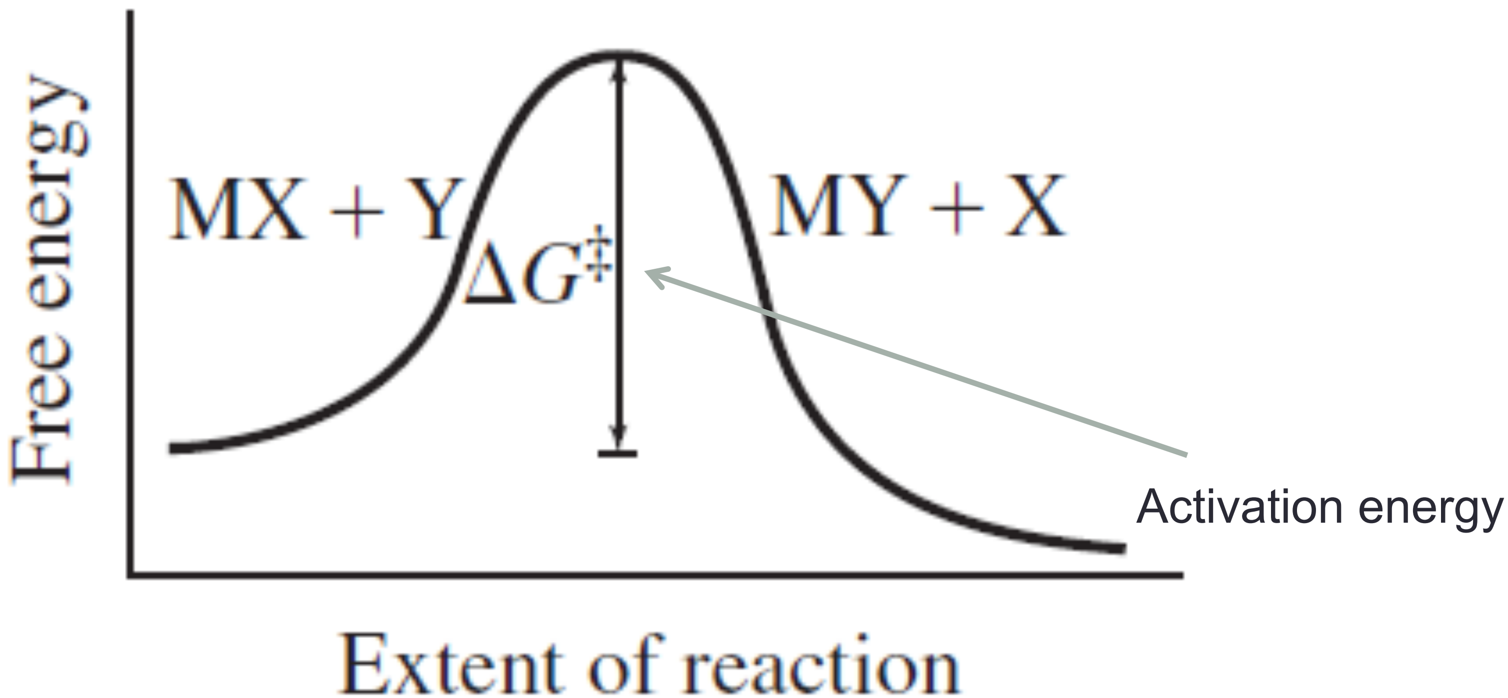
Reaction coordinate for ligand substitution



Labile and inert electronic configurations

Slow Reactions (Inert)
d^3, low-spin d^4, d^5, and d^6
Strong-field d^8 (square planar)

Moderate Rate
Weak-field d^8

Fast Reactions (Labile)
d^1, d^2, high-spin d^4, d^5, and d^6
d^7, d^9, d^{10}

The *trans* effect

- Final ligand ranking a result of both pi and sigma effects

Ligand ranking for trans effect

$CN^- \sim CO \sim C_2H_4 > PH_3 \sim SH_2 > NO_2^- > I^- > Cl^- > NH_3 \sim py > OH^- > H_2O$

Large trans effect **Small trans effect**

Strong pi acceptor → strong sigma donor → neither strong sigma donor or pi acceptor

TABLE 6.14 Hard and Soft Bases

Hard Bases	Borderline Bases	Soft Bases
		H^-
F^-, Cl^-	Br^-	I^-
H_2O, OH^-, O^{2-}		H_2S, SH^-, S^{2-}
ROH, RO^-, R_2O, CH_3COO^-		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	NO_2^-, N_3^-	SCN^-, CN^-, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^{2-}$
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_2	PR_3, $P(OR)_3$, AsR_3, C_2H_4, C_6H_6

Classifications from R. G. Pearson, *J. Chem. Educ*, **1968**, *45*, 581.

TABLE 6.15 Hard and Soft Acids

Hard Acids	Borderline Acids	Soft Acids
H^+, Li^+, Na^+, K^+		
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}		
BF_3, BCl_3, $B(OR)_3$	$B(CH_3)_3$	BH_3, Tl^+, $Tl(CH_3)_3$
Al^{3+}, $Al(CH_3)_3$, $AlCl_3$, AlH_3		
Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Rh^{3+}, Ir^{3+} Ru^{3+}, Os^{2+}	Cu^+, Ag^+, Au^+, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, CH_3Hg^+, $[Co(CN)_5]^{2-}$, Pd^{2+}, Pt^{2+}, Pt^{4+}, Br_2, I_2
Ions with formal oxidation states of 4 or higher		Metals with zero oxidation state
HX (hydrogen-bonding molecules)		π acceptors: e.g., trinitrobenzene, quinines, tetracyanoethylene

Classifications from R. G. Pearson, *J. Chem. Educ*, **1968**, *45*, 581.

OXIDATION-REDUCTION REACTIONS

CH 431

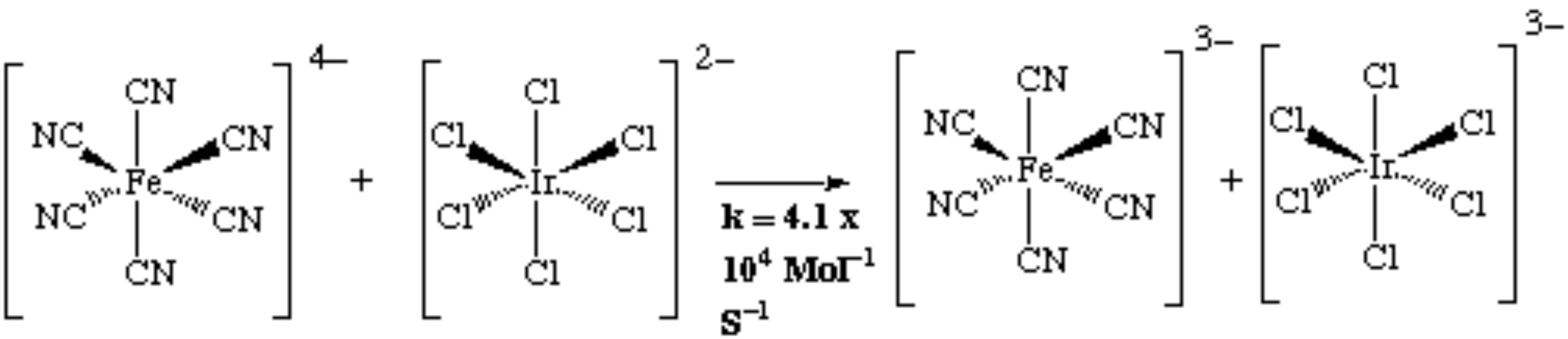
MFT Ch 12

Review material from CH302

Oxidation-reduction reactions

- In addition to ligand substitution, metal complexes can undergo oxidation-reduction reactions

- These involve electron transfer one metal complex to another
- Example:



Terminology

- **Redox**: refers to oxidation/reduction chemistry

- **Reduction**: gain of electrons
- **Oxidation**: loss of electrons

  Pneumonic: OIL RIG (oxidation is loss, reduction is gain)

- **Oxidizing agent**: a substance that oxidizes a substrate by being reduced
- **Reducing agent**: a substance that reduces a substrate by being oxidized

https://ch302.cm.utexas.edu/echem/index.php#redox/intro-redox.html

Reduction potential

- A reduction potential is a measure of the tendency of a species to be reduced, reported in volts

$$A^{n+} + e^- \rightarrow A^{(n-1)+} \qquad E° = \_\_\_\_ \ V$$

- More positive reduction potentials indicate greater tendency to be reduced

- Standard reduction potentials are measured vs. the standard hydrogen electrode (SHE)

$$2H^+ + 2e^- \rightarrow 2H_2 \qquad E° = 0.00 \ V$$

TABLE 17.1 Standard Reduction Potentials at 25 °C

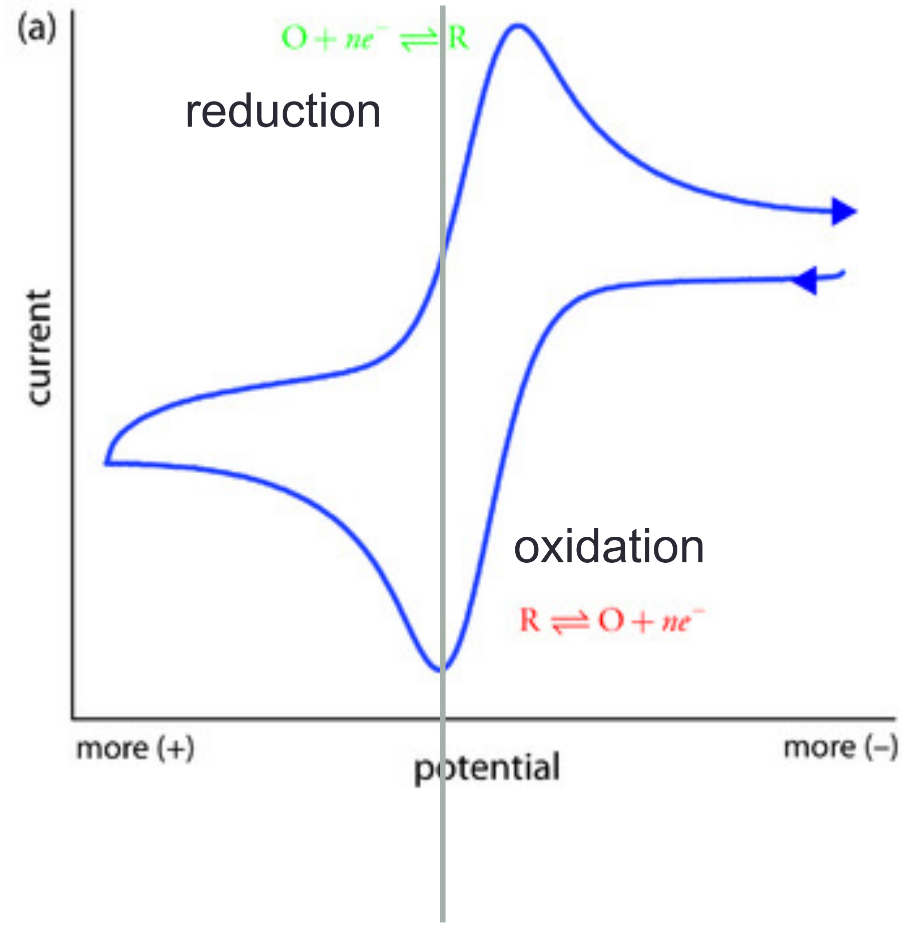
	Reduction Half-Reaction		$E°$ (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(aq) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	- 0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	- 0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	- 0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	- 0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	- 0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	- 0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	- 1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	- 2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	- 2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	- 3.04	Stronger reducing agent

https://ch302.cm.utexas.edu/echem/index.php#echem-cells/std-red-potentials.html

Measuring redox potentials

- Cyclic voltammetry (CV) is a method that can be used to measure redox potentials
- CV monitors electron flow (current) to and from a complex, electron flow increases around a complex's redox potential

- You will use (have used) this technique to characterize the ferrocene you make in lab. Ferrocene is a commonly used standard for CV



E°

Factors that contribute to the reduction potential of a metal complex

1. HSAB theory: softer ligands will shift potential more in favor of softer oxidation state, harder ligands will shift potential more in favor of harder oxidation state

Cu(II)–Cu(I) Reactions	$E°$ (V)
$Cu^{2+} + 2\,CN^- + e^- \rightleftharpoons [Cu(CN)_2]^-$	+1.103
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.153
$[Cu(NH_3)_4]^{2+} + e^- \rightleftharpoons [Cu(NH_3)_2]^+ + 2\,NH_3$	−0.01

CN- soft ligand, NH_3 hard
Cu^+ soft metal ion, Cu^{2+} borderline metal ion

Factors that contribute to the reduction potential of a metal complex

2. LFSE: species that has highest LFSE will be favored

Co(III)–Co(II) Reactions	$E°$ (V)
$[Co(H_2O)_6]^{3+} + e^- \rightleftharpoons [Co(H_2O)_6]^{2+}$	+1.808
$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$	+0.108
$[Co(CN)_6]^{3-} + e^- \rightleftharpoons [Co(CN)_6]^{4-}$	−0.83

Δ_o $H_2O < NH_3 < CN^-$ (spectrochemical series)

Co^{3+} complexes are low spin d^6 (LFSE: $-12/5\ \Delta_o$)

Δ_o for CN^- complex is very large. Thus, even though the soft CN^- ligand forms more stable complexes with the softer Co^{2+}, the Co^{3+} complex is favored (remember, reduction will add an electron to the e_g orbital set, which will be the most destabilized in the CN- complex)

Factors that contribute to the reduction potential of a metal complex

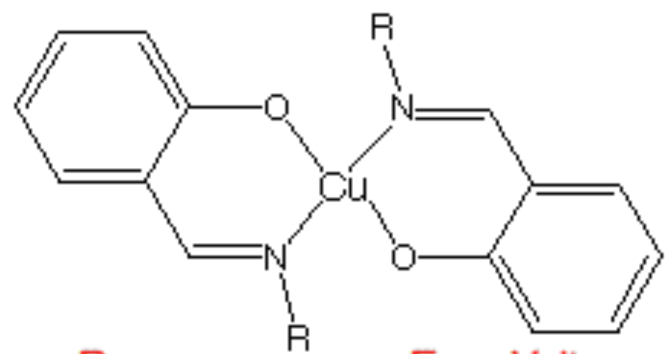
3. Coordination geometry: The geometry and coordination number that a ligand set imposes can modulate the redox potential of a metal complex

Geometry:

Cu(II): prefers square planar geometry

Cu(I): prefers tetrahedral geometry

Bulky R groups favor more tetrahedral configuration, E° is the least negative (most positive) for tBu ligand



R	$E_{1/2}$ Volts
O	- 1.21
Et	- 0.86
Me	- 0.90
S	- 0.83
iPr	- 0.74
tBu	- 0.66

Factors that contribute to the reduction potential of a metal complex

3. Coordination geometry: The geometry and coordination number that a ligand set imposes can modulate the redox potential of a metal complex

Coordination number:

Comparing a 5-coordinate vs. a 4-coordinate Cu^{2+} complex, which complex would you expect to have the higher reduction potential?

In this case, we can think of coordinate ligands around the metal center as electron density: the 5-coordinate complex has more electron density around the metal than the 4-coordinate complex. Which would be more likely to accept additional electrons?

Electron transfer reactions

- Two metal complexes can react by simply transferring an electron from one complex to another
- Favorable reactions have positive net E° value

$$A^{n+} + e^- \rightarrow A^{(n-1)+} \qquad E° = +1.0\ V$$

$$B^{m+} + e^- \rightarrow B^{(m-1)+} \qquad E° = +0.7\ V$$

$$B^{(m-1)+} \rightarrow B^{m+} + e^- \qquad E° = -0.7\ V$$ (oxidation potential)

$$A^{n+} + B^{(m-1)+} \rightarrow A^{(n-1)+} + B^{m+} \qquad E° = +0.3\ V$$

https://ch302.cm.utexas.edu/echem/index.php#echem-cells/std-cell-potentials.html

Example question

- Which of the following metallocenes is the strongest reducing agent?

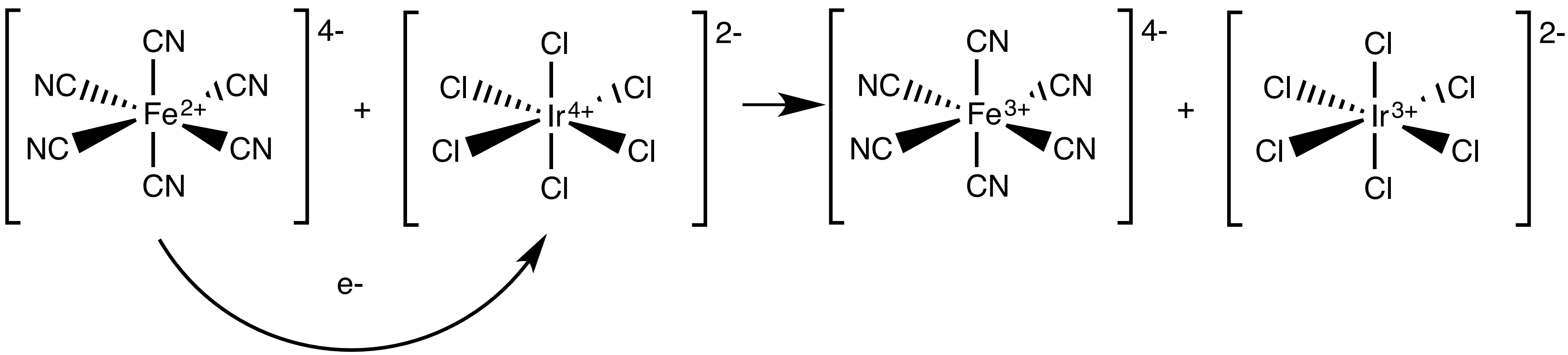
Half-reaction	**E° (V) (Ferrocene potential set to 0)**
Ferrocene: $Fe(C_5H_5)_2^+ + e^- \rightleftharpoons Fe(C_5H_5)_2$	0
Decamethyl ferrocene: $Fe(C_5Me_5)_2^+ + e^- \rightleftharpoons Fe(C_5Me_5)_2$	−0.59
Cobaltocene: $Co(C_5H_5)_2^+ + e^- \rightleftharpoons Co(C_5H_5)_2$	−1.33
Decamethyl cobaltocene: $Co(C_5Me_5)_2^+ e^- \rightleftharpoons Co(C_5Me_5)_2$	−1.94

- Which of the above metallocene(s) could be used as a reducing agent for the following reaction?

$$A^{n+} + e^- \rightarrow A^{(n-1)+} \quad E° = -1.0\ V$$

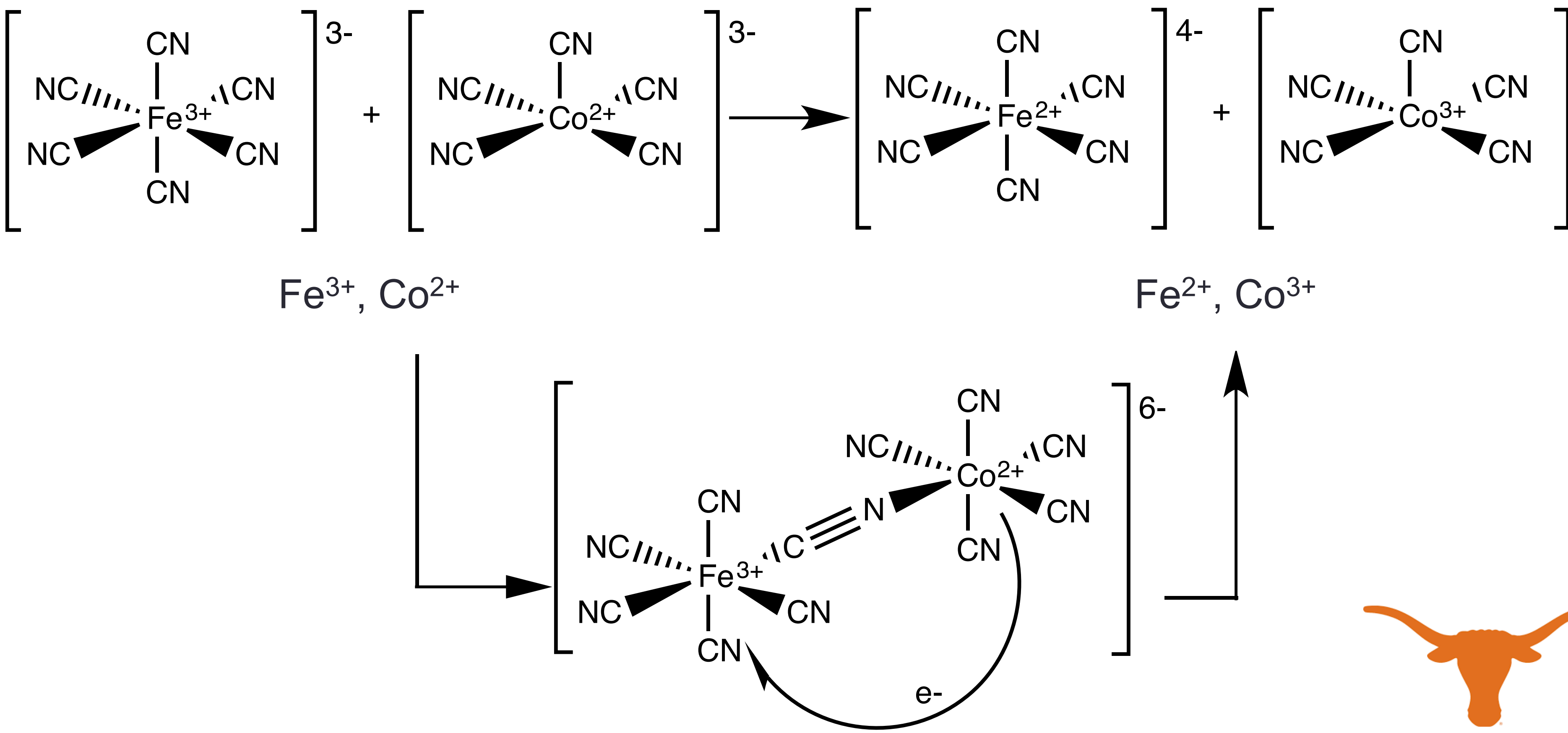
Mechanisms of electron transfer: Outer sphere

In outer sphere electron transfer, transfer occurs between two separate coordination spheres (no linking ligand)



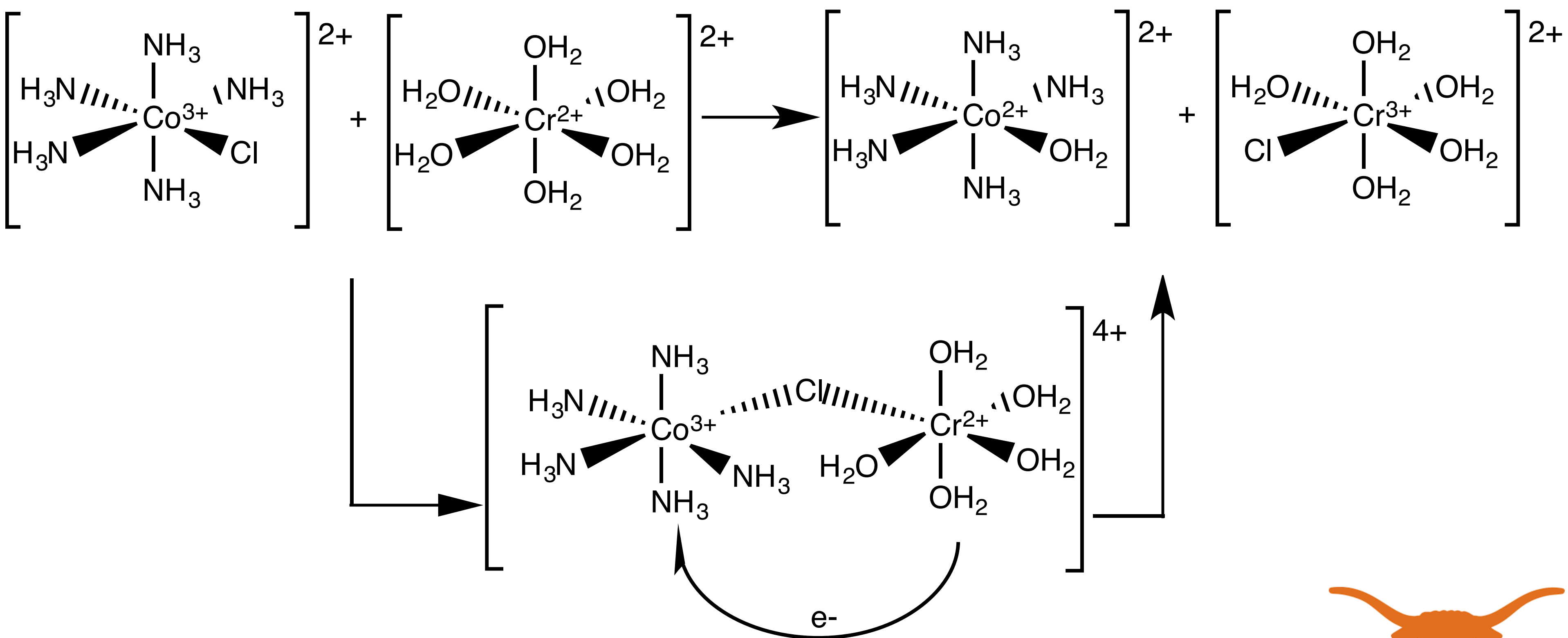
Mechanisms of electron transfer: Inner sphere

In inner sphere electron transfer, two molecules are connected by a ligand through which the electron is transferred



Mechanisms of electron transfer: Inner sphere

Inner sphere electron transfer can sometimes be accompanied by exchange of bridging ligand between metal complexes



Take away messages

- Reduction is gain of electrons, oxidation is loss of electrons
- Reductions with more positive reduction potentials are more thermodynamically favored
- Ligand coordination environment can tune reduction potentials
- Electron transfer reactions involve the reduction of one species and the oxidation of another
- Inner sphere and outer sphere mechanisms exist for electron transfer (know the basics from this lecture but you do not need to know all the material in MFT 12.8.1)