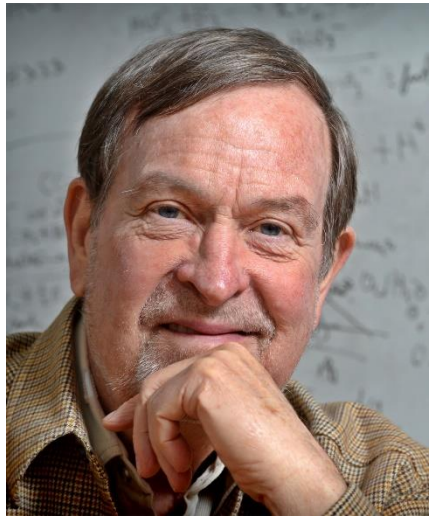


Thomas J. Meyer

CAREER RETROSPECTIVE

LEVIN GROUP MEETING 4/16/20

PATRICK KELLY

Career Summary

1963-1966 – PhD Stanford University (Henry Taube)

1967 – NATO Postdoctoral fellowship University College, London

1968 – Joined faculty at University of North Carolina

1972 – Promoted to Associate Professor

1975 – Promoted to Full Professor

1982 – Smith Professor

1985 – Kenan Professor

1994-1996 – Dean of the Graduate School UNC

2000-2004 – Los Alamos National Lab

2005-present – Arey Distinguished Professor of Chemistry, UNC

As of 2016 – 756 publications, 6 patents

Selected Awards

Alfred P. Sloan Fellow (1975-1977)

Medal of Merit Award, Ohio University Alumni Association, Ohio University (1988)

Dwyer Medalist, University of New South Wales, Australia (1989)

ACS Award in Inorganic Chemistry (1990)

Centenary Medalist, Royal Society of Chemistry (1991)

Southern Chemist of the Year Award, Memphis Section of ACS (1992)

American Academy of Arts and Sciences, Cambridge, Massachusetts (1994)

National Academy of Sciences, Washington, DC (1994)

Nyholm Award, Royal Australian Chemical Institute, Inorganic Division (1996)

Inter-American Photochemical Society Award in Photochemistry (1997)

Basolo Medalist, Northwestern Universtiy (1999)

ACS Award for Distinguished Service to Inorganic Chemistry (2002)

Research Triangle Institute President's Award (2008)

ACS Voices of Inorganic Chemistry Feature (2001)

Special Symposium to Honor Professor Thomas Meyer; Manipulating Energy and Electron Transfer in Molecules and Devices. Fall 2016 ACS National Meeting August 21-25, Philadelphia, PA

Electrochemistry 101: Basics

$\Delta G = -nFE_{cell}$

E_{cell} = cell potential in volts

$E_{cell} > 0$ means $\Delta G < 0$

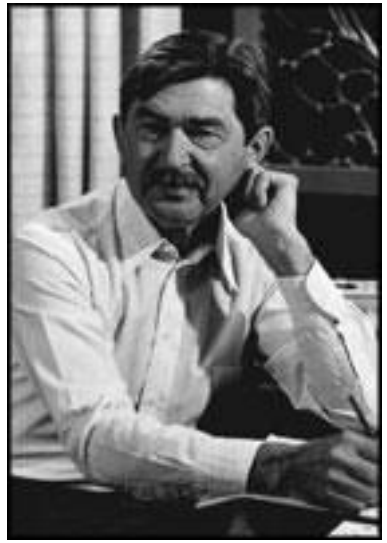
For a 1 electron transfer:

- 1 V => 2.3 kcal/mol
- 0.1 V => 0.23 kcal/mol

Graduate Work

Electron Transfer reactions of Ruthenium Amines

Couple	μ	$-E_{measd}$,[b] V	ΔE,[c] V	$-E$,[d,e] V	$-E°$, V[f]
$Ru(NH_3)_6^{2+,3+}$	0.21	0.088	0.015	0.073	0.10 ± 0.01
$Ru(NH_3)_6^{2+,3+}$	0.061	0.092	0.012	0.080	...
$Ru(NH_3)_6^{2+,3+}$	0.011	0.099	0.009	0.090	...
$Ru(en)_3^{2+,3+}$	0.21	0.187	0.015	0.172	0.21 ± 0.01
$Ru(en)_3^{2+,3+}$	0.061	0.196	0.012	0.184	...
$Ru(en)_3^{2+,3+}$	0.011	0.206	0.009	0.197	...
$Ru(NH_3)_5OH_2^{2+,3+}$	0.011	0.16	0.01	0.15 ± 0.01	0.16



Henry Taube

$$[Ru(NH_3)_6]^{2+} + [Ru(ND_3)_6]^{3+} \underset{\text{faster}}{\rightleftharpoons} [Ru(NH_3)_6]^{3+} + [Ru(ND_3)_6]^{2+}$$

$$[Ru(en_3)_6]^{2+} + [Ru(enD)_6]^{3+} \underset{\text{slower}}{\rightleftharpoons} [Ru(en_3)_6]^{3+} + [Ru(enD)_6]^{2+}$$

Both are outer sphere electron transfer!

Inorg. Chem. 1968, 7, 11, 2369-2379

Electrochemistry 201: Mechanism

$\Delta G = -nFE_{cell}$

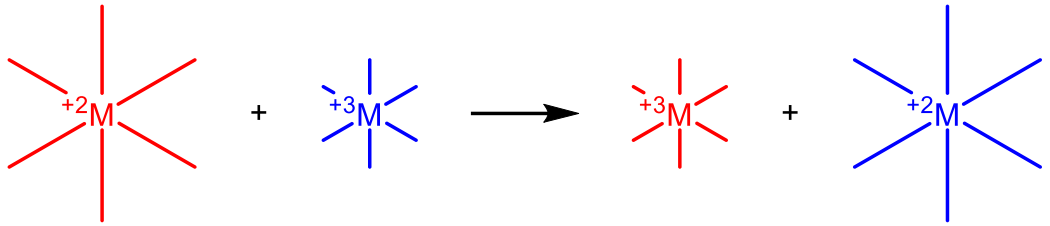
E_{cell} = cell potential in volts

$E_{cell} > 0$ means $\Delta G < 0$

For a 1 electron transfer:

- 1 V => 2.3 kcal/mol
- 0.1 V => 0.23 kcal/mol

Reorganization



Outer Sphere Electron Transfer

$Fe^{II}(CN)_6^{4-} + Mo^{V}(CN)_8^{3-} \longrightarrow Fe^{III}(CN)_6^{3-} + Mo^{IV}(CN)_8^{4-}$

No bonds made or formed
Penalty is reorganization

Inner Sphere Electron Transfer

$(H_3N)_5Co^{III}{-}Cl^{2+} + Cr^{II}(H_2O)_5^{2+} \longrightarrow Co^{II}(NH_3)_5^{2+} + Cl{-}Cr^{III}(H_2O)_5^{2+}$

Bonds broken and formed
More complicated thermodynamics

Graduate Work

Electron Transfer reactions of Ruthenium Amines

Couple	μ	$-E_{measd}$,[b] V	ΔE,[c] V	$-E$,[d,e] V	$-E^\circ$, V[f]
$Ru(NH_3)_6^{2+,3+}$	0.21	0.088	0.015	0.073	0.10 ± 0.01
$Ru(NH_3)_6^{2+,3+}$	0.061	0.092	0.012	0.080	...
$Ru(NH_3)_6^{2+,3+}$	0.011	0.099	0.009	0.090	...
$Ru(en)_3^{2+,3+}$	0.21	0.187	0.015	0.172	0.21 ± 0.01
$Ru(en)_3^{2+,3+}$	0.061	0.196	0.012	0.184	...
$Ru(en)_3^{2+,3+}$	0.011	0.206	0.009	0.197	...
$Ru(NH_3)_5OH_2^{2+,3+}$	0.011	0.16	0.01	0.15 ± 0.01	0.16

$[Ru(NH_3)_6]^{2+} \xrightarrow{Fe^{3+}} [Ru(NH_3)_6]^{3+}$

$[Ru(NH_3)_6]^{2+} \xrightarrow{[Fe(OH)]^{2+}}$ 6x less reactive! $[Ru(NH_3)_6]^{3+}$

$[Ru(NH_3)_5(H_2O)]^{2+} \xrightarrow{Fe^{3+}} [Ru(NH_3)_6(H_2O)]^{3+}$

$[Ru(NH_3)_5(H_2O)]^{2+} \xrightarrow{[Fe(OH)]^{2+}}$ 6x more reactive! $[Ru(NH_3)_6(H_2O)]^{3+}$

k_{H2O}/k_{D2O} = ~36

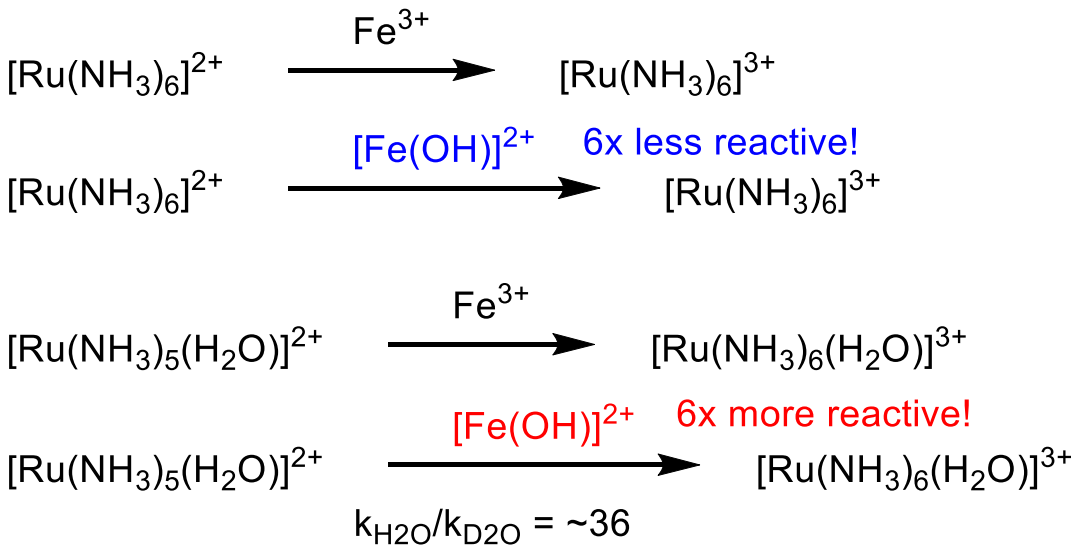
$[Ru(NH_3)_6]^{2+} + [Ru(ND_3)_6]^{3+} \underset{\text{faster}}{\rightleftharpoons} [Ru(NH_3)_6]^{3+} + [Ru(ND_3)_6]^{2+}$

$[Ru(en_3)_6]^{2+} + [Ru(enD)_6]^{3+} \underset{\text{slower}}{\rightleftharpoons} [Ru(en_3)_6]^{3+} + [Ru(enD)_6]^{2+}$

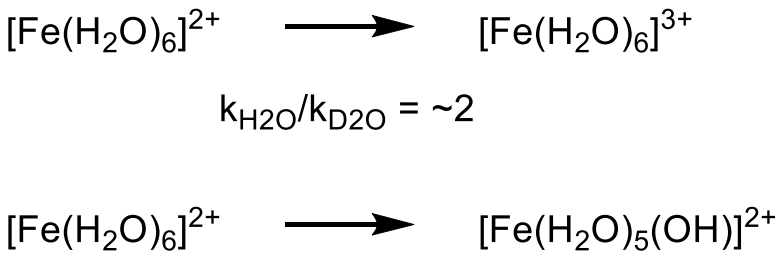
Both are outer sphere electron transfer!

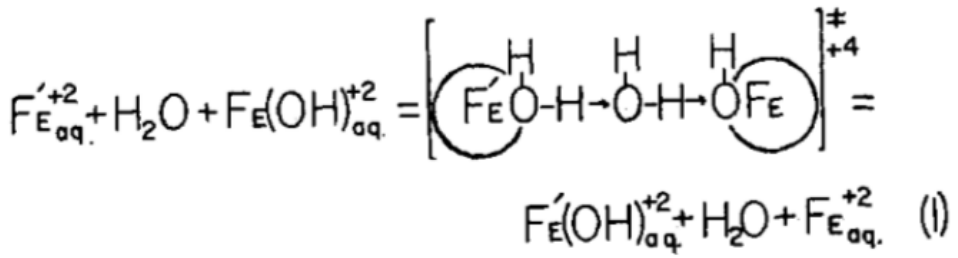
The Beginnings of PCET

Meyer and Taube (1968) - Meyer's graduate work



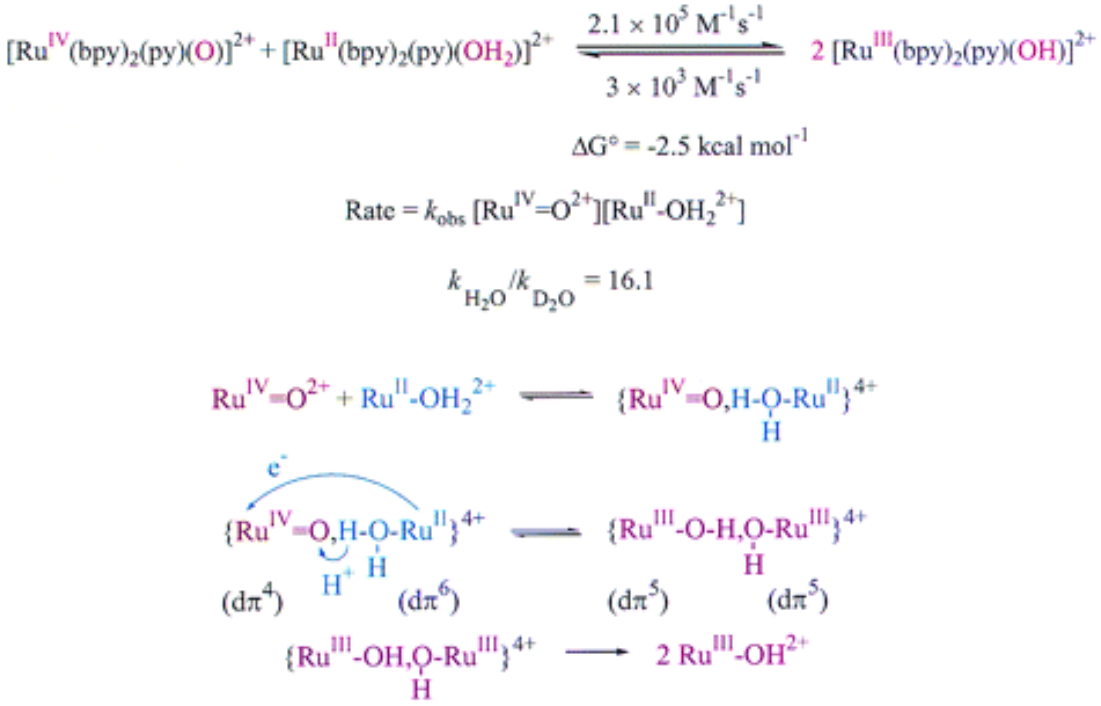
Lumry (1955) and Dodson (1956)

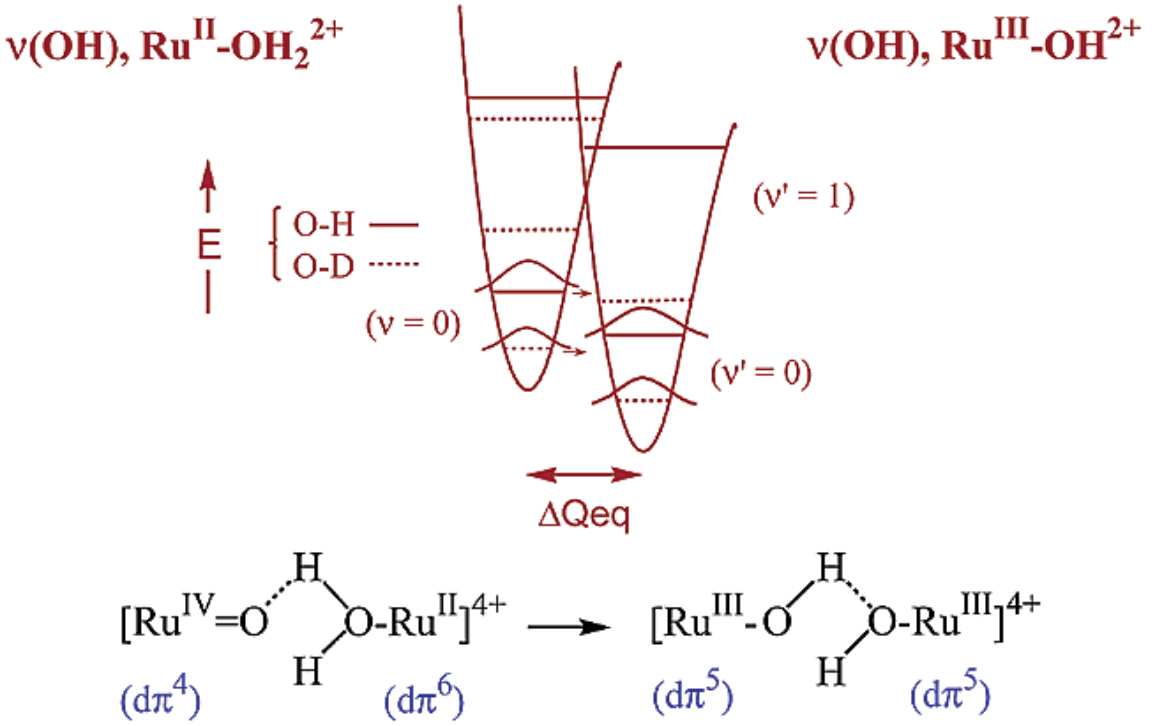




J. Chem. Phys. 1955, 23, 12, 2460
J. Am. Chem. Soc. 1956, 78, 5, 911-913
Inorg. Chem. 1968, 7, 11, 2369-2379
J. Am. Chem. Soc. 1981, 103, 10, 2897-2899

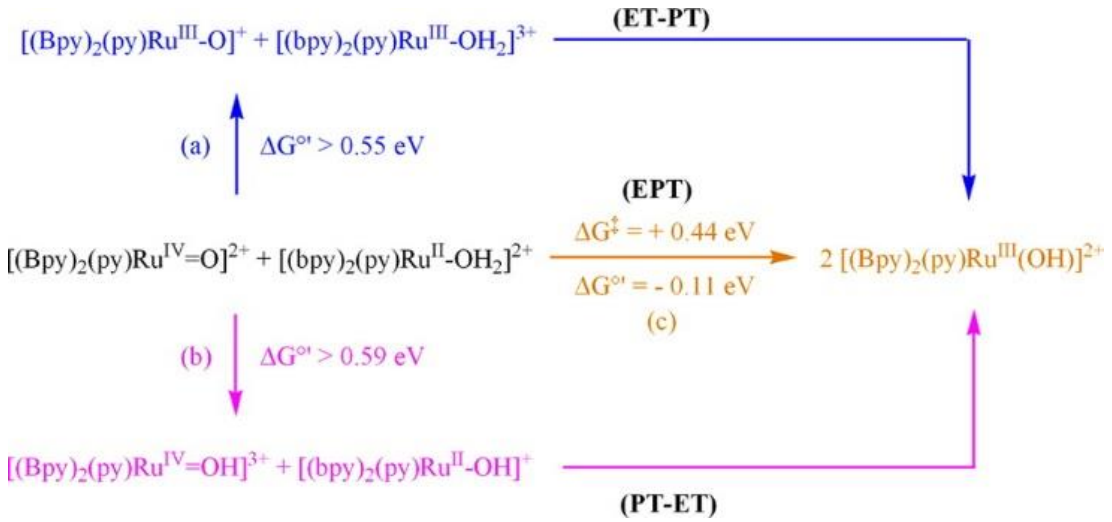
The first characterized PCET

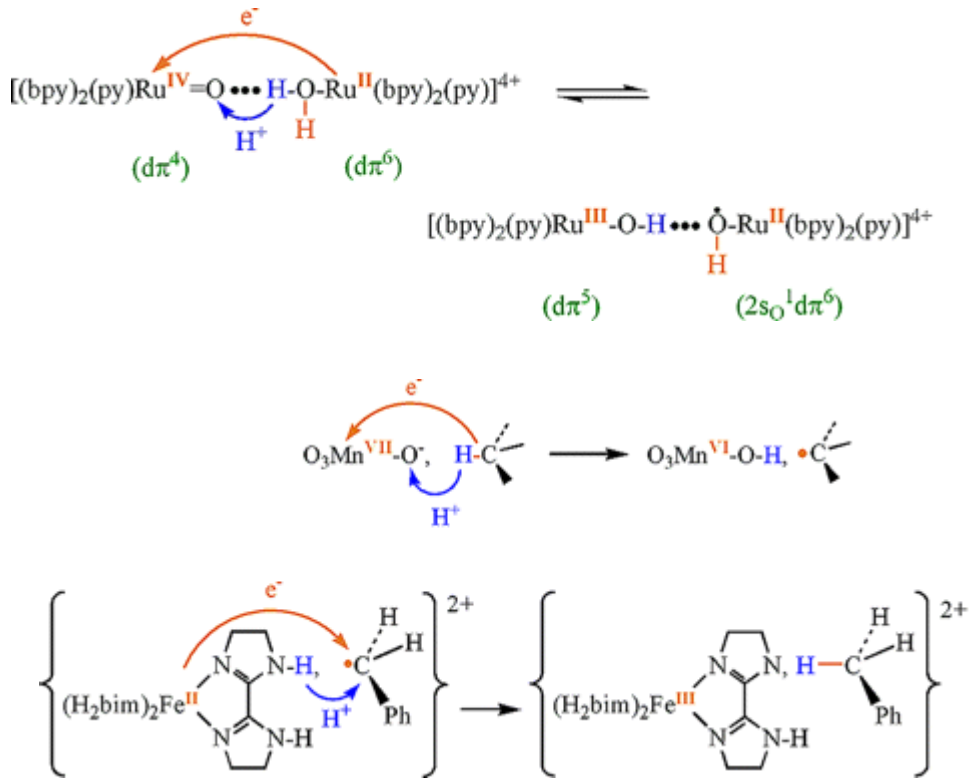




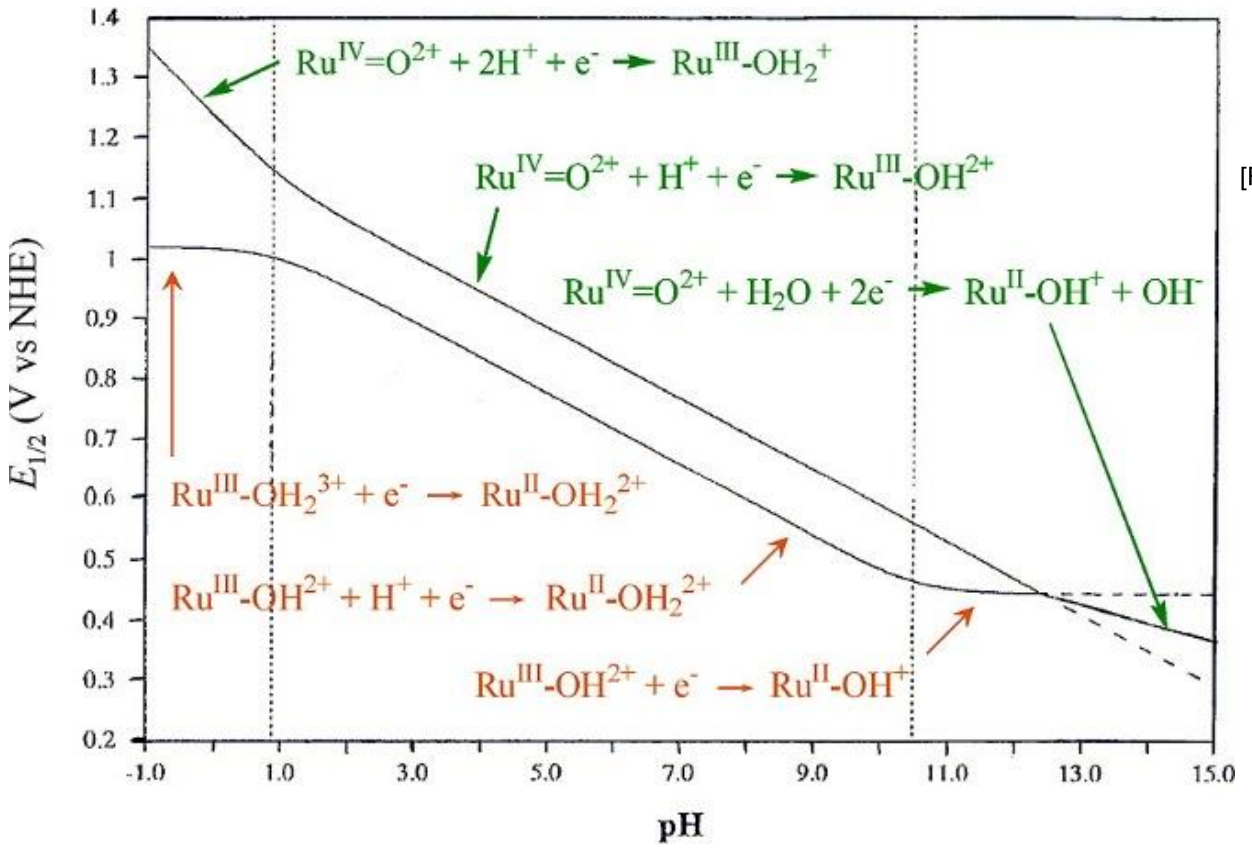
J. Am. Chem. Soc. 1981, 103, 10, 2897-2899
Inorg. Chem. 2003, 42, 25, 8140-8160

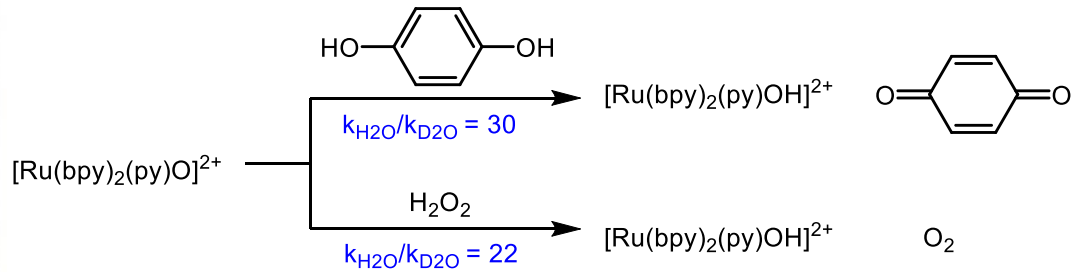
PCET Mechanisms





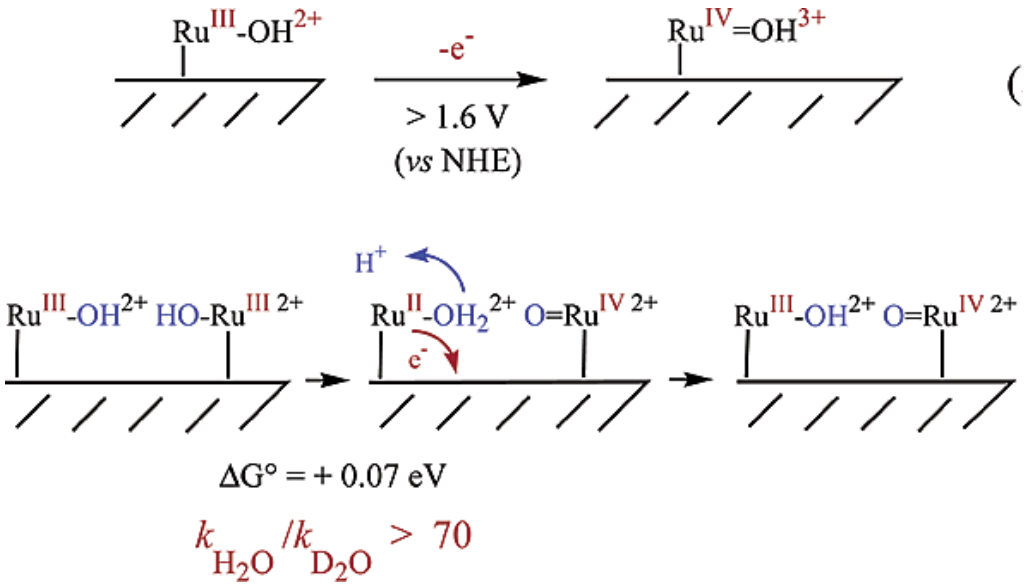
Coining the term PCET

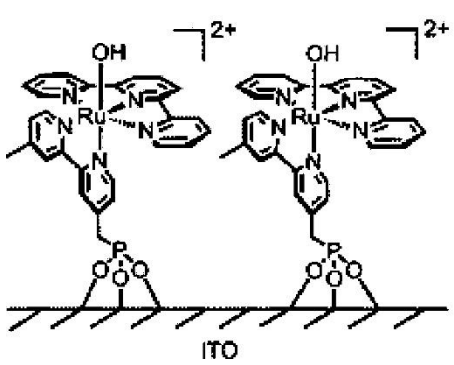


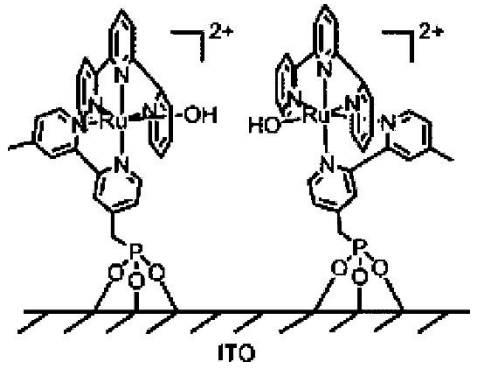


J. Am. Chem. Soc. 1981, 103, 10, 2897-2899
J. Am. Chem. Soc. 1982, 104, 24, 6872-6873
J. Am. Chem. Soc. 1992, 114, 1, 173-186
Inorg. Chem. 1987, 26, 7, 1126-1132
Chem. Rev. 2007, 107, 11, 5004-5064

PCET on Surfaces



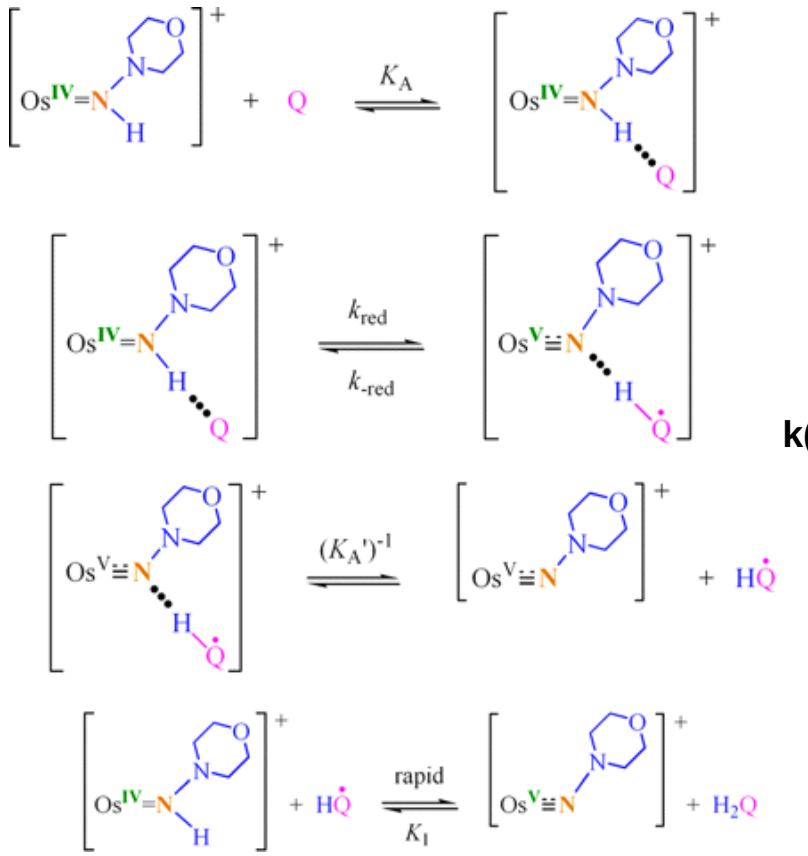




Features of PCET

Reaction[a]	k_{H_2O}/k_{D_2O} 25 °C	$(D_2O - H_2O)$ $\Delta\Delta H^{\ddagger}$ kcal/mol	$\Delta\Delta S^{\ddagger}$ cal/°C mol
$Ru^{IV}=O^{2+} + Ru^{II}\text{-}OH_2^{2+}$ [7-9] ($d\pi^4$) ($d\pi^6$)	16.1 ± 0.2	+1.6	-0.3
$Ru^{IV}=O^{2+}$ + HO-⟨⟩-OH ($d\pi^4$) (π^2)	28.7 ± 1.0	+1.5	-1.7
$Ru^{IV}=O^{2+}$ + H-O-O-H ($d\pi^4$) (σ^2)	21.6 ± 1.2	+3.2	+2.0
$Ru^{III}\text{-}OH^{2+}$ + HO-⟨⟩-OH ($d\pi^5$) (π^2)	9.3 ± 0.1	NA	NA
$Ru^{III}\text{-}OH^{2+}$ + H-O-O-H ($d\pi^4$) (σ^2)	16.2 ± 0.7	NA	NA

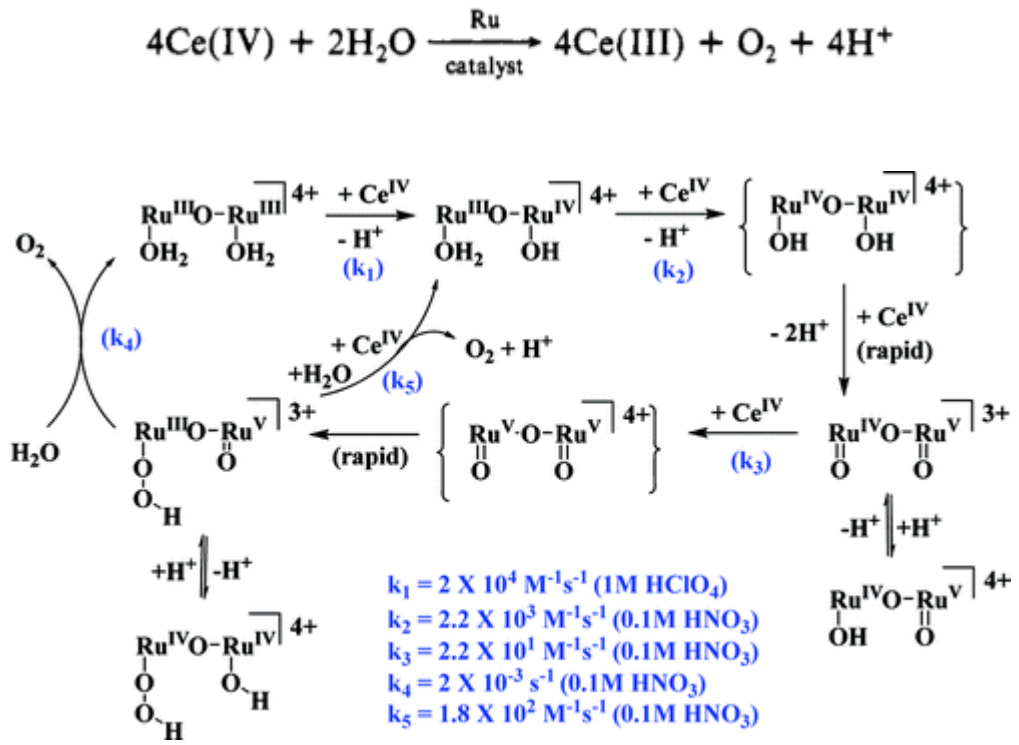
[a]The electronic configurations of the electron transfer donors and acceptors are indicated for the individual entries.

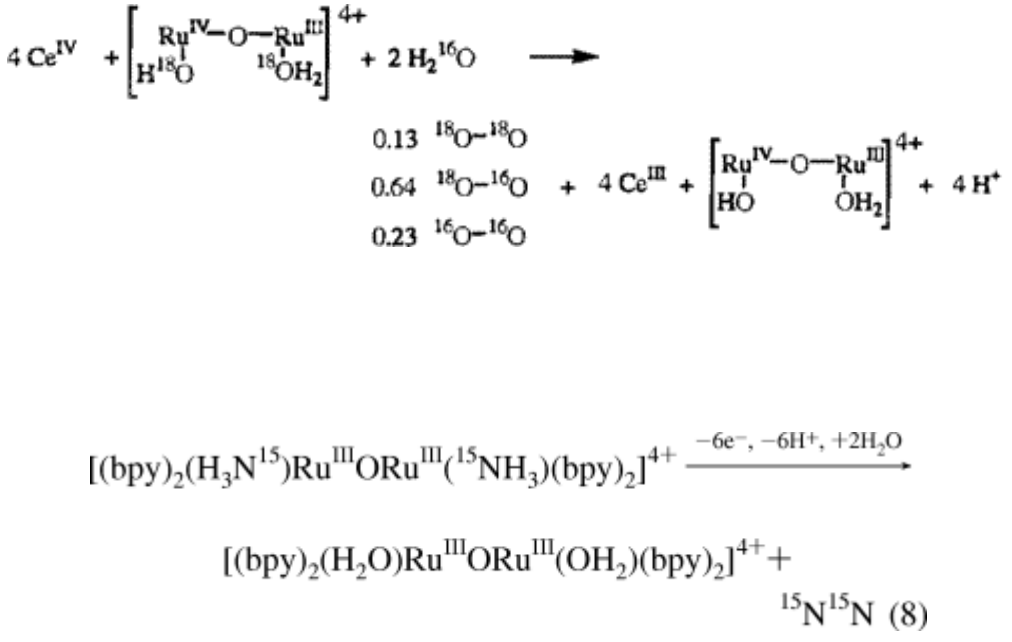


Colossal KIE!
k(H2O)/k(D2O) = 439

Proc. Natl. Acad. Sci. U.S.A. 2004, *101*, 13138.
J. Am. Chem. Soc. 1999, 121, 18, 4530-4531
Chem. Rev. 2007, 107, 11, 5004-5064

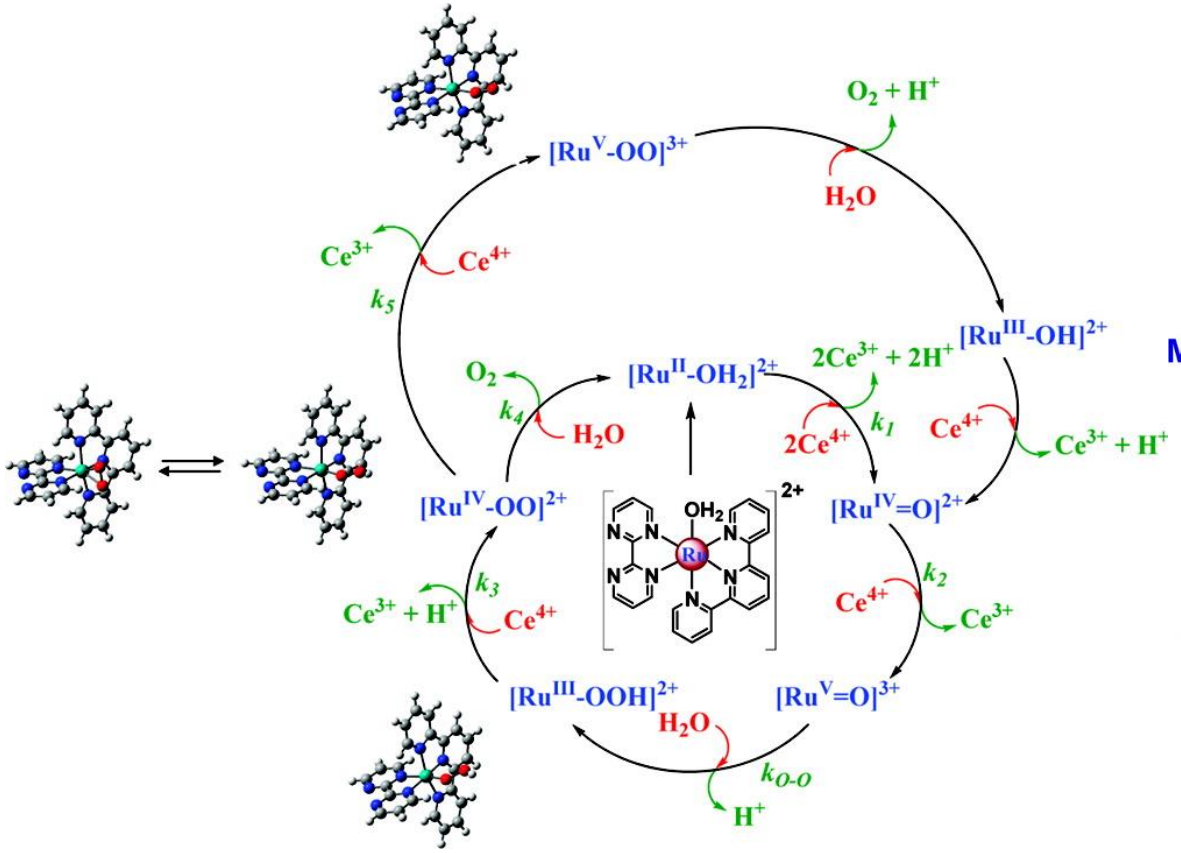
Water oxidation

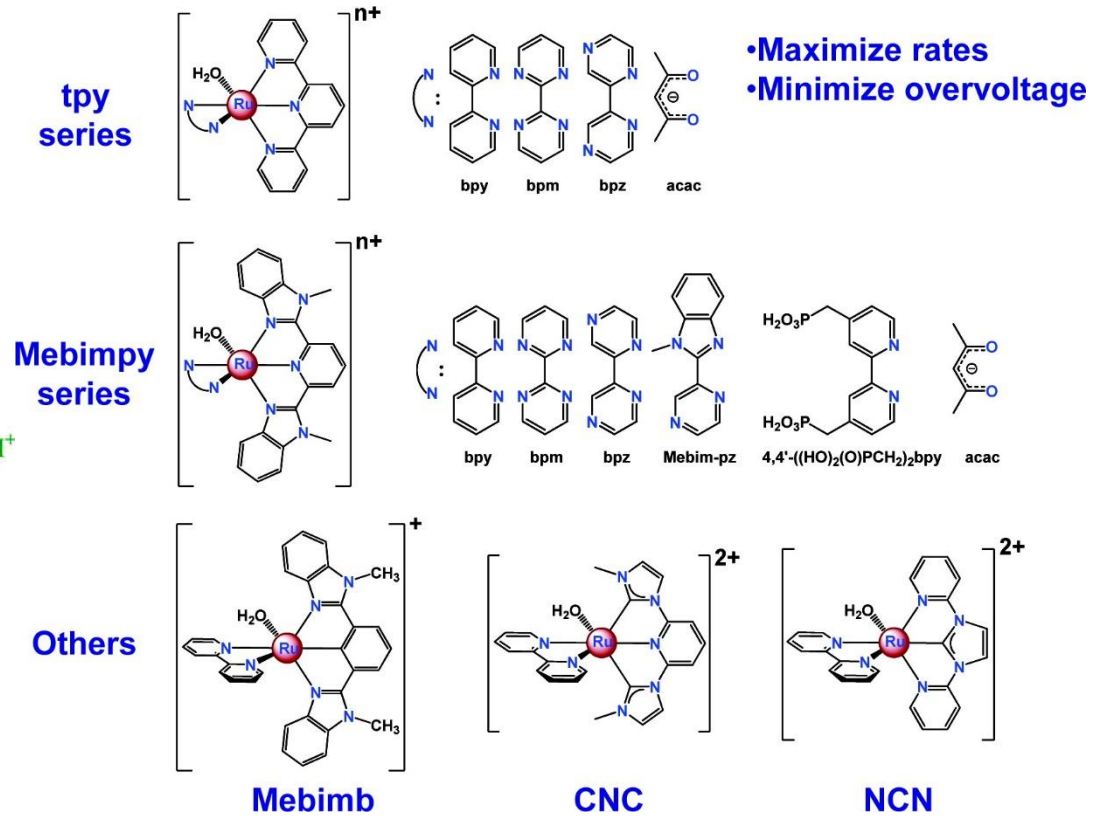




J. Am. Chem. Soc. 1982, 104, 14, 4029-4030
J. Am. Chem. Soc. 1985, 107, 13, 3855-3864
Inorg. Chem. 2008, 47, 6, 1727-1752
J. Am. Chem. Soc. 2000, 122, 35, 8464-8473
Inorg. Chem. 2003, 42, 25, 8140-8160

Single Site Water Oxidation



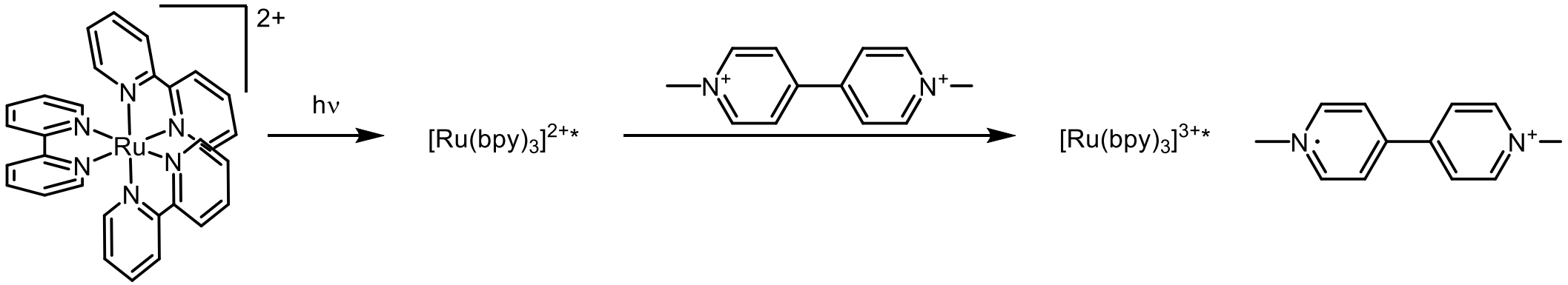


J. Am. Chem. Soc. 2010, 132, 5, 1545-1557
Acc. Chem. Res. 2009, 42, 12, 1954-1965

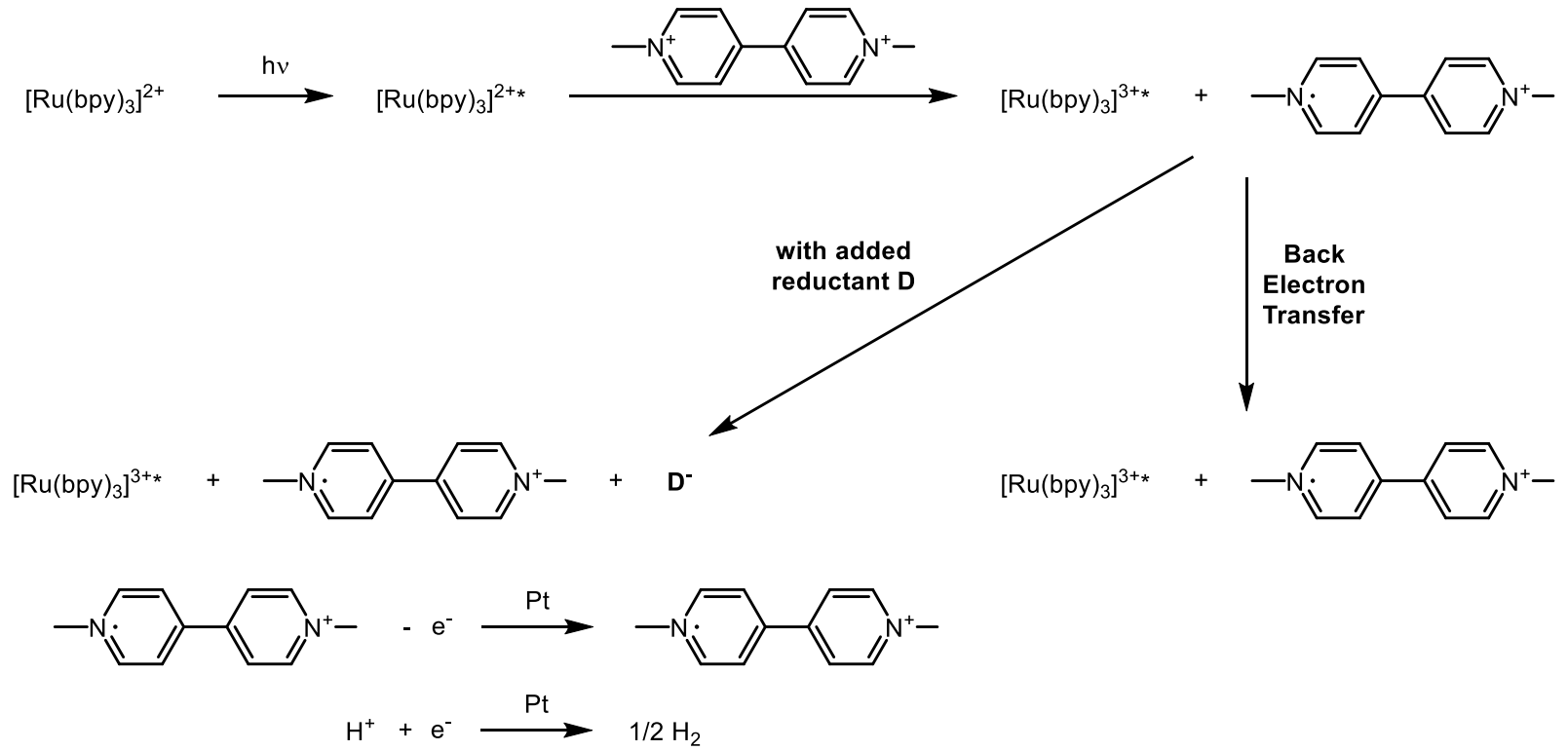
Early work

https://youtu.be/NCQWEUiwyGo?t=348

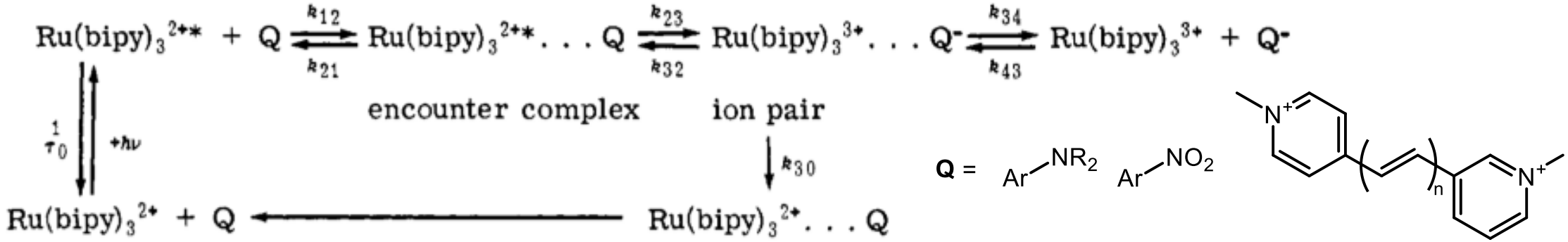
Excited State Charge Transfer



Making Stuff with Excited State Charge Transfer

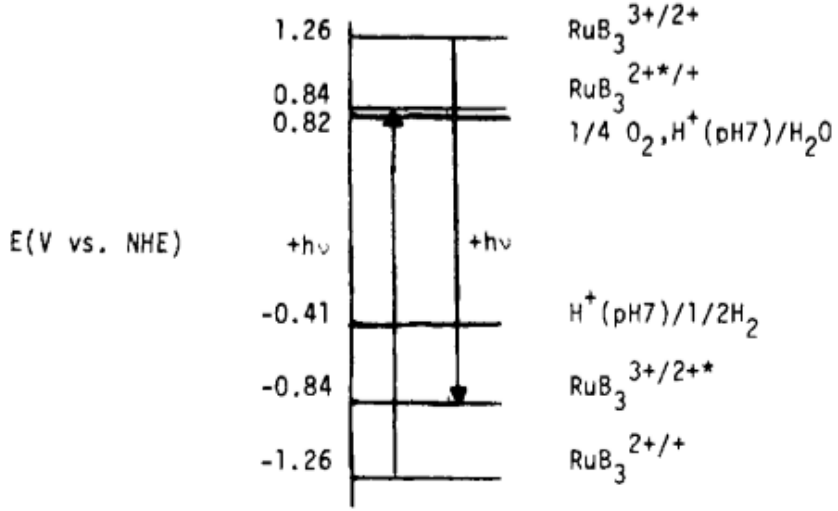


Mechanistic photoredox



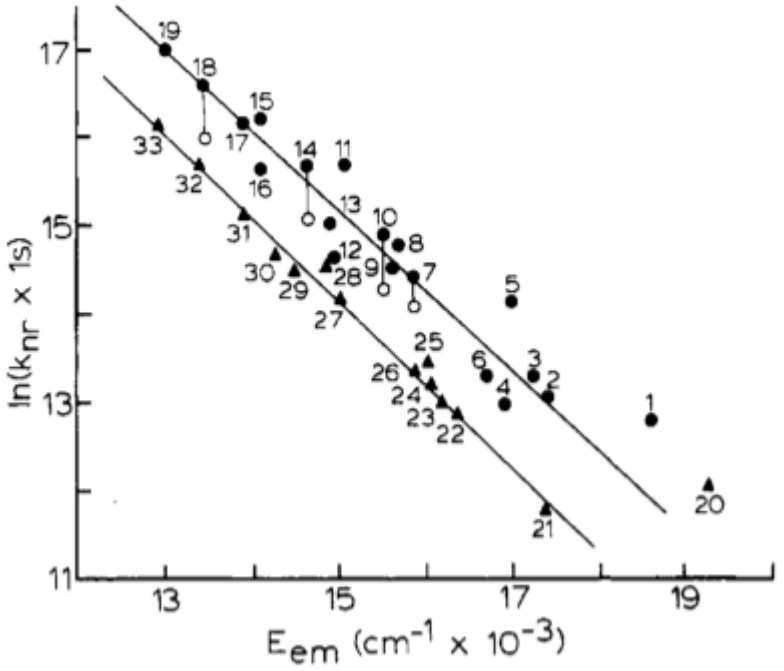
Q =

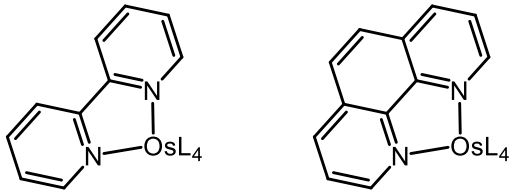
couple	E, V (CH_3CN vs. SCE)	E, V (H_2O vs. NHE)[a]
$Ru(bpy)_3^{3+/2+}$	1.29 ± 0.07	1.26
$Ru(bpy)_3^{2+*/+}$	0.77 ± 0.07	0.84
$Ru(bpy)_3^{3+/2+*}$	−0.81 ± 0.07	−0.84
$Ru(bpy)_3^{2+/+}$	−1.33 ± 0.07	−1.26



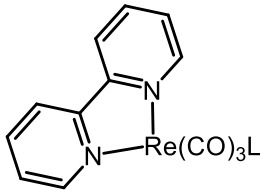
J. Am. Chem. Soc. 1974, 96, 14, 4710-4712
J. Am. Chem. Soc. 1975, 97, 10, 2909-2911
J. Am. Chem. Soc. 1975, 97, 16, 4781-4782
J. Am. Chem. Soc. 1979, 101, 17, 4815-4824

The Energy Gap Law





L = CO, X, PR_3, NR_x

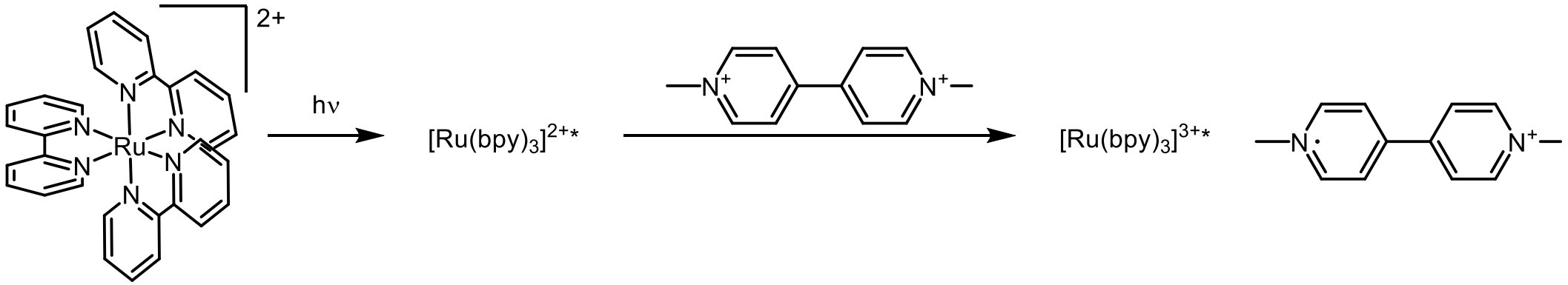


$Rh(NH_3)_5L$

(Various Solvents)

J. Phys. Chem. 1986, *90*, 3722-3734
J. Phys. Chem. 1983, *87*. 952-957

Excited State Charge Transfer



Ultimately, a related sequence of reactions may lead to the permanent storage of light energy as chemical energy.

J. Am. Chem. Soc. 1974, 96, 14, 4710-4712
J. Am. Chem. Soc. 1975, 97, 16, 4781-4782

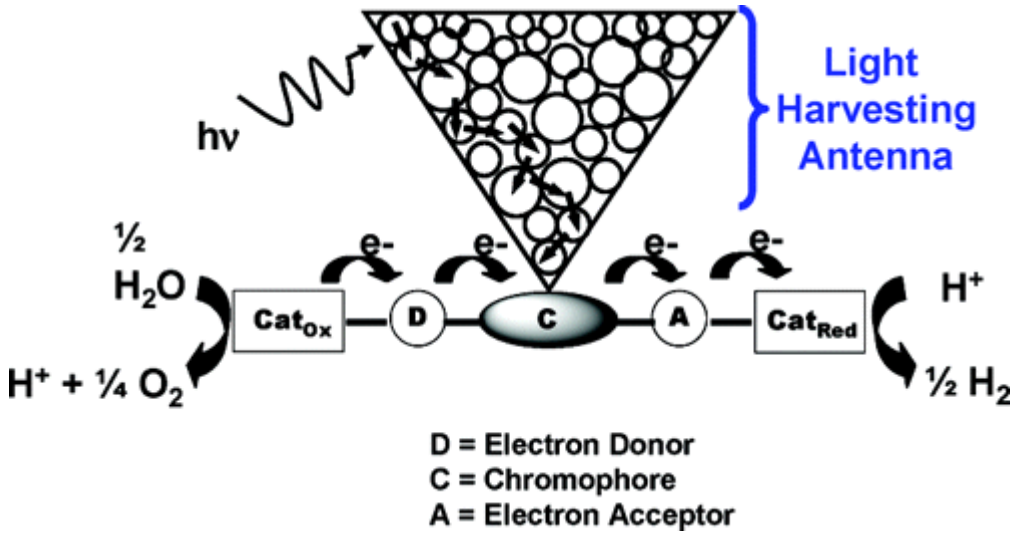
Solar Fuel Cells

$$6H_2O + 6CO_2 + 48h\nu \rightarrow C_6H_{12}O_6 + 6O_2$$

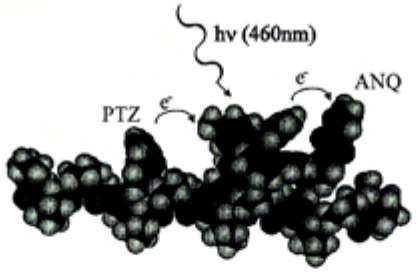
$$2H_2O + 4h\nu \rightarrow 2H_2 + O_2$$

$$2H_2O + 2CO_2 + 4h\nu \rightarrow 2HCOOH + O_2$$

Water Oxidation is KEY to artificial photosynthesis!!

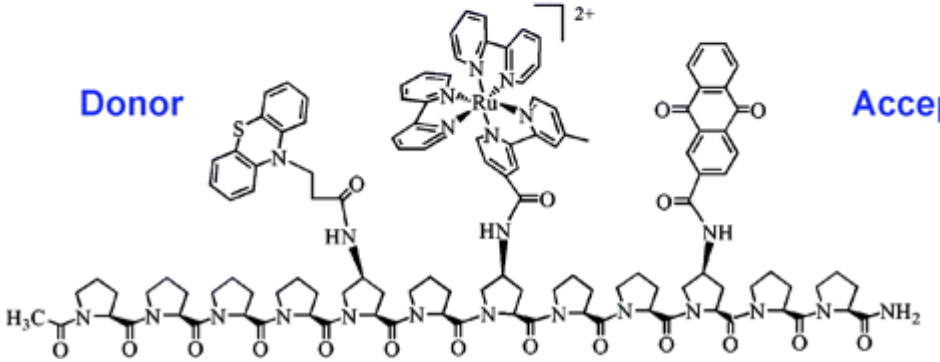


Bringing Parts Together

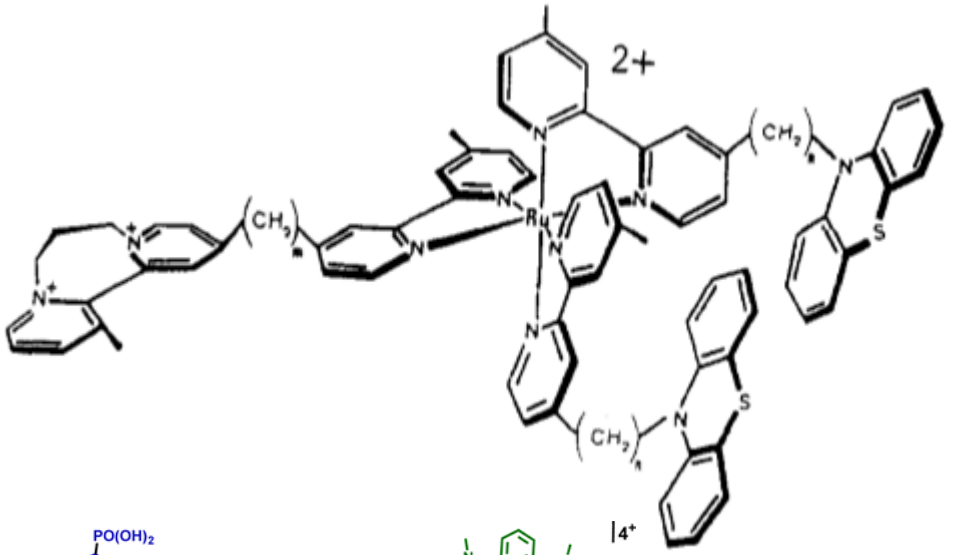


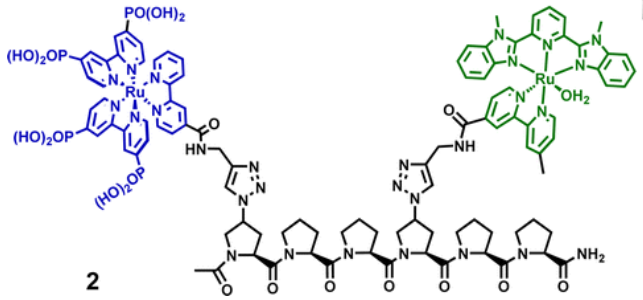
Chromophore

Donor



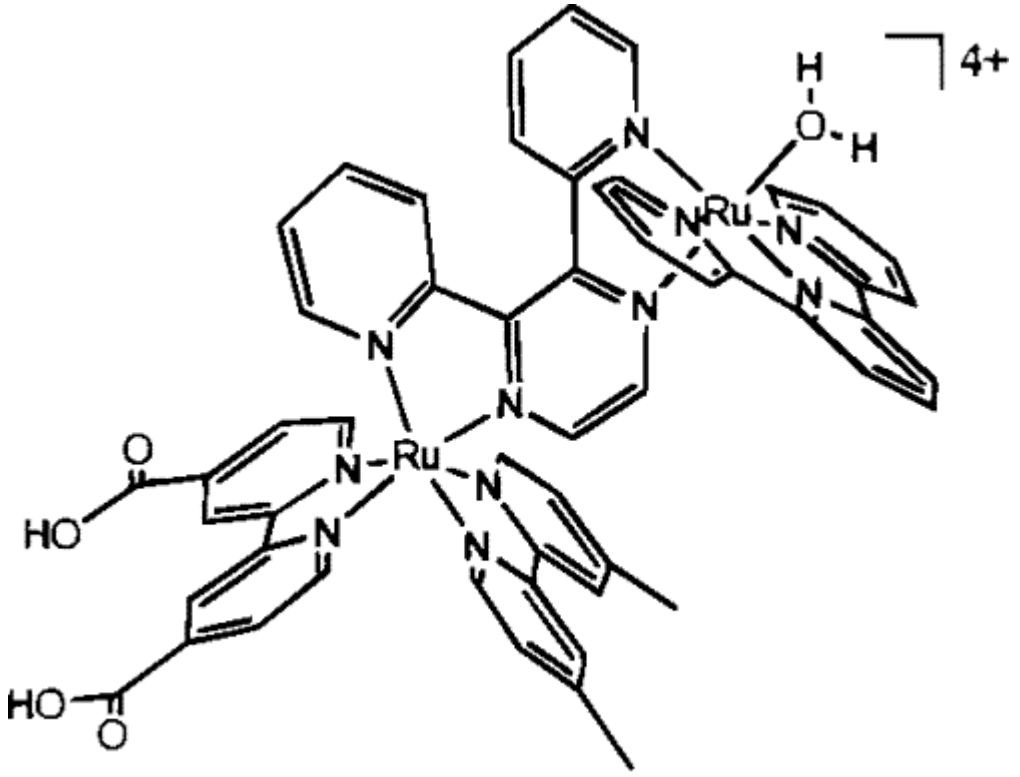
Acceptor





2

The First Dye-Sensitized Photoelectrosynthetic Cell



1

i) $TiO_2 | -[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+} + H^+(Pt) \xrightarrow{h\nu} \longrightarrow$
$TiO_2 | [-Ru_a^{II}\text{-}Ru_b^{III}\text{-}OH]^{4+} + H^+ + \frac{1}{2}H_2(Pt)$

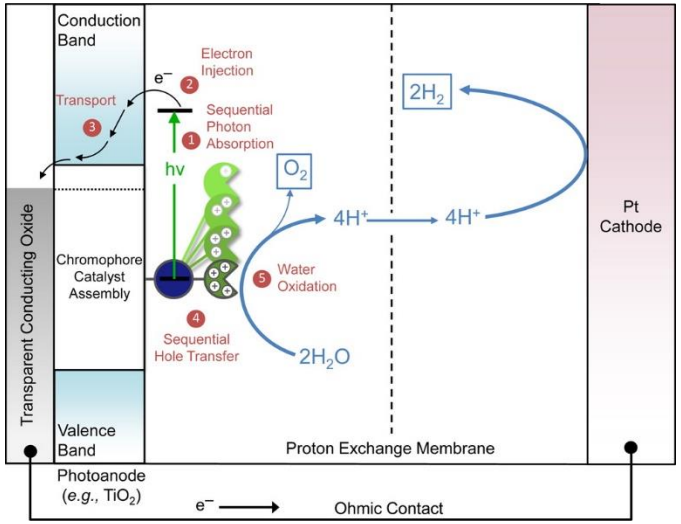
ii) $TiO_2 | -[Ru_a^{II}\text{-}Ru_b^{III}\text{-}OH]^{4+} + H^+(Pt) \xrightarrow{h\nu} \longrightarrow$
$TiO_2 | -[Ru_a^{III}\text{-}Ru_b^{III}\text{-}OH]^{5+} + \frac{1}{2}H_2(Pt)$

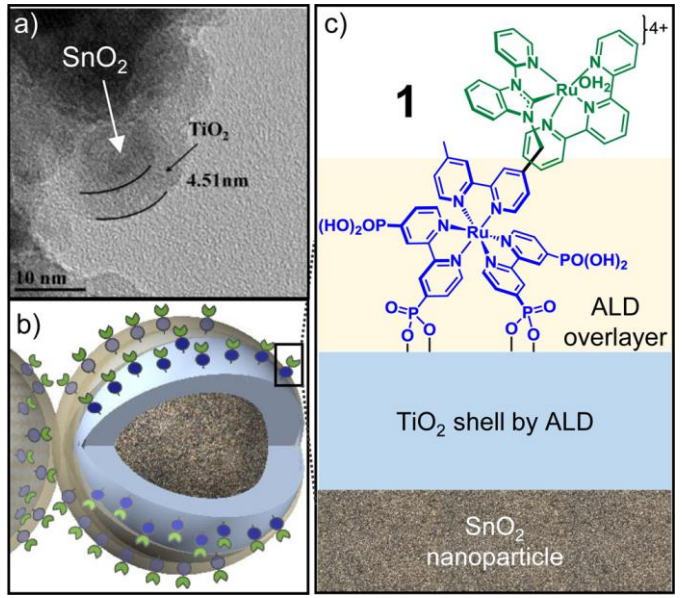
iii) $TiO_2 | -[Ru_a^{III}\text{-}Ru_b^{III}\text{-}OH]^{5+} \longrightarrow TiO_2 | -[Ru_a^{II}\text{-}Ru_b^{IV}{=}O]^{4+} + H^+$

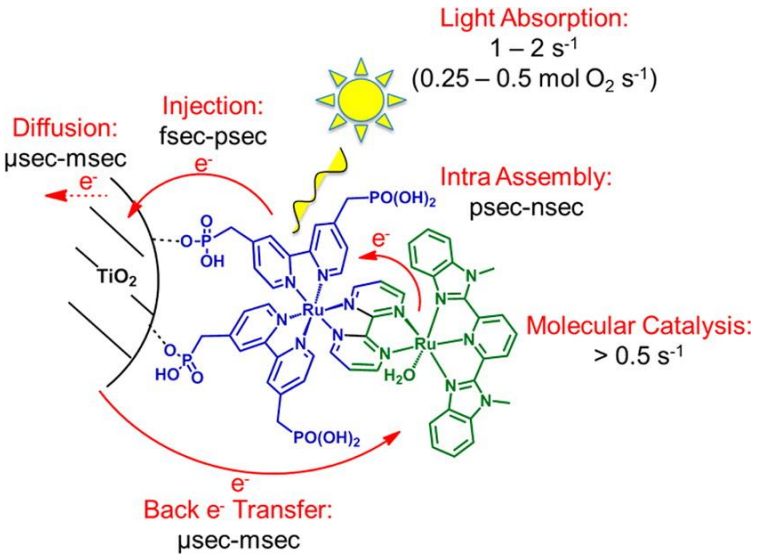
iv) $TiO_2 | -[Ru_a^{II}\text{-}Ru_b^{IV}{=}O]^{4+} + H^+(Pt) \xrightarrow{h\nu} \longrightarrow$
$TiO_2 | -[Ru_a^{III}\text{-}Ru_b^{IV}{=}O]^{5+} + \frac{1}{2}H_2(Pt)$

Inorg. Chem. 1999, 38, 20, 4386-4387

Dye-Sensitized Photoelectrosynthesis Cells

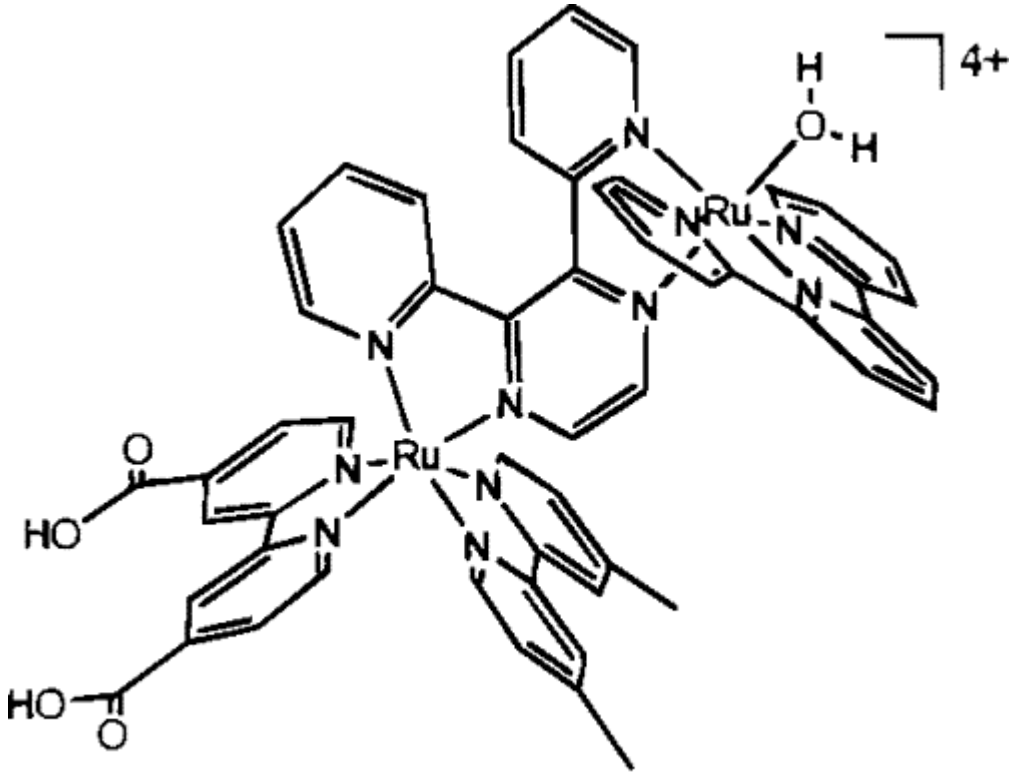






Chem. Rev. 2015, 115, 23, 13006-13049
J. Am. Chem. Soc. 2016, 138, 40, 13085-13102

The First Dye-Sensitized Photoelectrosynthetic Cell



1

i) $TiO_2 \mid -[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+} + H^+(Pt) \xrightarrow{h\nu} \longrightarrow$
$TiO_2 \mid [-Ru_a^{II}\text{-}Ru_b^{III}\text{-}OH]^{4+} + H^+ + \tfrac{1}{2}H_2(Pt)$

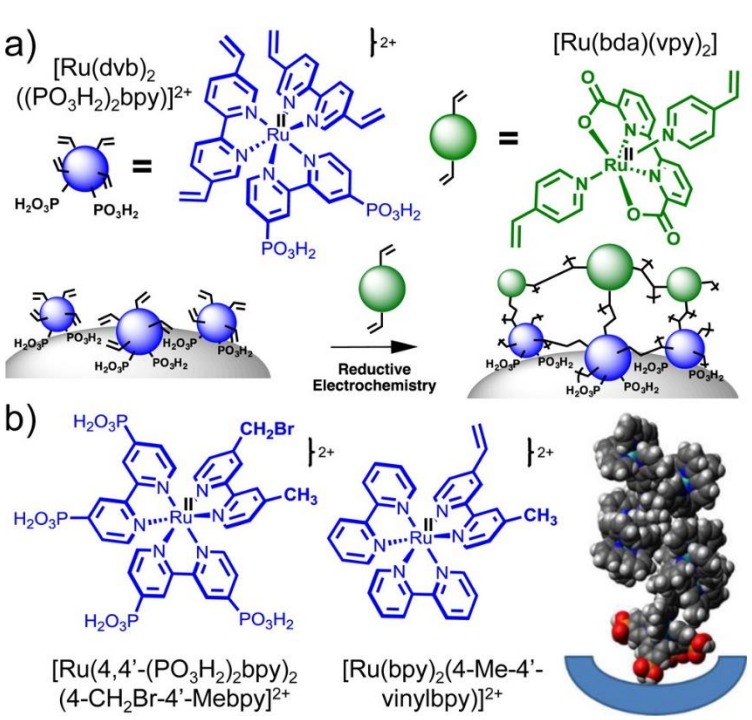
ii) $TiO_2 \mid -[Ru_a^{II}\text{-}Ru_b^{III}\text{-}OH]^{4+} + H^+(Pt) \xrightarrow{h\nu} \longrightarrow$
$TiO_2 \mid -[Ru_a^{III}\text{-}Ru_b^{III}\text{-}OH]^{5+} + \tfrac{1}{2}H_2(Pt)$

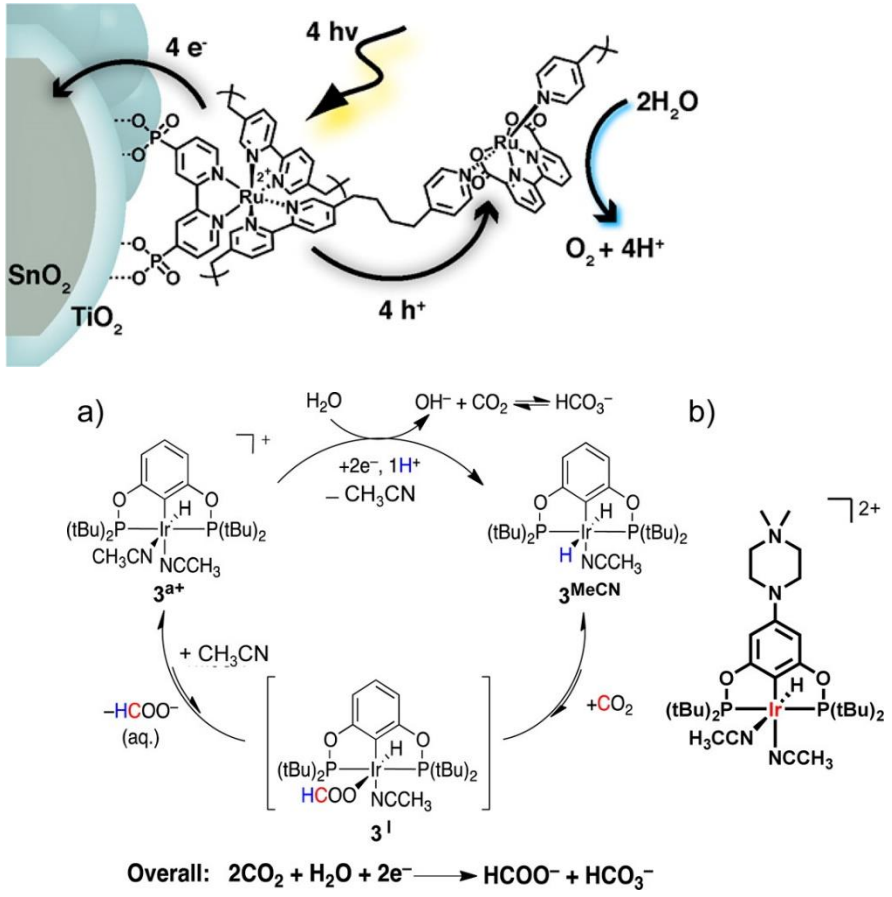
iii) $TiO_2 \mid -[Ru_a^{III}\text{-}Ru_b^{III}\text{-}OH]^{5+} \longrightarrow TiO_2 \mid -[Ru_a^{II}\text{-}Ru_b^{IV}{=}O]^{4+} + H^+$

iv) $TiO_2 \mid -[Ru_a^{II}\text{-}Ru_b^{IV}{=}O]^{4+} + H^+(Pt) \xrightarrow{h\nu} \longrightarrow$
$TiO_2 \mid -[Ru_a^{III}\text{-}Ru_b^{IV}{=}O]^{5+} + \tfrac{1}{2}H_2(Pt)$

Inorg. Chem. 1999, 38, 20, 4386-4387

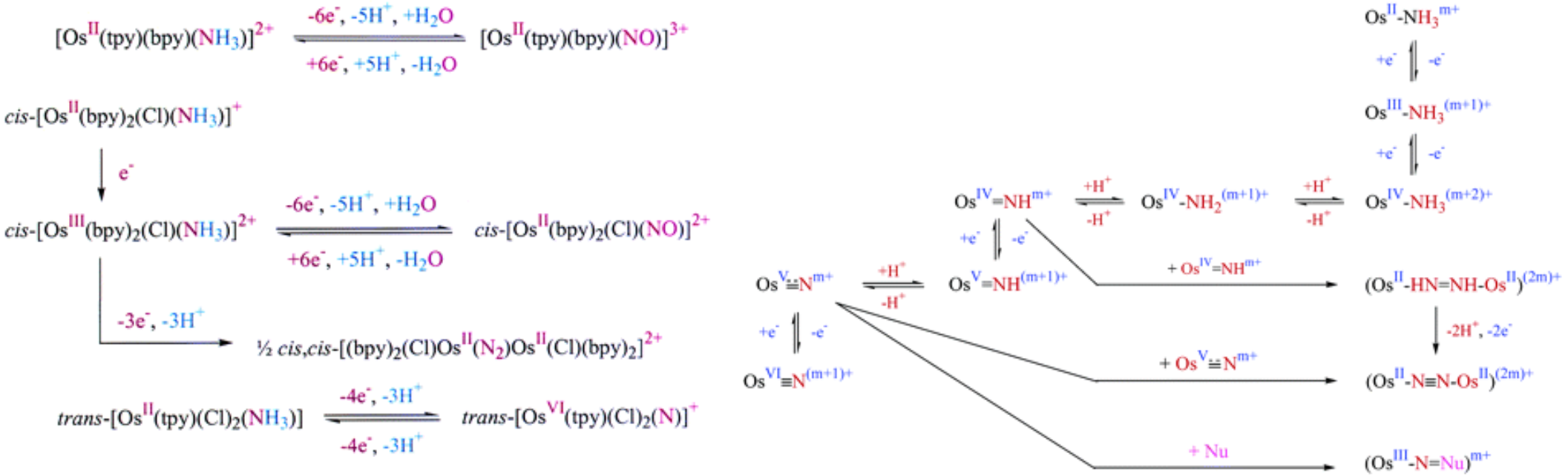
Current Research



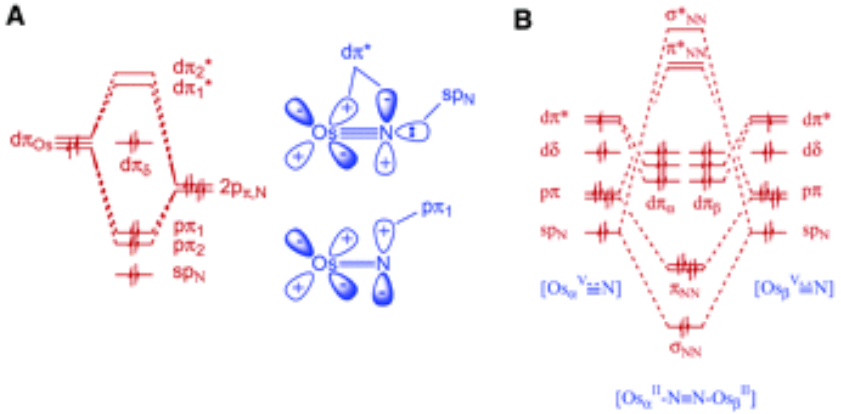


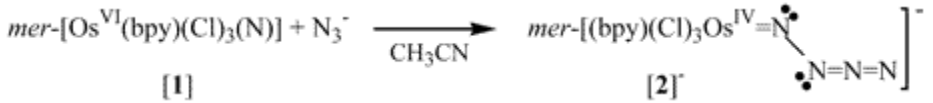
Angew. Chem., Int. Ed. **2015**, 54, 4778– 4781
Angew. Chem., Int. Ed. **2014**, 53, 8709– 8713
Chem. Sci. **2013**, 4, 3497– 3502
J. Phys. Chem. Lett. **2015**, 6, 3213– 3217

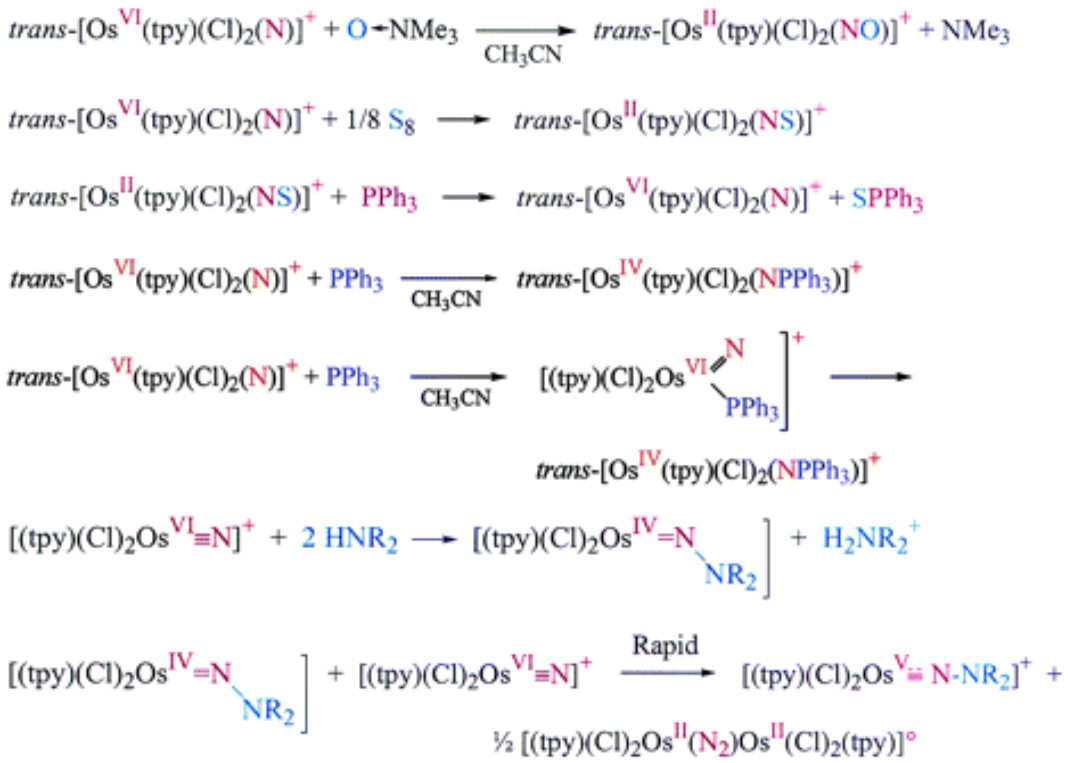
Nitrogen is not Oxygen



Osmium Nitrido Complexes

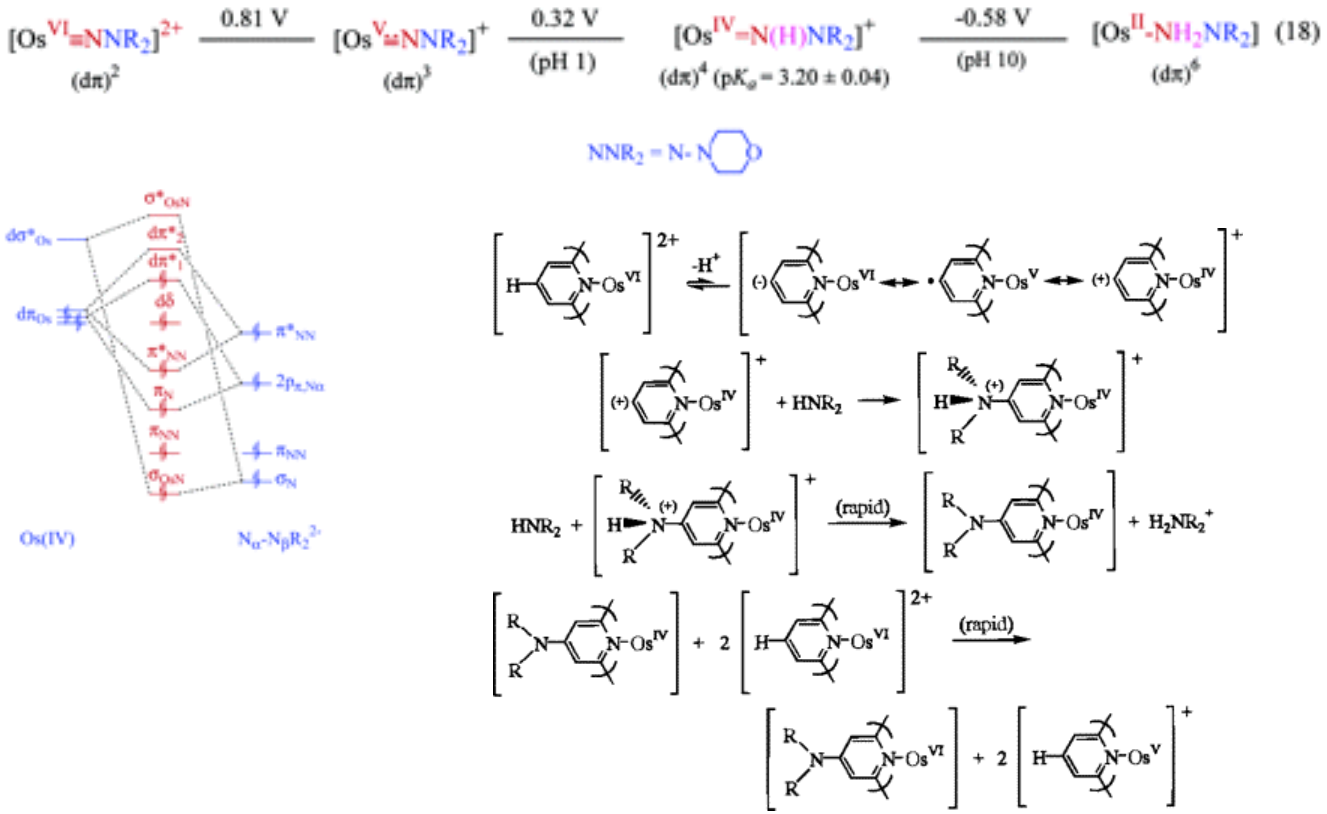


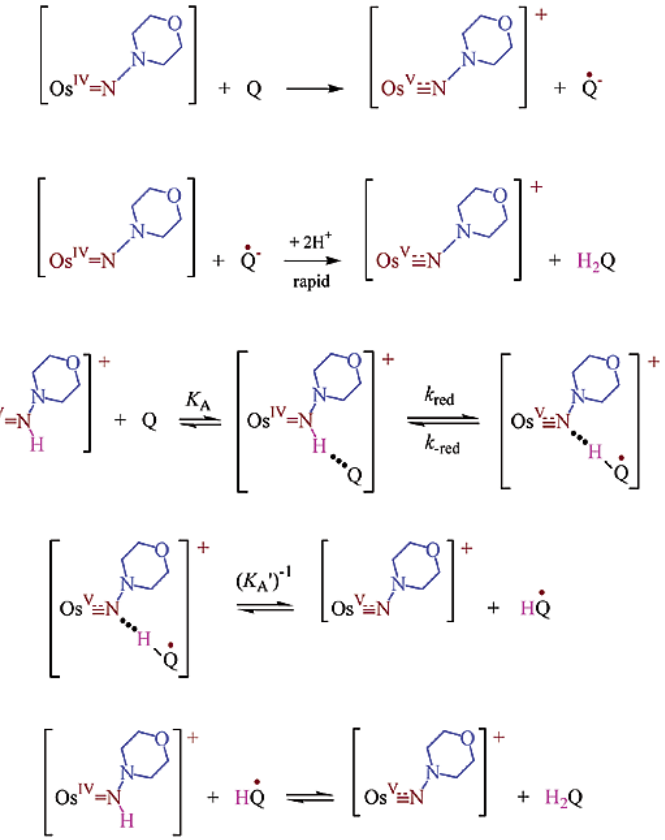




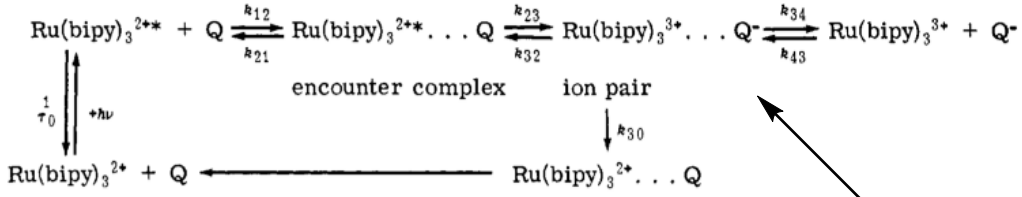
Inorg. Chem. 2003, 42, 25, 8140-8160
J. Am. Chem. Soc. 2002, 124, 17, 4580-4582

Osmium Hydrazido Complexes





Summary



Firsts:

- Characterized PCET
- Electron transfer quenching
- Molecular water oxidation catalyst
- Dye sensitized photoelectrosynthetic cell