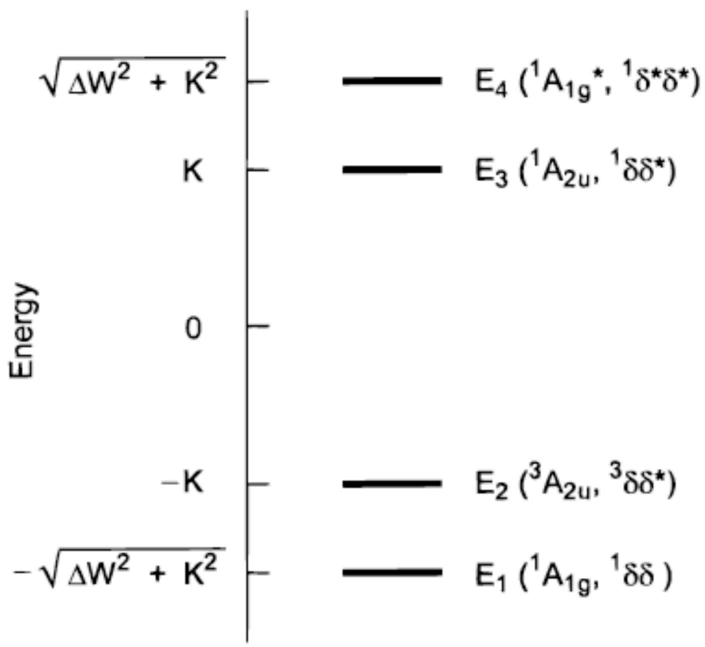
Engebretson, D.S.; Zaleski, J. M.; Lero, G. E.; Nocera, D. G. *Science* **1994**, *265*, 759.

Is this true?

Isn't this limited to NdYAG Laser Chemistry? (No)

Accessing Zwitterionic State

- Singlet Excited State Has (Large) Zwitterionic Character



ΔW = Bond Strength (essentially)

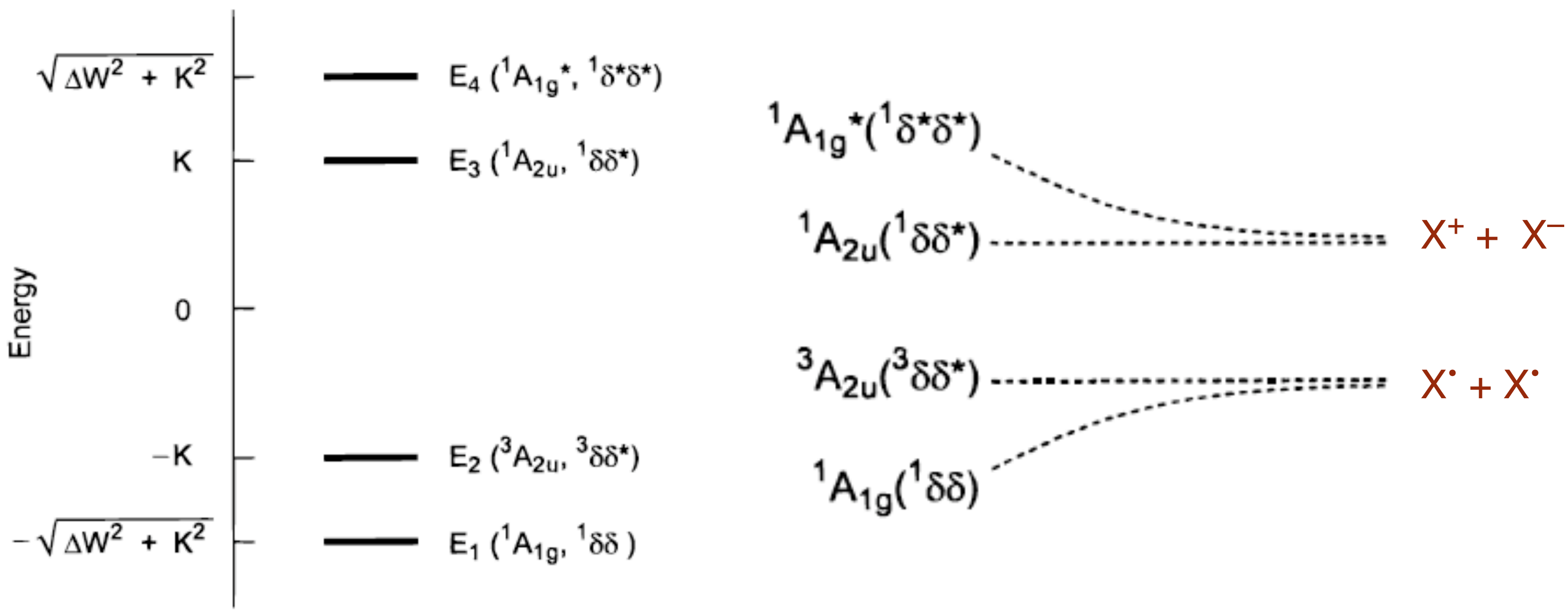
2K = Exchange Energy $X^\bullet + X^\bullet \longrightarrow X^+ + X^-$

What happens when bond is very weak?

Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

Accessing Zwitterionic State

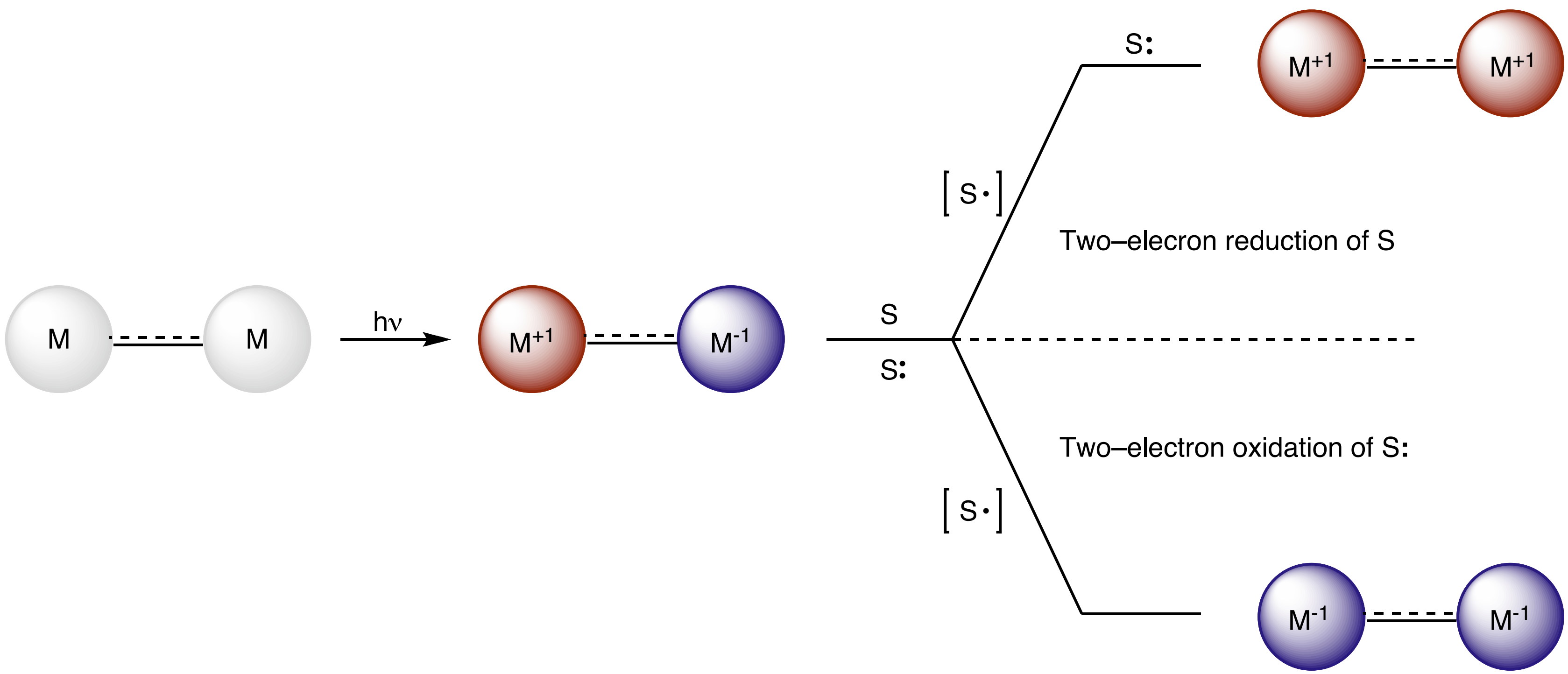
- Singlet Excited State Has (Large) Zwitterionic Character



Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

Design Plan

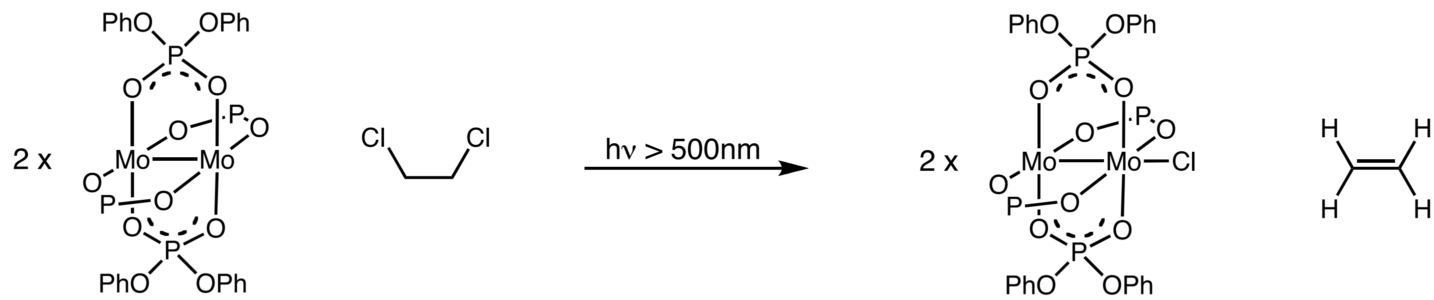
■ Excitation of Weak M—M Bond



Nocera, D. G. *Acc. Chem. Res.* **1995**, *28*, 209.

Dimolybdenum Phosphates

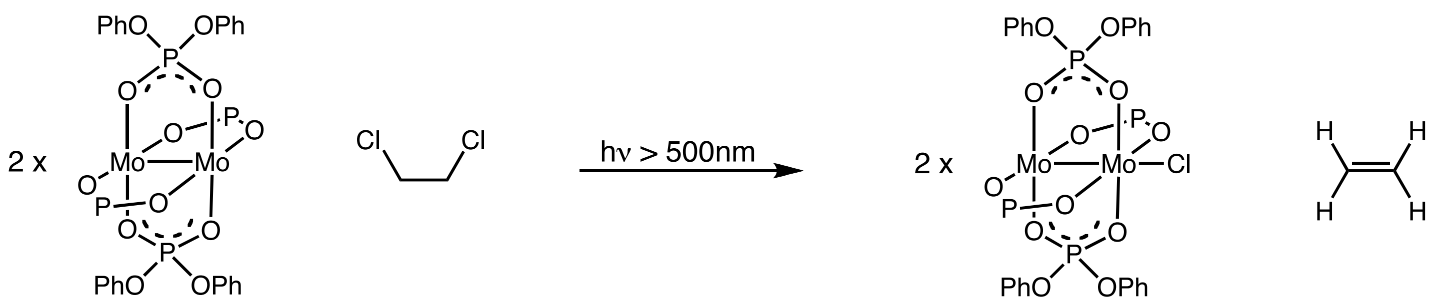
Proof of Concept

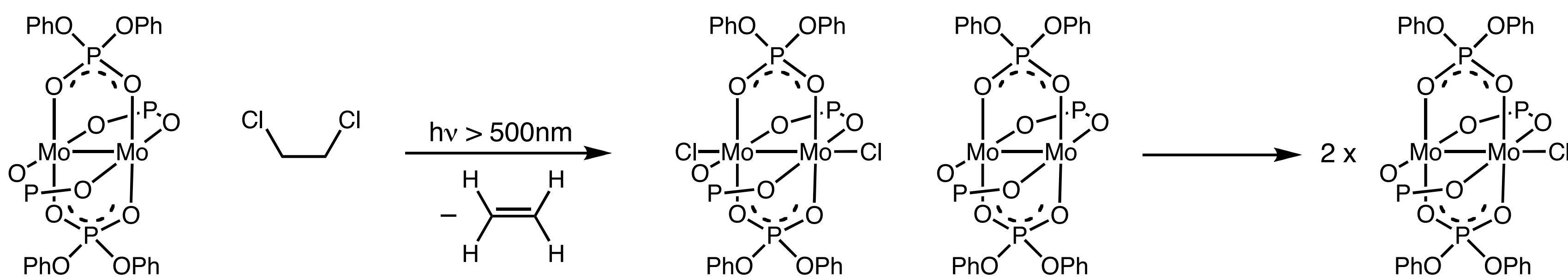


Chang, I. J.; Nocera, D. G. *Inorg. Chem.* **1989**, *28*, 4309.

Dimolybdenum Phosphates

■ Proof of Concept

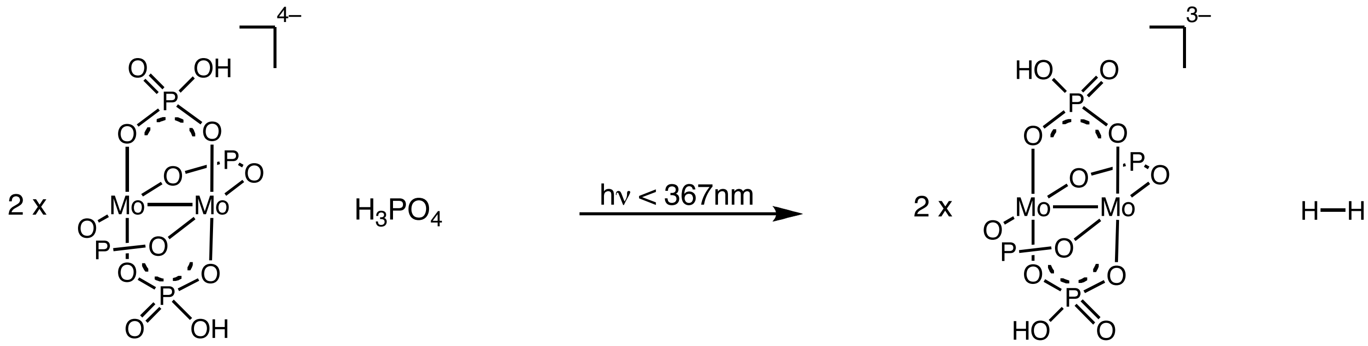




Chang, I. J.; Nocera, D. G. *Inorg. Chem.* **1989**, *28*, 4309.

Dimolybdenum in Acid

■ Early Hydrogen Production



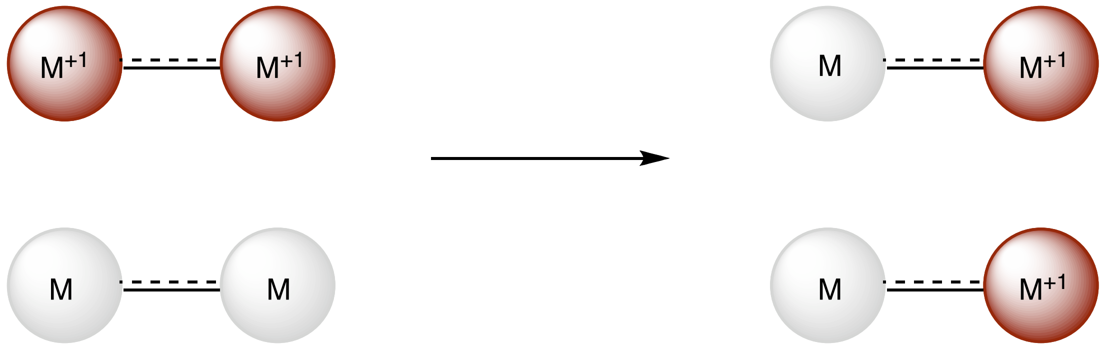
Molybdenum subject to same disproportionation

UV excitation required (π* <— π)

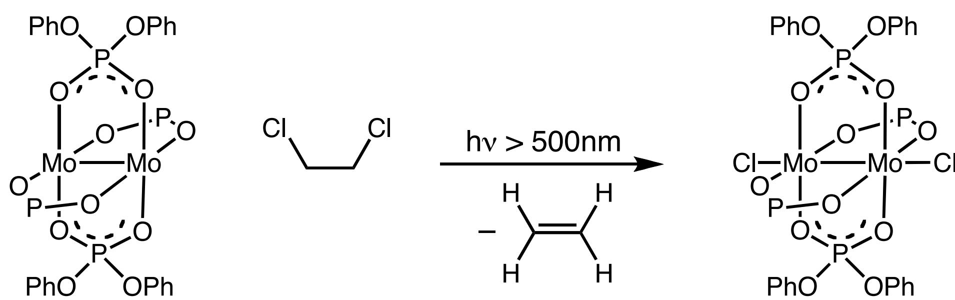
Chang, I. J.; Nocera, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 4901.

Consistent Problems

■ Catalyst Disproportionation



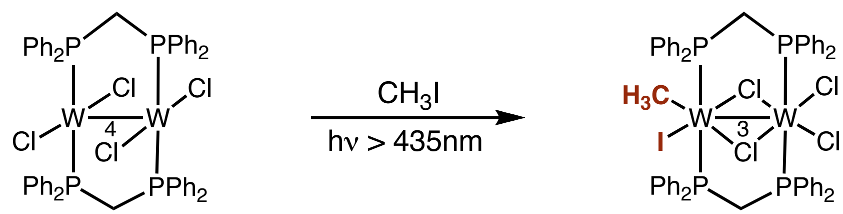
■ Independent (Though Coordinated) Reactivity



Chang, I. J.; Nocera, D. G. *Inorg. Chem.* **1989**, *28*, 4309.

Photooxidative Addition

■ Reaction at Single Metal Center



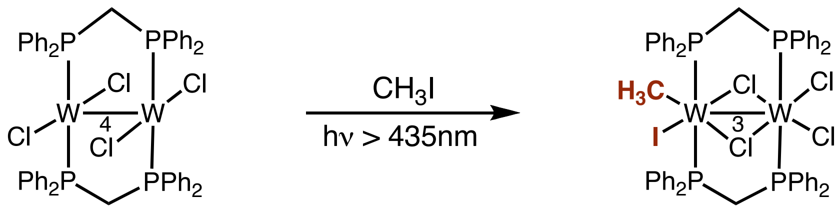
No reaction in dark

Radical reaction ruled out

Partigianoni, C. M.; Nocera, D. G. *Inorg. Chem.* **1990**, *29*, 2033.

Photooxidative Addition

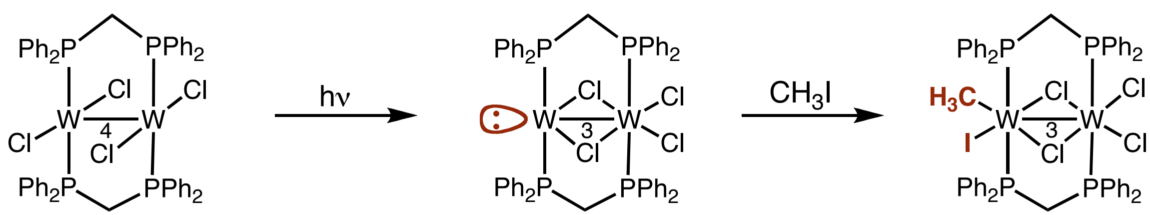
■ Reaction at Single Metal Center



No reaction in dark

Radical reaction ruled out

■ Stabilization of Zwitterionic Intermediate



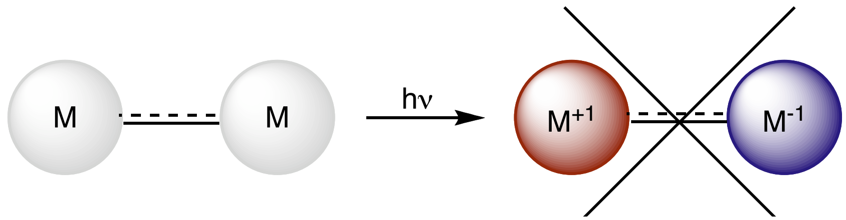
$W^{II}—W^{II}$ $W^{I}—W^{III}$ $W^{III}—W^{III}$

DIFFERENT COORDINATION GEOMETRY

Partigianoni, C. M.; Nocera, D. G. *Inorg. Chem.* **1990**, *29*, 2033.

Ground–State Mixed Valency

- Analogous Exicted State Reativity?

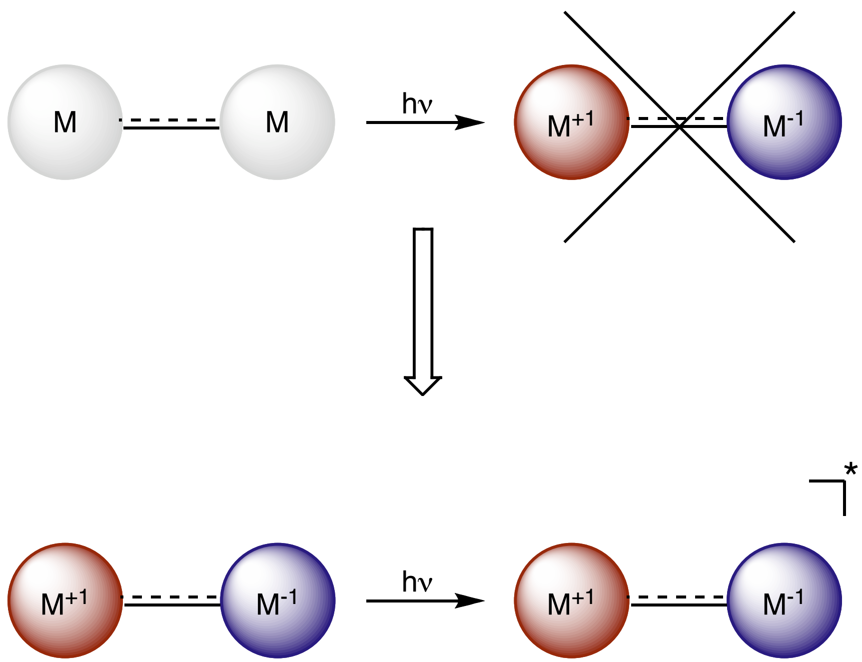


Identical metal centers tend to react by $1e^{-}$ each

Nocera, D. G. *Acc. Chem. Res.* **1995**, *28*, 209.

Ground–State Mixed Valency

■ Analogous Exicted State Reativity?



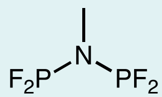
Identical metal centers tend to react by 1e⁻ each

Can mixed valence system still capture useful energy from light?

Nocera, D. G. *Acc. Chem. Res.* **1995**, *28*, 209.

Crucial Ligand Set

- Mixed Valence Complexes (With $M^{n}-M^{n+2}$) Rare

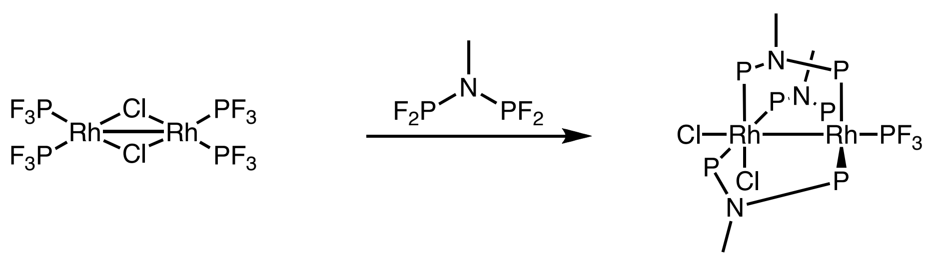


dfpma = bis(difluorophosphine)methylamine

Discovery: Nixon, J.F. *J. Chem. Soc. A* **1968**, 269.

Widely explored: King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243.

- Induces Spontaneous Disproportionation



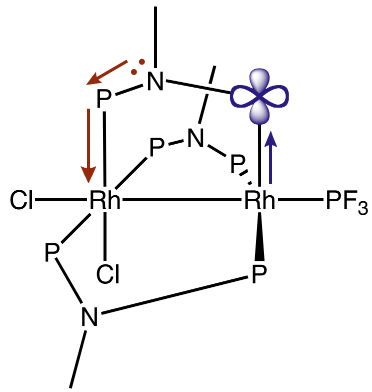
$Rh^{I}-Rh^{I}$

$Rh^{II}-Rh^{0}$

Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 4054.

DPFMA

■ Electronic Communication



Methylamine linker donates lone pair towards Rh^{II}

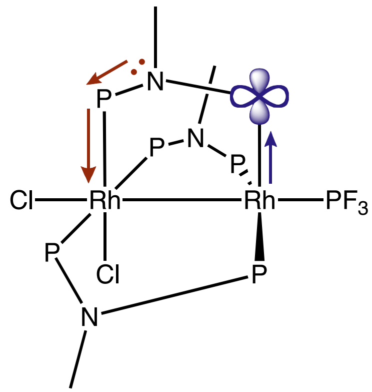
PF_2 groups a Rh^0 very π–acidic, strong backbonding

Confirmed by crystal structure

Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 2969.

DPFMA

■ Electronic Communication

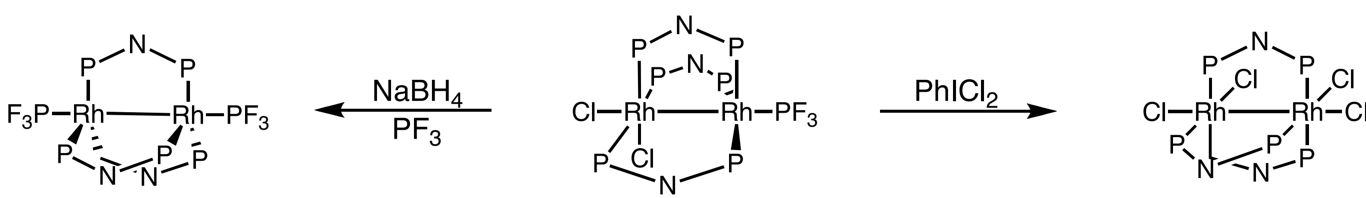


Methylamine linker donates lone pair towards Rh^{II}

PF_2 groups a Rh^0 very π–acidic, strong backbonding

Confirmed by crystal structure

■ Bis–Oxidized and Bis–Reduced Products Accessible



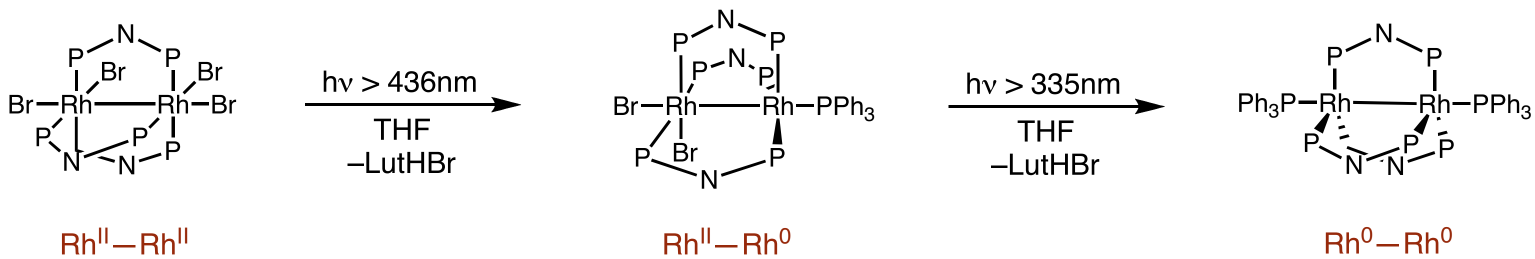
Rh^0—Rh^0 Rh^{II}—Rh^0 Rh^{II}—Rh^{II}

NB: Actual geometry is twisted

Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 2969.

X_2 Reductive Elimination

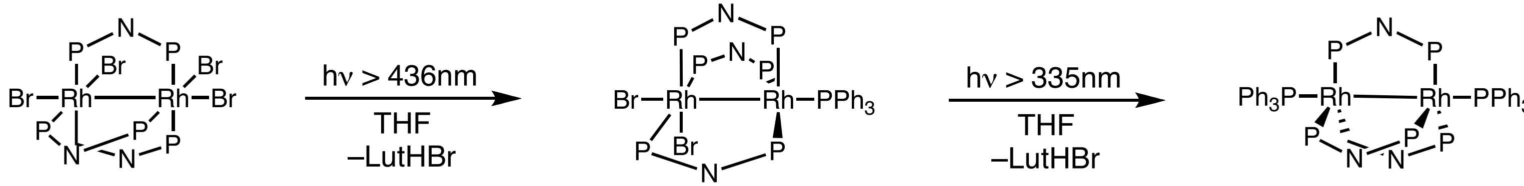
■ Four–Electron Rh_2 Series



Heyduk, A. F.; Macintosh, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **1999**, *121*, 5023.

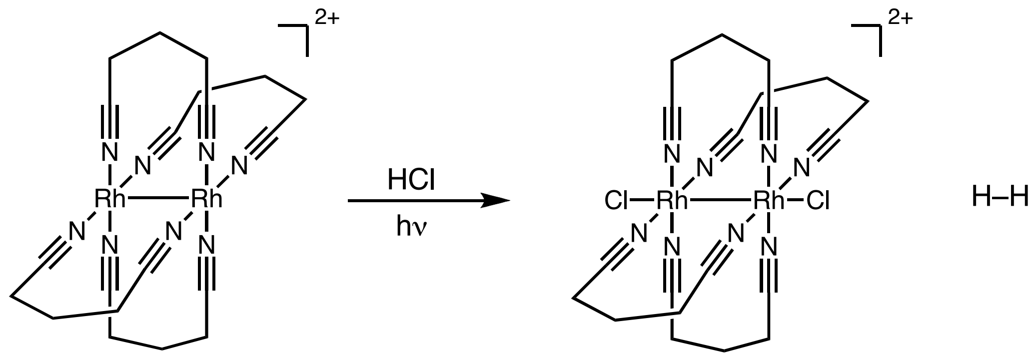
X_2 Reductive Elimination

■ Four–Electron Rh_2 Series



$Rh^{II}—Rh^{II}$ $Rh^{II}—Rh^{0}$ $Rh^{0}—Rh^{0}$

■ Rh–X Typically Dead End



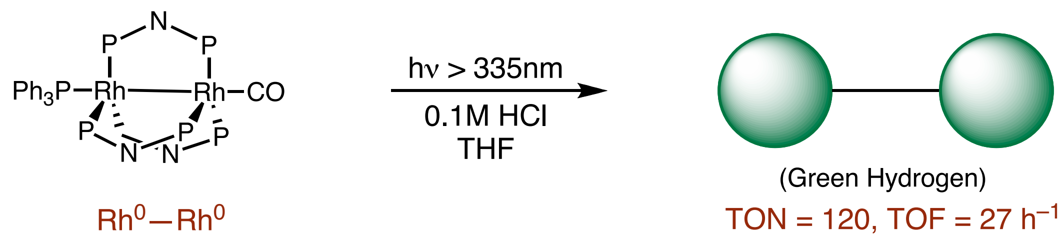
$Rh^{I}—Rh^{I}$ $Rh^{II}—Rh^{II}$

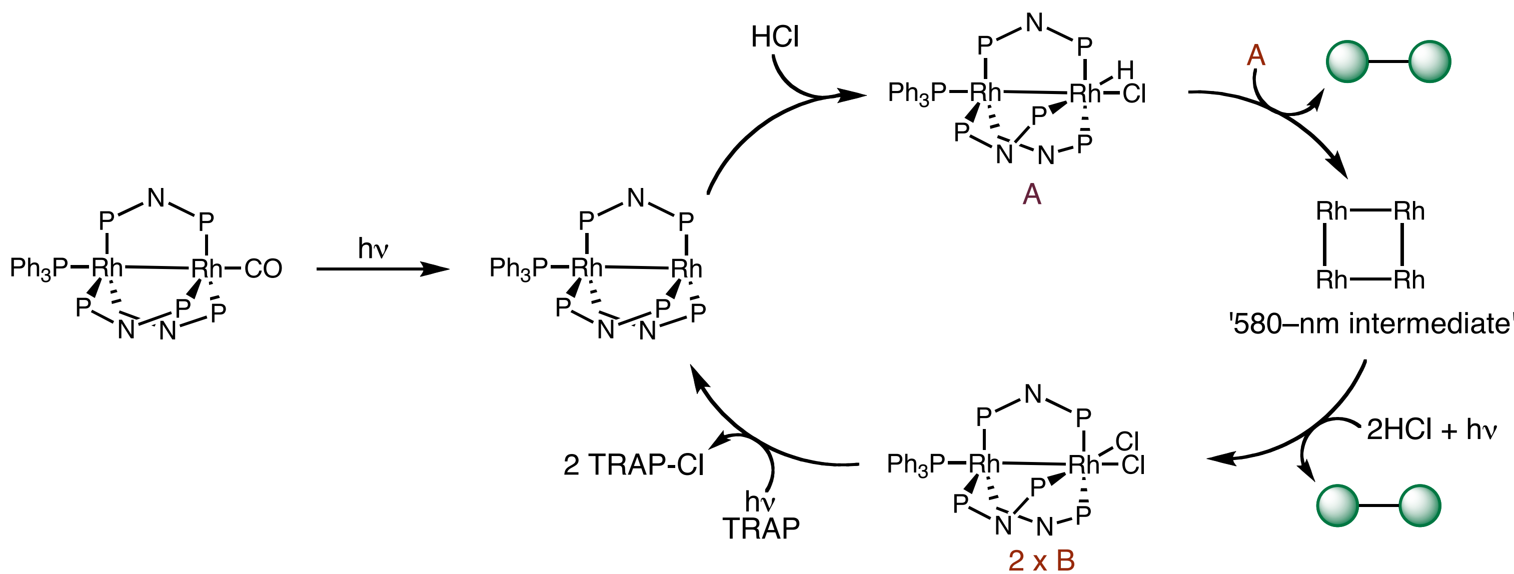
Heyduk, A. F.; Macintosh, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **1999**, *121*, 5023.

Gray, H. B.; Maverick, A. W. *Science*, **1981**, *214*, 1201.

Photocatalytic H_2 Production

■ Complicated, But Possible

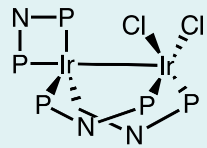




Heyduk, A. F.; Nocera, D. G. *Science*, **2001**, *293*, 1639.

Iridium Analogues

Slightly Altered Ligand



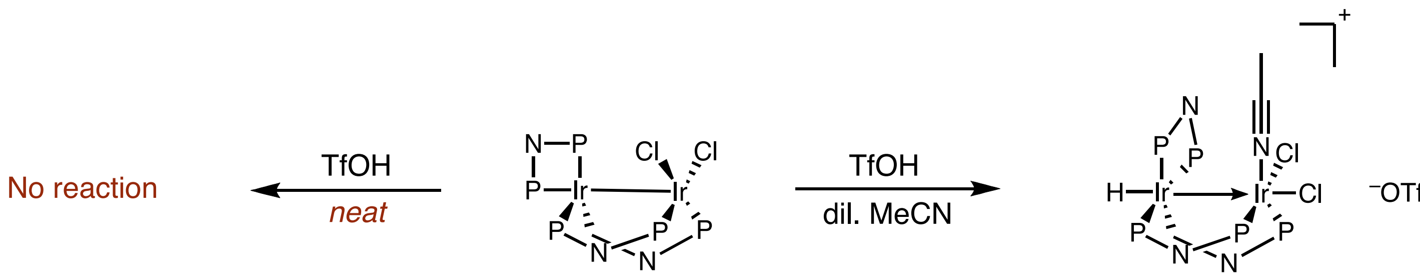
Ir^{0}—Ir^{II}

P = $P(OCH_2CF_3)_2$

Larger group prevents Ir oligmerization

Heyduk, A. F.; Nocera, D. G. *J. Am. Chem. Soc.* **2000**, *122*, 9415.

Incredible Protonation Characteristics

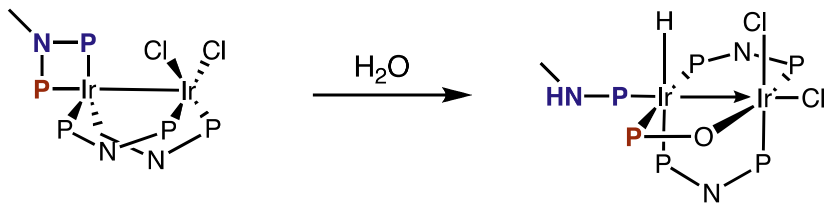


Ir^{0}—Ir^{II}

Ir^{I}—Ir^{III}

Water Splitting at Ir

■ Reaction With H_2O To Deliver Ir–H



Ir^{0}—Ir^{II} Ir^{I}—Ir^{III}

Free ligand stable to H_2O

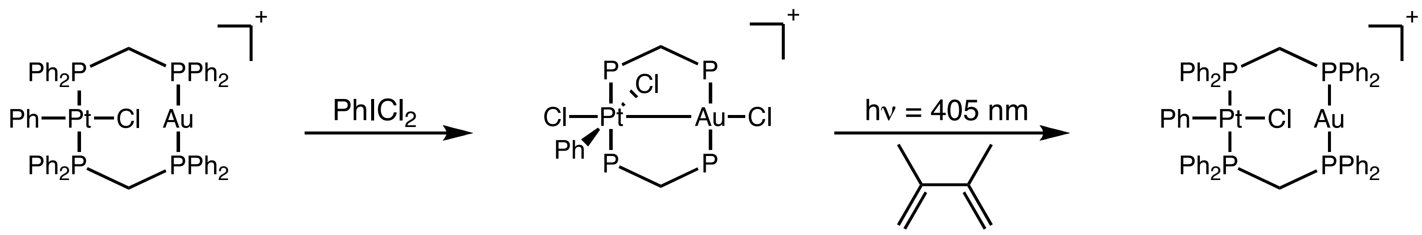
Ir complex stable to TfOH

Veige, A. S.; Nocera, D. G. *Chem. Comm.* **2004**, 1958.

Could advantages of separate metals (e.g. Rh and Ir) be combined into a single catalyst?

Pt–Au Bimetallics

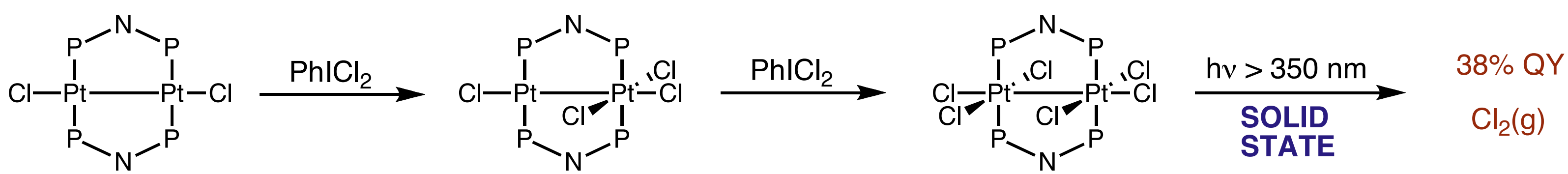
Increased Halogen Elimination at Au



Pt^{II}—Au^{I} Pt^{III}—Au^{II} 10x Increased Quantum Yield (6%)

Cook, T. R.; Esswein, A. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 10094.

Trap–Free Hydrogen Production

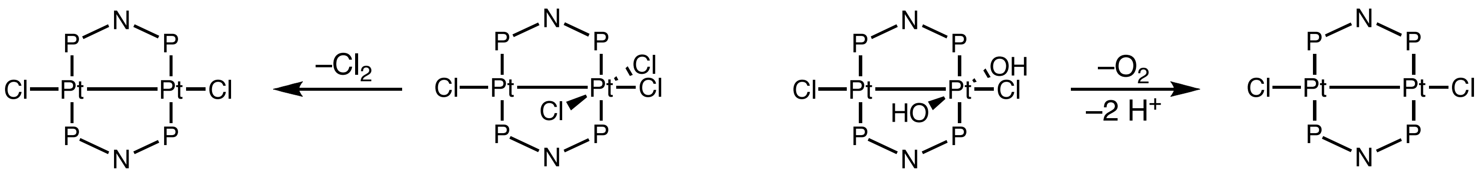


Pt^{I}—Pt^{I} Pt^{I}—Pt^{III} Pt^{III}—Pt^{III}

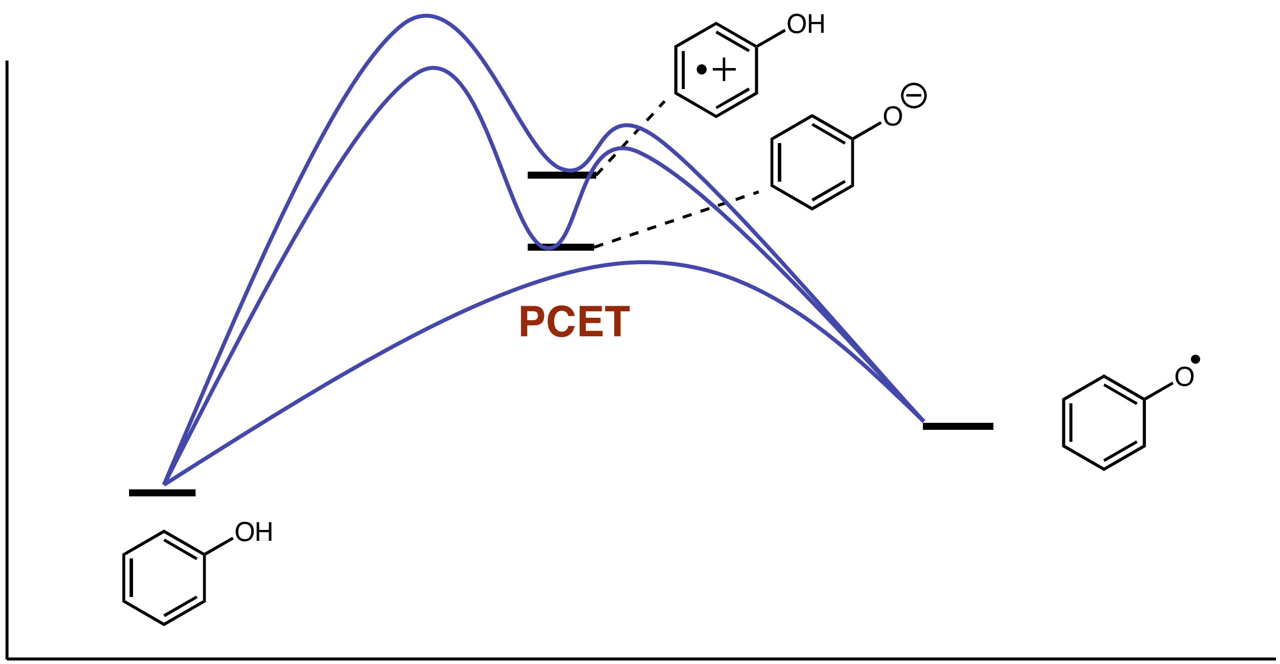
Cook, T. R.; Surendranath, Y.; Nocera, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 28.

X_2 vs O_2 Elimination

- Halogen Elimination Couples No Protons

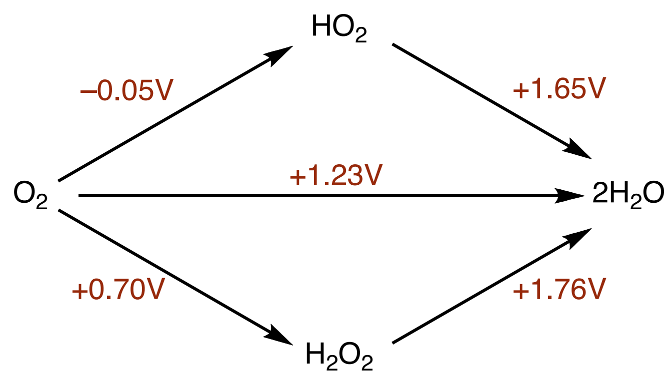


- PCET Often Lowest Energy Path



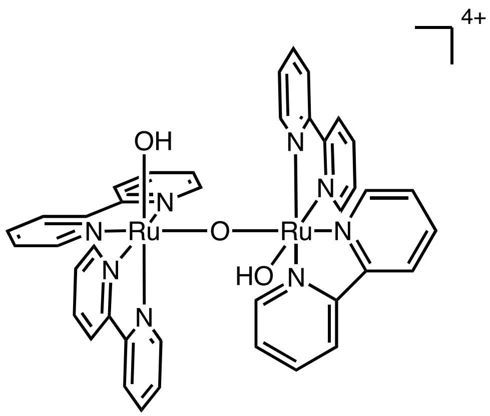
Maximum Power With O_2 Reduction

- Want To Avoid Semi–Reduced Pathways



Collman, J. P.; Wagenknecht, P. S.; Hutchinson, J. E. *Angew. Chem. Int. Ed.* **1994**, *33*, 1537.

- Difficult to Prevent H_2O_2 Release in Solution



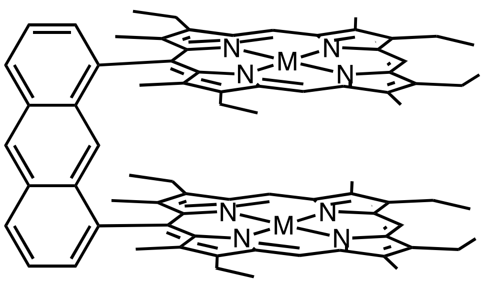
Catalyzed H_2O oxidation by Ce(IV)

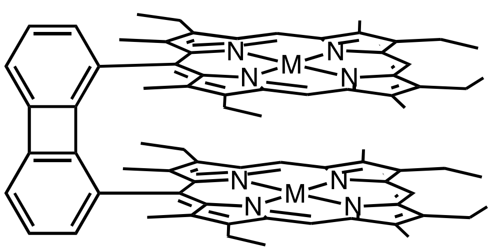
Mechanism unknown

Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029.

Bisporphyrin Electroreduction

- Introduced Late 70s by Collman, Kagan, Ogoshi and Chang



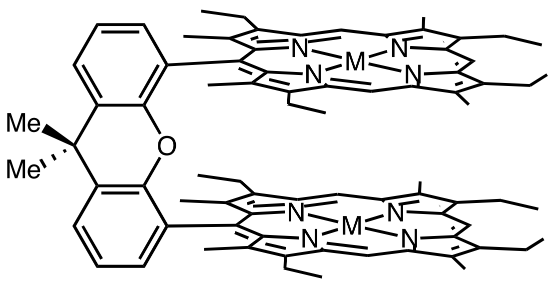


Used as Co complex deposited on C electrode

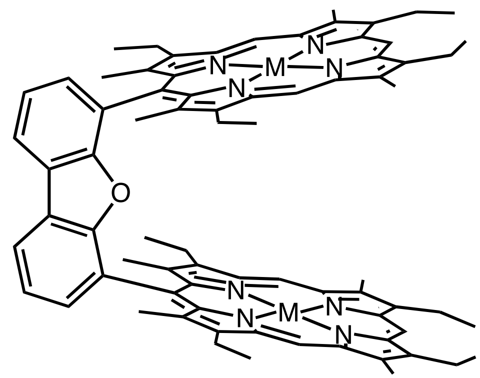
Collman, J. P.; Wagenknecht, P. S.; Hutchinson, J. E. *Angew. Chem. Int. Ed.* **1994**, *33*, 1537.

Expanding Framework

■ Significant Change in Cleft Size



DPX



DPD

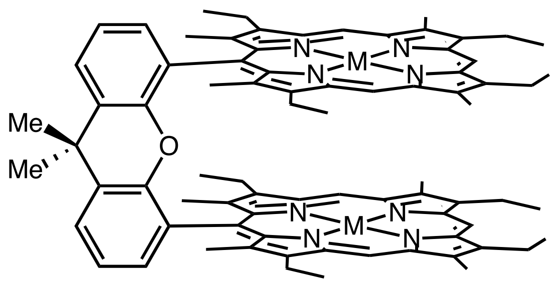
M = (Fe–O–Fe) 3.5Å

M = H_2 >7.5 Å

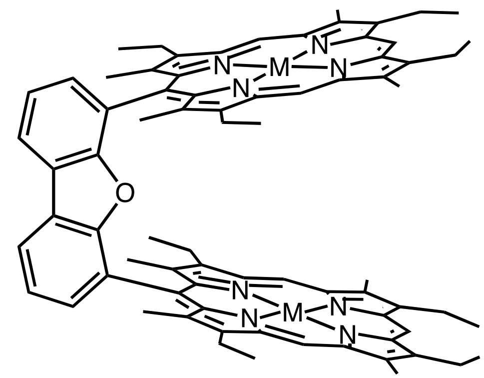
Chang, C. J.; Deng, Y.; Heyduk, A. F.; Chang, C. K.; Nocera, D. G. *Inorg. Chem.* **2000**, *39*, 959.

Expanding Framework

■ Significant Change in Cleft Size



DPX

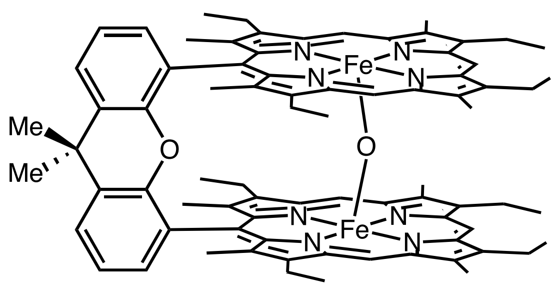


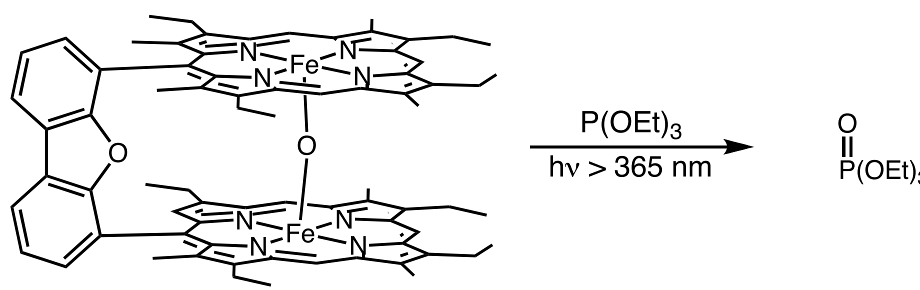
DPD

M = (Fe–O–Fe) 3.5Å

M = H_2 >7.5 Å

Chang, C. J.; Deng, Y.; Heyduk, A. F.; Chang, C. K.; Nocera, D. G. *Inorg. Chem.* **2000**, *39*, 959.



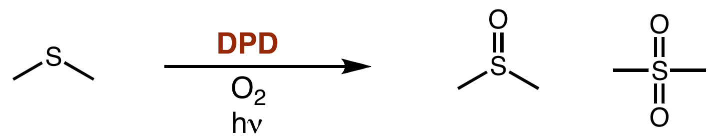


10,000x Greater Rate

Chang, C. J.; Baker, E. A.; Pistorio, B. J.; Deng, Y.; Loh, Z.–H.; Miller, S. E.; Carpenter, S. D.; Nocera, D. G. *Inorg. Chem.* **2002**, *41*, 3102.

'Pacman' Effect

■ Effective in Catalytic Oxidation

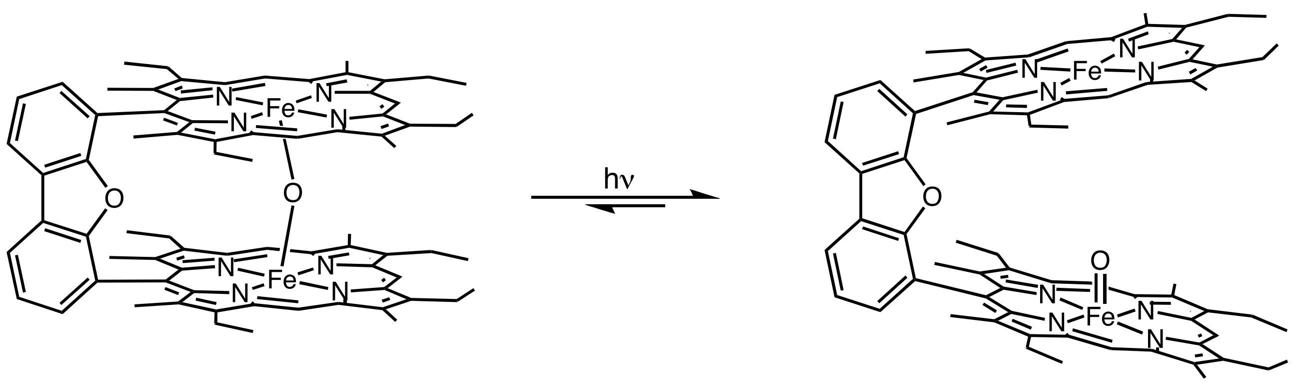


TON = 600

Selectivity 10 : 1

Pistorio, B. J.; Chang, C. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 7884.

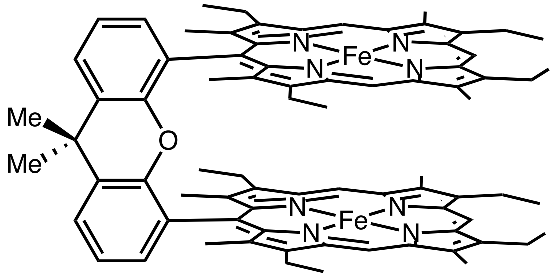
■ Recapture Ability



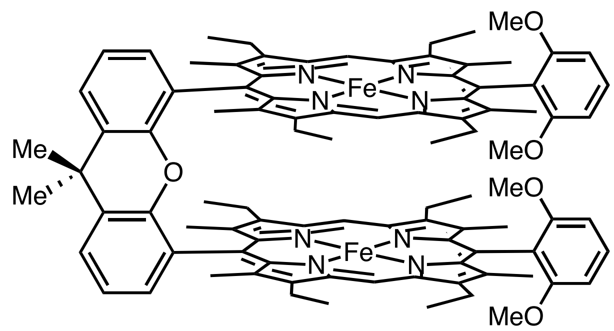
Deng, Y.; Chang, C. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2000**, *122*, 410.

Picosecond Laser Observations

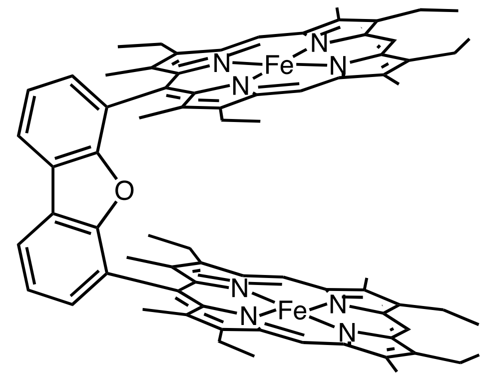
■ Oxyl Liftime ≠ Reactivity



ΔD = 0.208Å
τ = 1.26 ns
RR = 1



ΔD = 2.424Å
τ = 1.27 ns
RR = 100

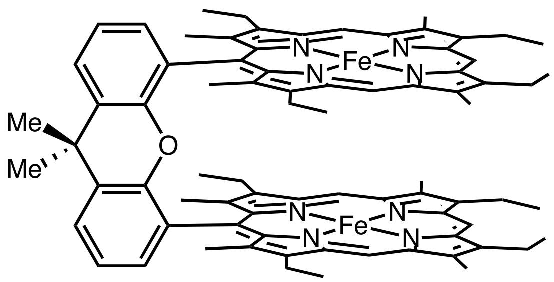


ΔD = 4.271Å
τ = 1.36 ns
RR = 10,000

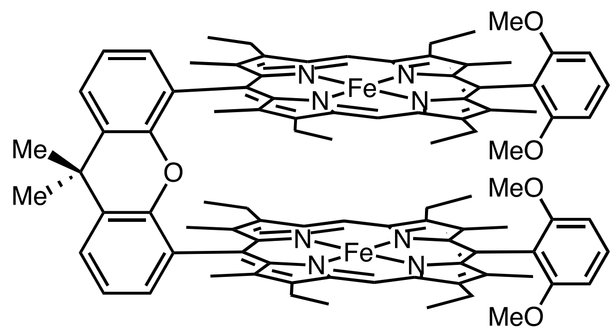
Hodgkiss, J. M.; Chang, C. J.; Pistorio, B. J.; Nocera, D. G. *Inorg. Chem.* **2003**, *42*, 8270.

Picosecond Laser Observations

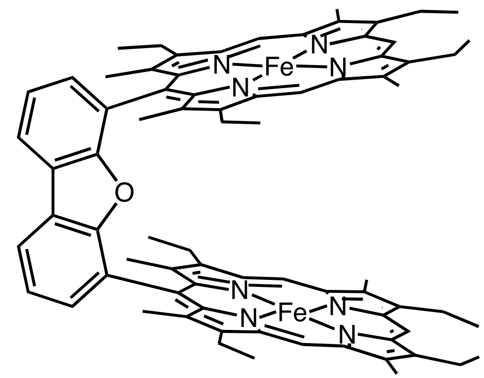
■ Oxyl Liftime ≠ Reactivity



ΔD = 0.208Å
τ = 1.26 ns
RR = 1



ΔD = 2.424Å
τ = 1.27 ns
RR = 100



ΔD = 4.271Å
τ = 1.36 ns
RR = 10,000

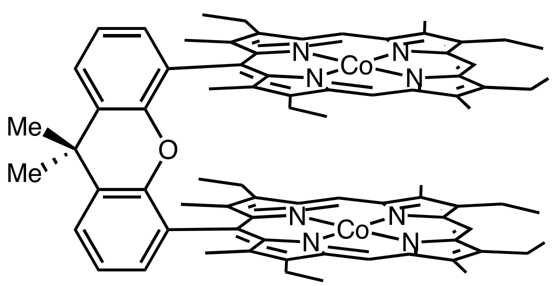
Hodgkiss, J. M.; Chang, C. J.; Pistorio, B. J.; Nocera, D. G. *Inorg. Chem.* **2003**, *42*, 8270.

DOES NOT INCLUDE PROTON TRANFER

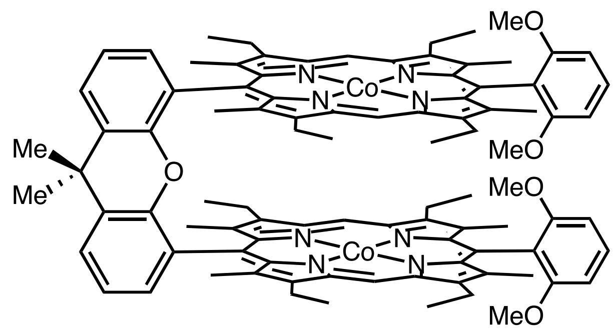
Co–Catalyzed O_2 Reduction

- Reduction at +0.3V (Ag/AgCl)

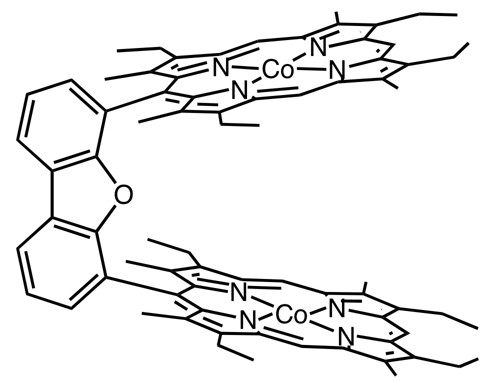
H_2O vs. H_2O_2 Selectivity



Ox = +0.28V



Ox = +0.31V



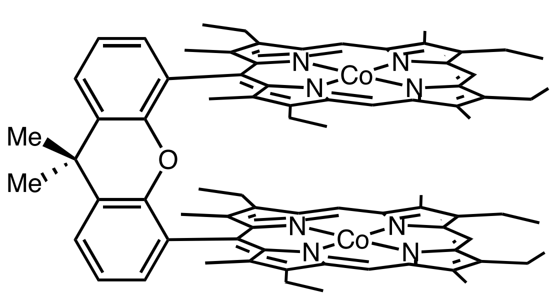
Ox = +0.33V

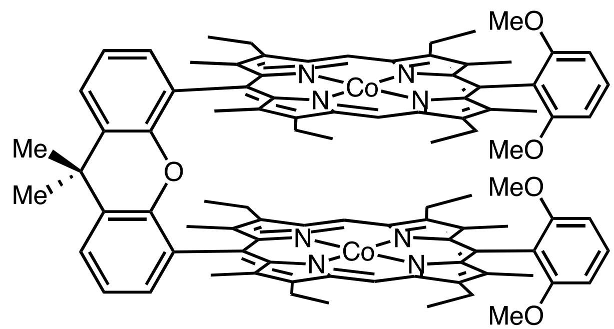
Chang, C. J.; Loh, Z.–H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013.

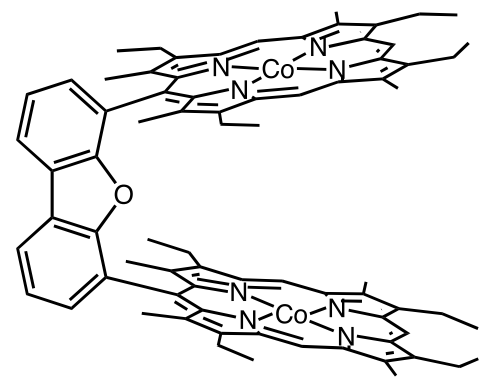
Co–Catalyzed O_2 Reduction

■ Reduction at +0.3V (Ag/AgCl)

H_2O vs. H_2O_2 Selectivity







Ox = +0.28V
% H_2O = 72

Ox = +0.31V
% H_2O = 52

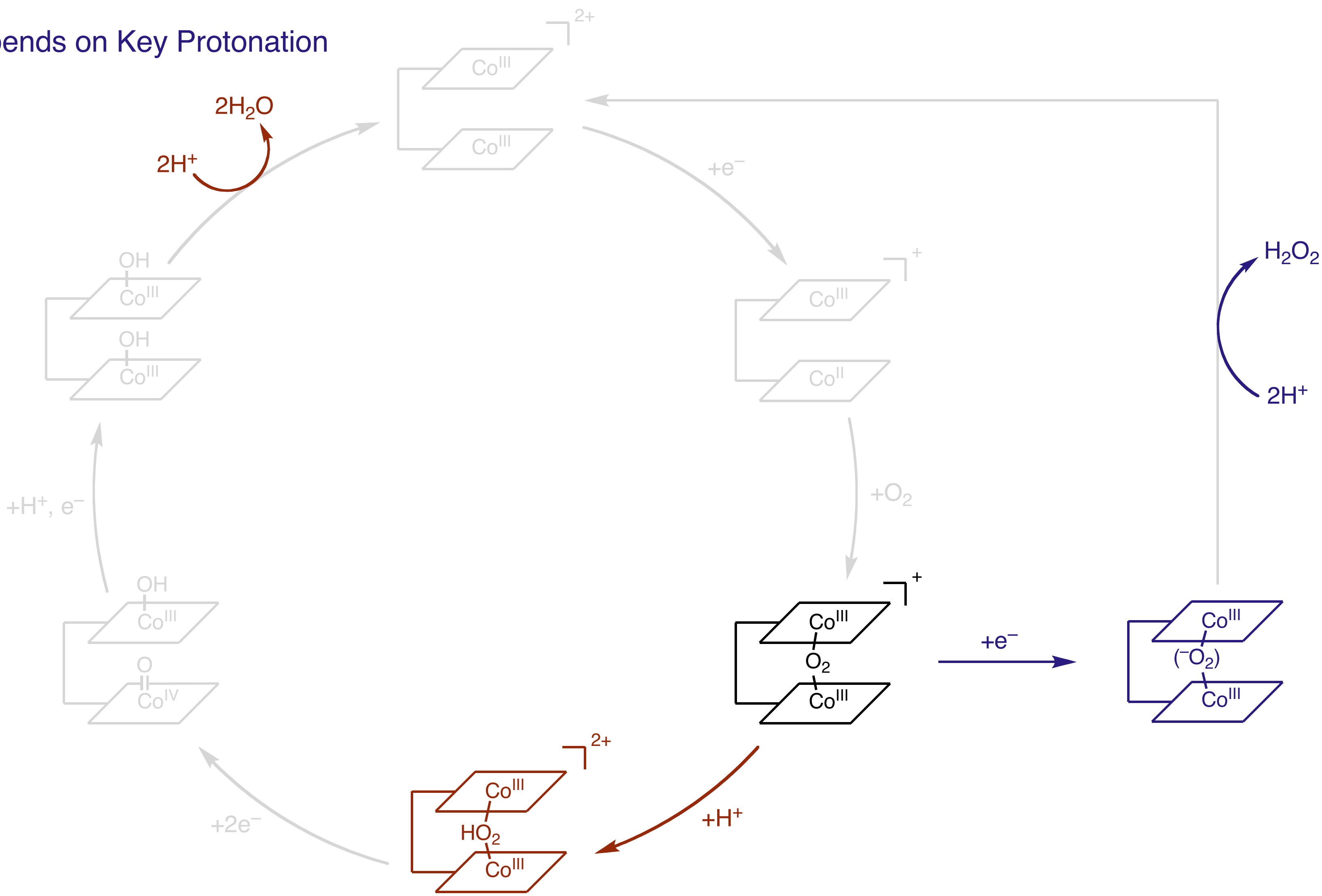
Ox = +0.33V
% H_2O = 80

KEY IS BALANCING PROTON INVENTORY

Chang, C. J.; Loh, Z.–H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013.

Product Selectivity

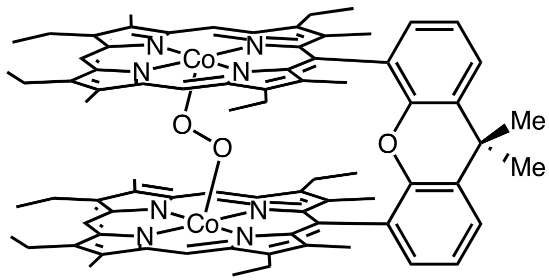
■ Depends on Key Protonation



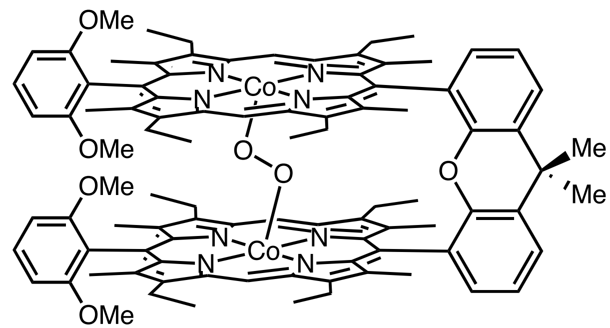
Chang, C. J.; Loh, Z.–H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013.

DFT Calculations

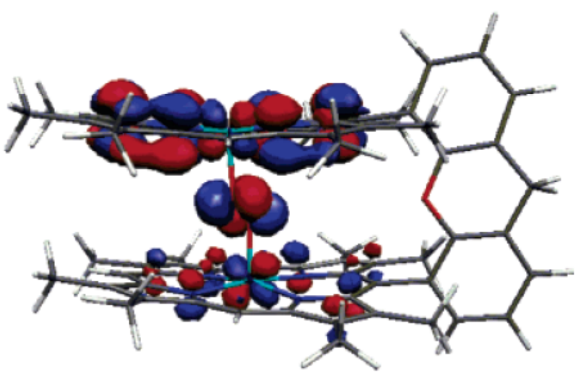
■ Stunning Difference

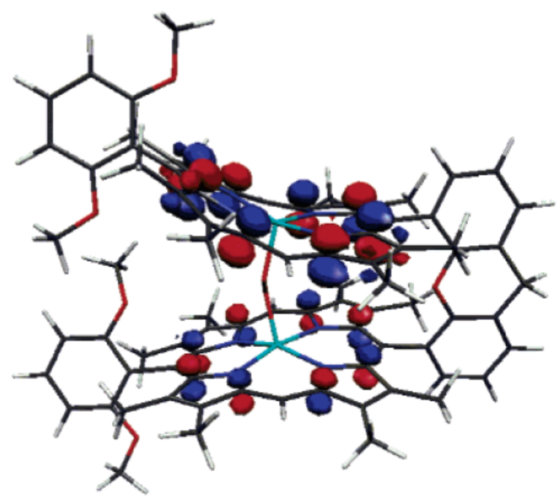


Ox = +0.28V
% H_2O = 72



Ox = +0.31V
% H_2O = 52

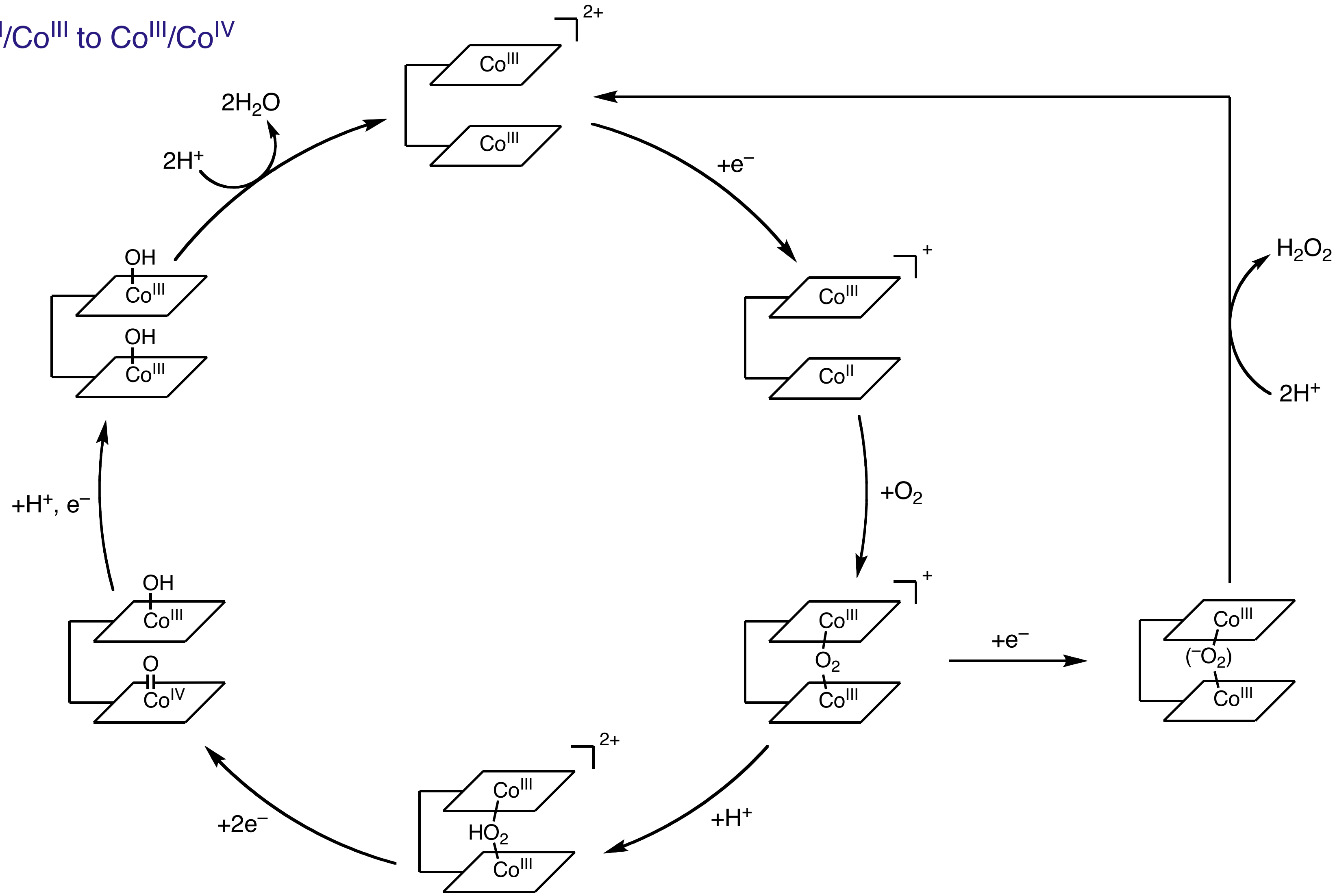




Chang, C. J.; Loh, Z.–H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013.

Co-Reduction Cycle

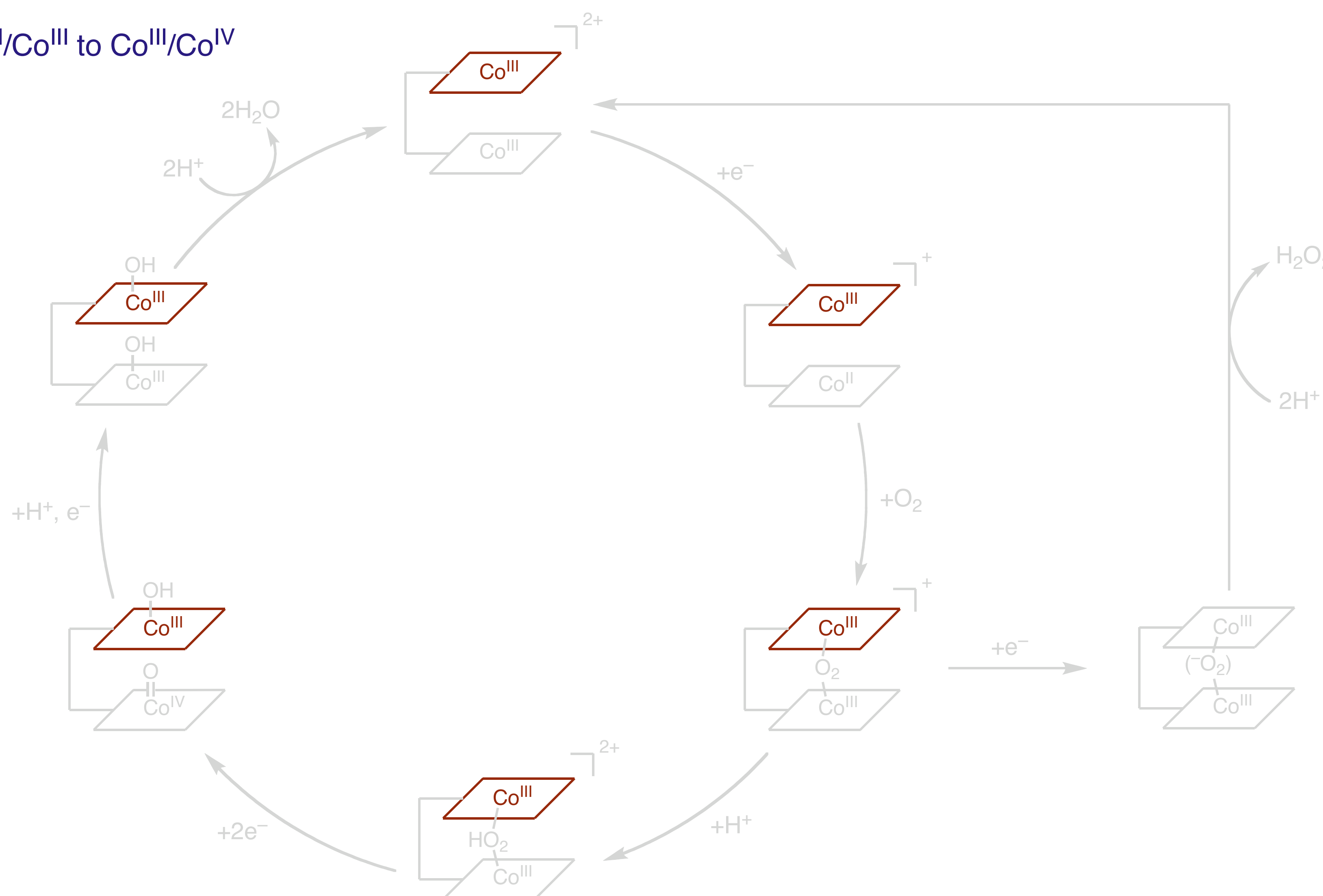
■ Co^{II}/Co^{III} to Co^{III}/Co^{IV}



Chang, C. J.; Loh, Z.–H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013.

Co-Reduction Cycle

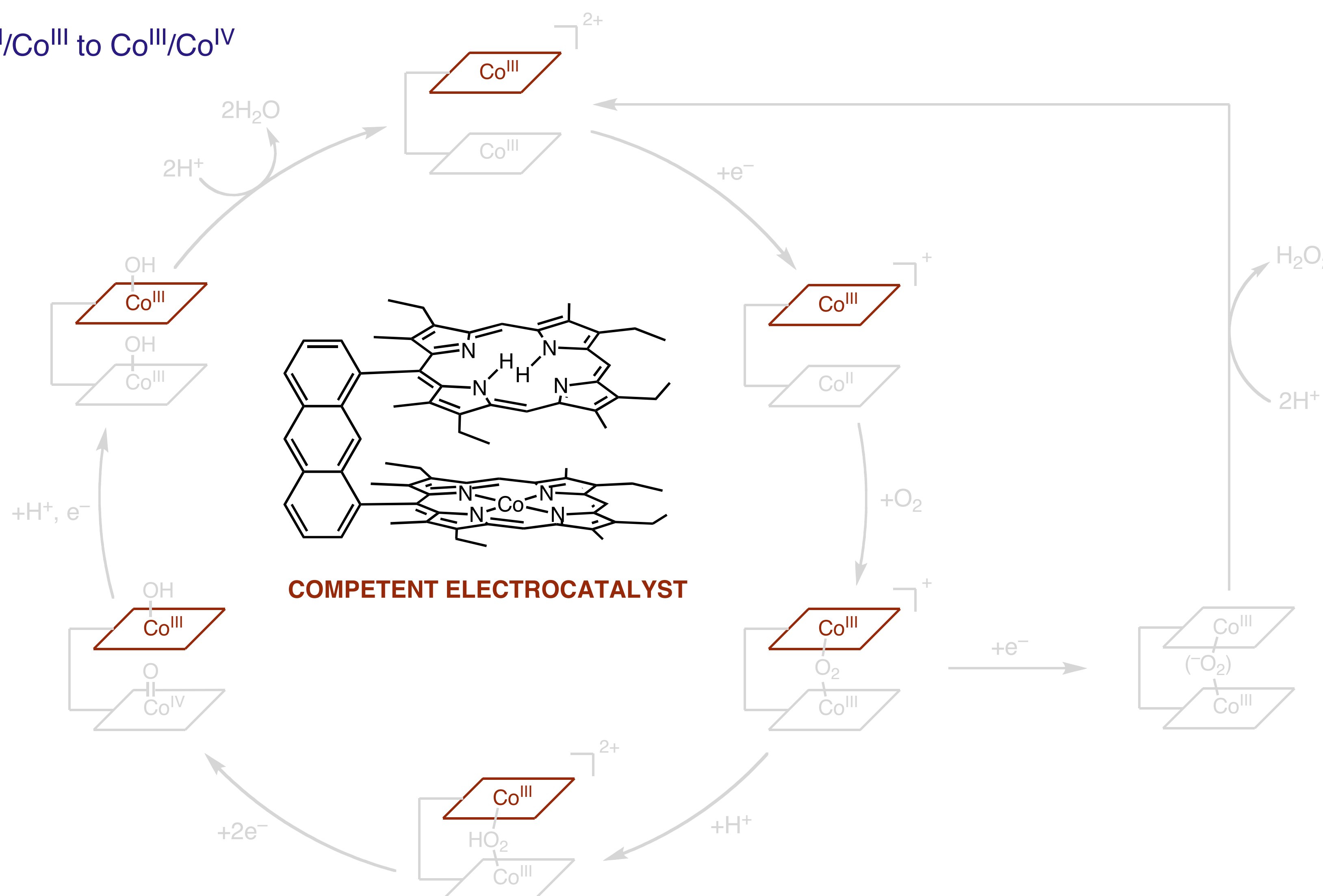
■ Co^{II}/Co^{III} to Co^{III}/Co^{IV}



Chang, C. J.; Loh, Z.–H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013.

Co-Reduction Cycle

■ Co^{II}/Co^{III} to Co^{III}/Co^{IV}



Chang, C. J.; Loh, Z.–H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013.

Second Pillar Site

- Why Two Cobalt Porphyrins?

Induce protonation of bound superoxide

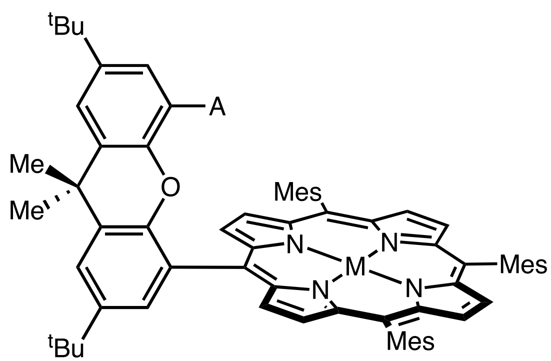
Chng, L. L.; Chang, C. J.; Nocera, D. G. *Org. Lett.* **2003**, *5*, 2421.

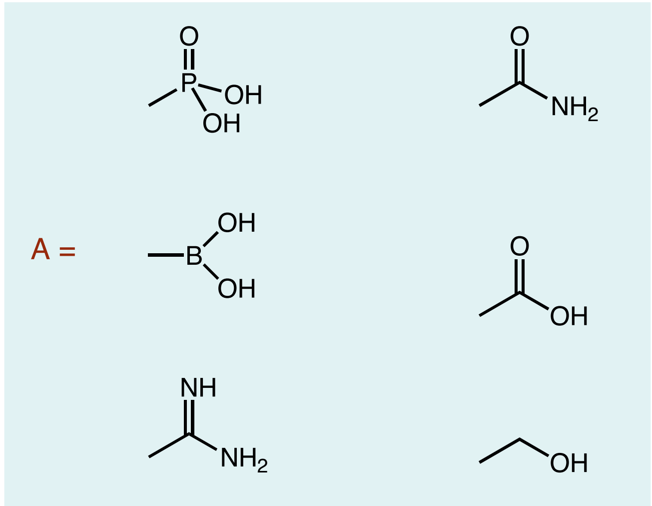
Second Pillar Site

- Why Two Cobalt Porphyrins?

Induce protonation of bound superoxide

- Hangman Architecture

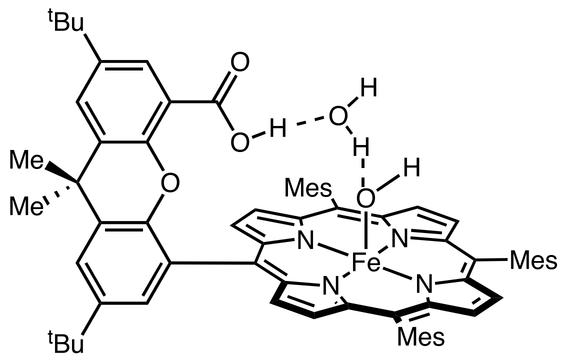




Chng, L. L.; Chang, C. J.; Nocera, D. G. *Org. Lett.* **2003**, *5*, 2421.

Water–Bound

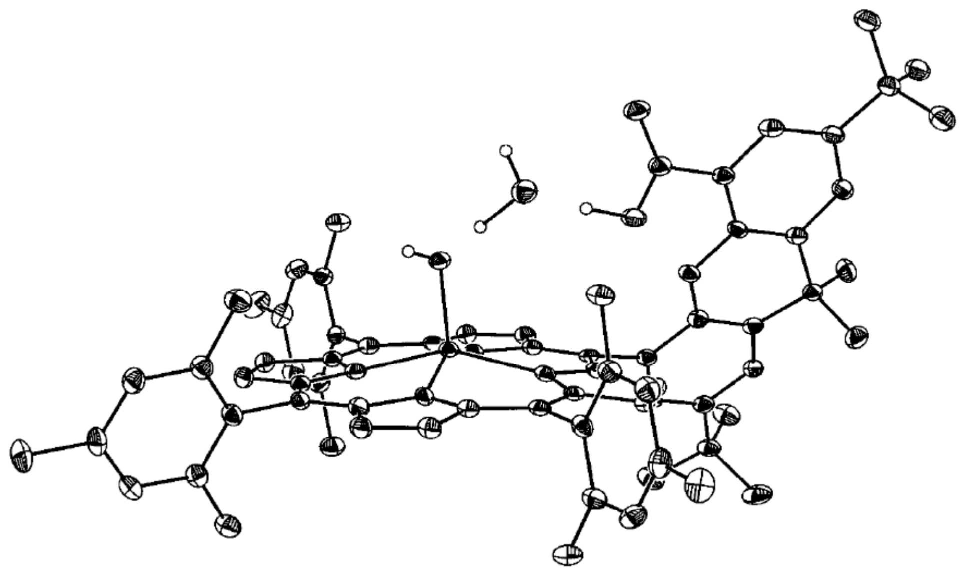
■ A Crystal Structure Surprise



Crystallographically resolved water

Maintained in solution

Binding energy ~6 kcal

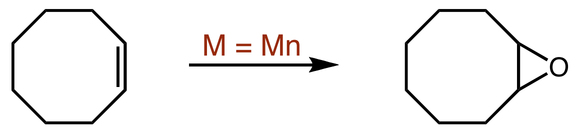


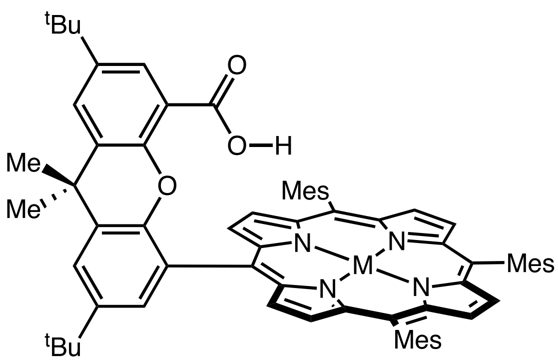
Yeh, C.–Y.; Chang, C. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 1513.

Exceptional Activity

■ Highly Active Catalyse and Epoxidation Activity

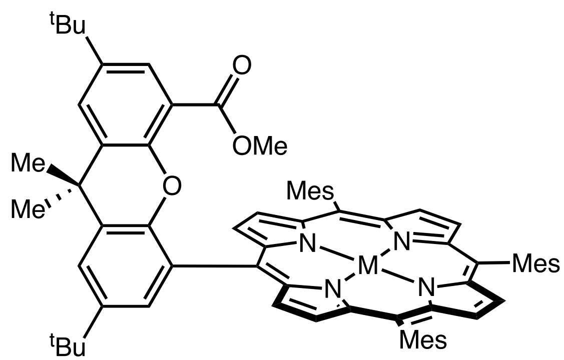
$$2H_2O_2 \xrightarrow{M = Fe} O_2 + H_2O$$





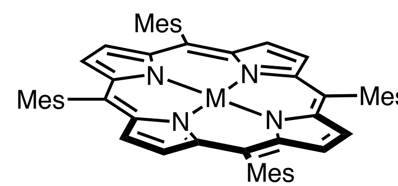
Fe TON = 436

Mn TON = 460



Fe TON = 48

Mn TON = 210



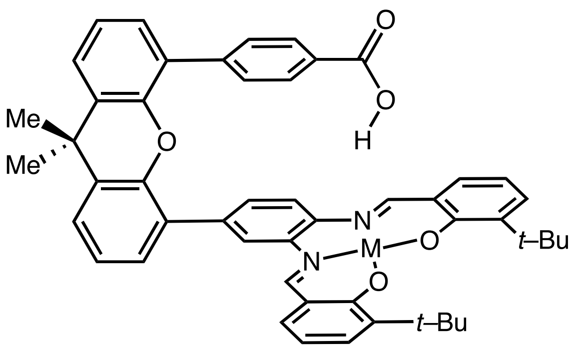
Fe TON = 4

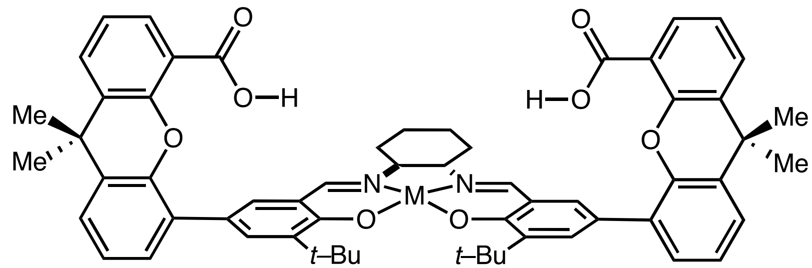
Mn TON = 45

Chang, C. J.; Chng, L. L.; Nocera, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 1866.

Salen Hangman

■ Simpler Synthesis





Large increase in synthetic simplicity

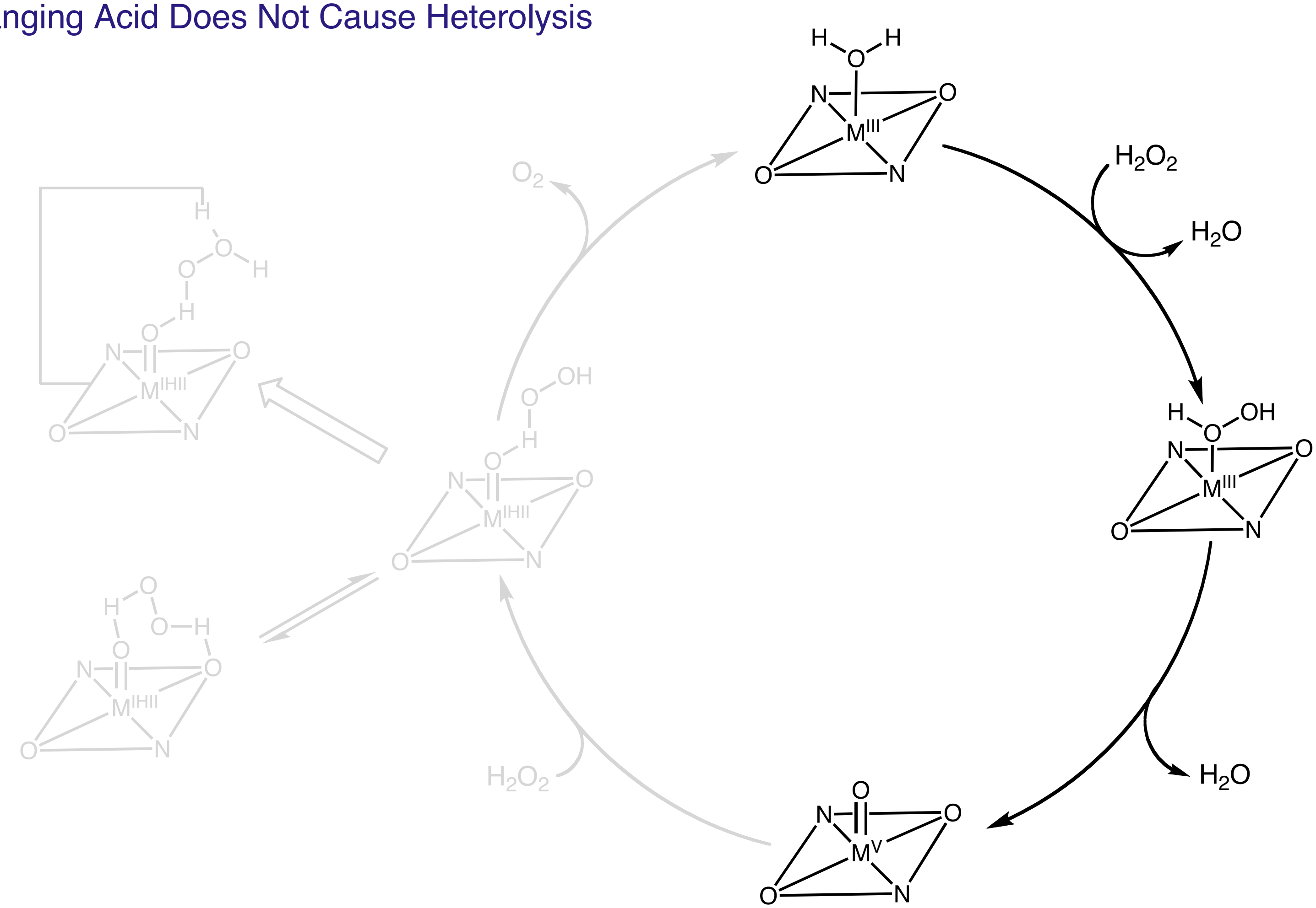
Small increase in TON

Liu, S.–Y.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 5278.

Yang, J. Y.; Bachmann, J.; Nocera, D. G. *J. Org. Chem.* **2006**, *71*, 8706.

Another Mechanistic Twist

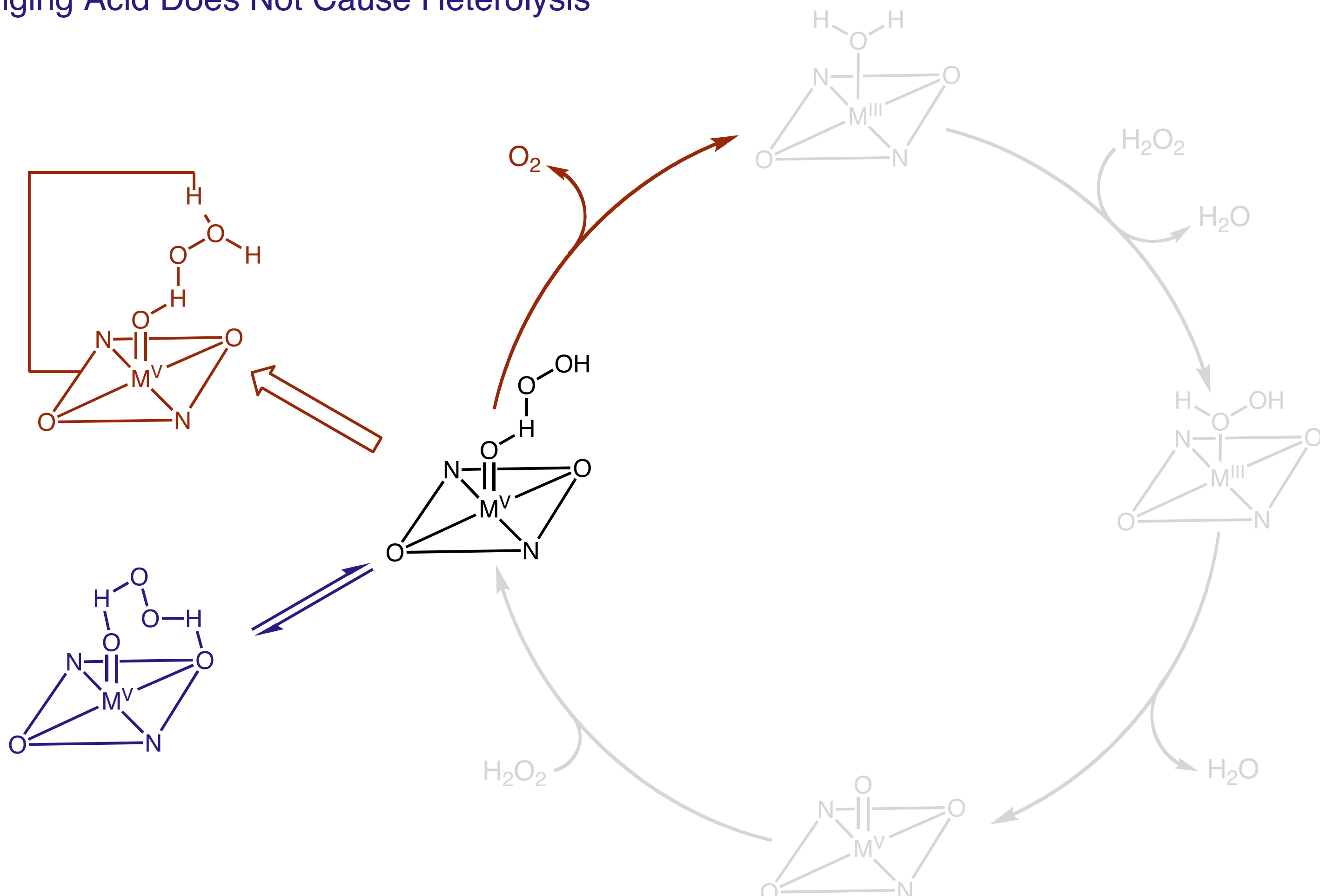
- Hanging Acid Does Not Cause Heterolysis



Liu, S.-Y.; Soper, J. D.; Yang, J. Y.; Rybak–Akimova, E. V.; Nocera, D. G. *Inorg. Chem.* **2006**, *45*, 7572.

Another Mechanistic Twist

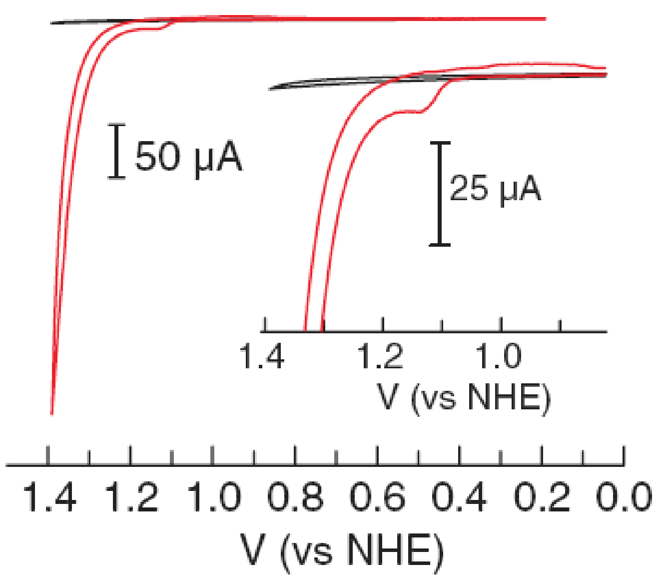
■ Hanging Acid Does Not Cause Heterolysis

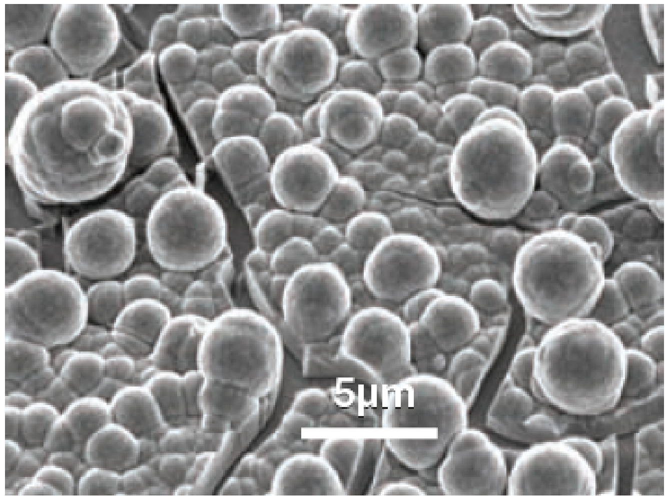


Liu, S.-Y.; Soper, J. D.; Yang, J. Y.; Rybak–Akimova, E. V.; Nocera, D. G. *Inorg. Chem.* **2006**, *45*, 7572.

- Co–Coated Electrodes

"Here we report such a catalyst that forms upon oxidative polarization. . .in phosphate buffered water containing Co(II)"





Kanan, M. W.; Nocera, D. G. *Science*, **2008**, *321*, 1072.

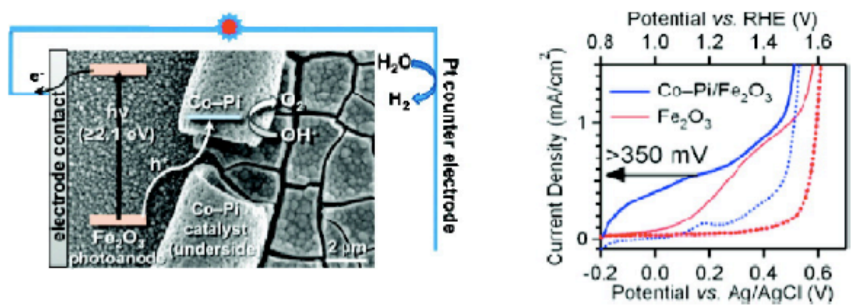
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Solar Water Oxidation by Composite Catalyst/#-FeO Photoanodes

Diane K. Zhong, Jianwei Sun, Hiroki Inumaru, and Daniel R. Gamelin

J. Am. Chem. Soc., **Article ASAP** • DOI: 10.1021/ja9016478 • Publication Date (Web): 08 April 2009



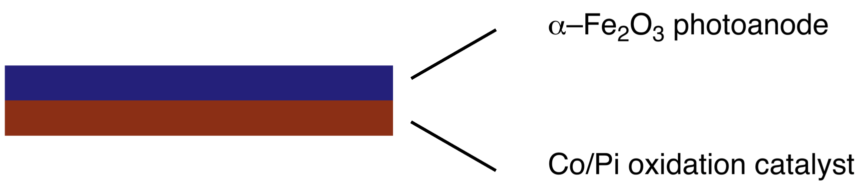
α–Fe_2O_3 Photoanodes

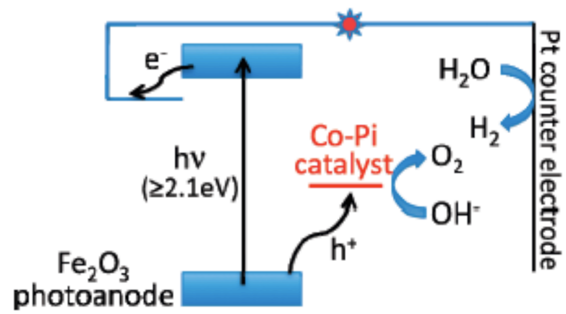
- Hematite is cheap, available, oxidatively stable
- Absorbs visible light to generate 2.1eV hole/charge combination (>1V overpotential for water oxidation)
- Kinetically, can't oxidize water very well

Zhong, D. K.; Sun, J.; Inumaru, H.; Gamelin, D. R. *J. Am. Chem. Soc.* **2009**, ASAP.

α–Fe_2O_3 Photoanodes

- Hematite is cheap, available, oxidatively stable
- Absorbs visible light to generate 2.1eV hole/charge combination (>1V overpotential for water oxidation)
- Kinetically, can't oxidize water very well

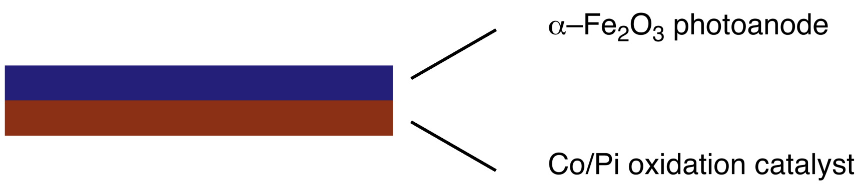


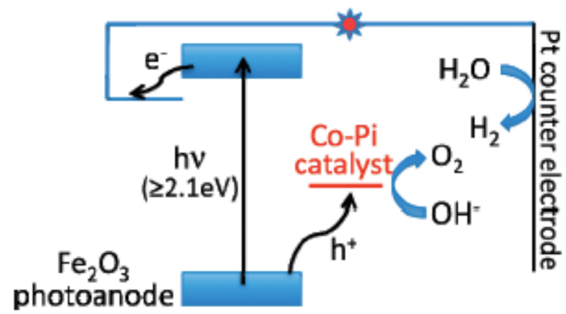


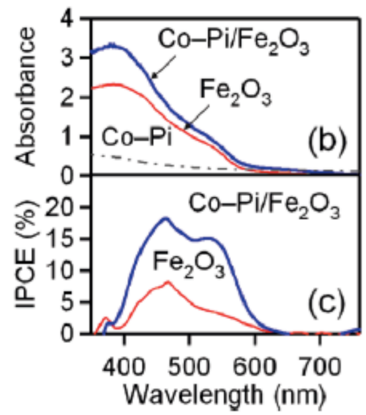
Zhong, D. K.; Sun, J.; Inumaru, H.; Gamelin, D. R. *J. Am. Chem. Soc.* **2009**, ASAP.

α–Fe_2O_3 Photoanodes

- Hematite is cheap, available, oxidatively stable
- Absorbs visible light to generate 2.1eV hole/charge combination (>1V overpotential for water oxidation)
- Kinetically, can't oxidize water very well







Zhong, D. K.; Sun, J.; Inumaru, H.; Gamelin, D. R. *J. Am. Chem. Soc.* **2009**, ASAP.