✓

Chem 432 Exam 3
Name Key
In-Class Portion
Useful information: $k_{12} = \sqrt{k_{11}k_{22}K_{12}f_{12}}$, $f_{12} \sim 1$

(+2) (1) (a) Rank the following in terms of increasing hardness.
Al^{3+}, Au^{+}, Hg^{2+}, Mg^{2+}
45.8 5.7 7.7 32.5

$Au^{+} < Hg^{2+} < Mg^{2+} < Al^{3+}$
5.7 7.7 32.5 45.8

(+3) (b) Which of the ~~following~~ above do you think would form the strongest bond with F^-? with NO_2^-? and why? F^- $\eta = 7.0$ NO_2^- $\eta = 4.5$

NO_2^- is a soft ion, so it would bond most strongly to Au^+, the softest metal
F^- is a hard ion, so it should bond best to Al^{3+}, the hardest acid.

(+4) (2) Which of the following are acids? Which are bases? Which definition of acid or base applies?

(a) SO_2 Lux-Flood acid, Lewis, Usanovich

(b) $HClO_4$ Arrhenius, Bronsted-Lowry acid

(c) NCl_3 Arrhenius, Bronsted-Lowry Lewis, Usanovich base

(d) MnO_4^- Usanovich base

(+5) 3) Order the following systems from slowest to fastest electron transfer and explain why.

a $[Ru(NH_3)_6]^{3+}$ + $[Ru(NH_3)_6]^{2+}$ ----> $[Ru(NH_3)_6]^{2+}$ + $[Ru(NH_3)_6]^{3+}$

b $[Rh(NH_3)_6]^{3+}$ + $[Rh(NH_3)_6]^{2+}$ ----> $[Rh(NH_3)_6]^{2+}$ + $[Rh(NH_3)_6]^{3+}$

c $[Ru(NH_3)_6]^{3+}$ + $[Rh(NH_3)_6]^{2+}$ ----> $[Ru(NH_3)_6]^{2+}$ + $[Rh(NH_3)_6]^{3+}$ K = 10^3

fastest (c) should be the fastest $k_{12} = \sqrt{k_{11} k_{22} K_{12} f_{12}}$ which means k for c should be ~ the average of a+b × $\sqrt{1000}$. This will probably be faster than

1a) $(Ru(NH_3)_6)^{3+}$ $[Ru(NH_3)_5]^{2+}$

_ _ Eg — — Eg

⥮ ⥮ ↿ T_{2g} ⥮ ⥮ ⥮ T_{2g}

The electron transfer involves an electron from a T_{2g} orbital to a T_{2g} orbital. Since the T_{2g} set is nonbonding in this molecule the inner sphere reorganization energy should be small and the activation barrier small.

1b) $(Rh(NH_3)_6)^{3+}$ $(Rh(NH_3)_5)^{2+}$

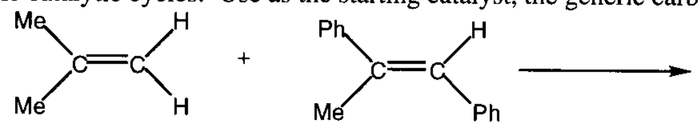
— — Eg ↿ — Eg

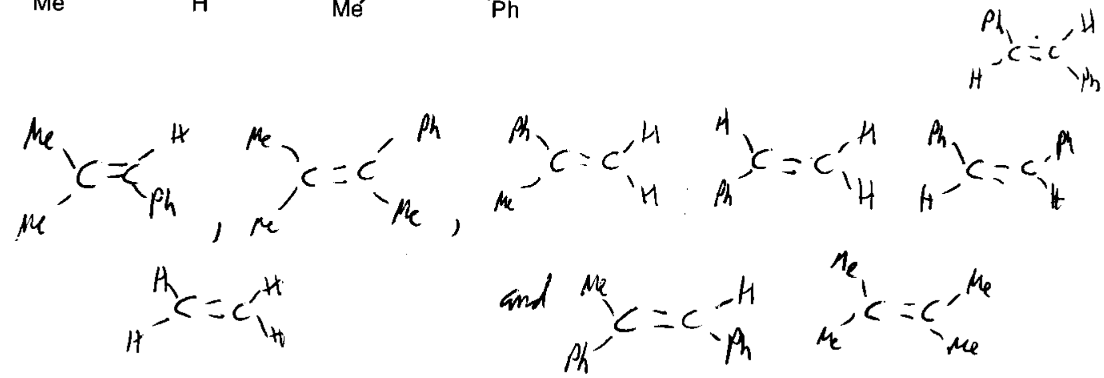
⥮ ⥮ ⥮ T_{2g} ⥮ ⥮ ⥮ T_{2g}

slow The electron transfer is from an Eg set. This means the inner sphere reorganization energy will be large (E_g is σ antibonding). The activation barrier will be large

(4) (a)List all of the possible products of the olefin metathesis reaction below. List products of multiple catalytic cycles. Use as the starting catalyst, the generic carbene catalyst $[M]=CH_2$.

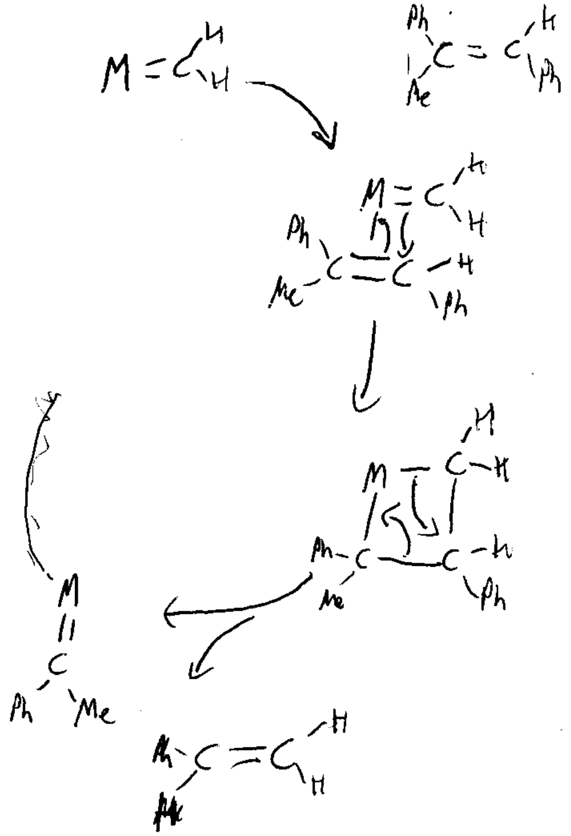
+5)





(b) Draw a catalytic cycle producing one of the products you listed above.

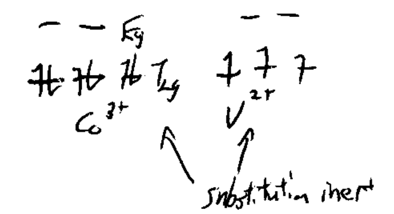
+5)



(5) Discuss the possibility for inner sphere electron transfer (in detail) in each system. If inner sphere electron transfer appears possible, how would it occur (what would the bound intermediate look like, etc).

$[Co(NH_3)_6]^{3+}_{(aq)} + [V(H_2O)_6]^{2+}_{(aq)} \text{------>} [Co(H_2O)_6]^{2+}_{(aq)} + [V(H_2O)_6]^{3+}_{(aq)}$

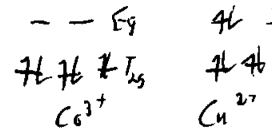
(+3)



Both of the starting materials are substitution inert, making the formation of a bridging intermediate sluggish. NH_3 ligands don't bridge metals and H_2O is a very poor bridging ligand so inner sphere electron transfer looks very remote.

$[Co(NH_3)_6]^{3+}_{(aq)} + [Cu(H_2O)_6]^{2+}_{(aq)} \text{------>} [Co(H_2O)_6]^{2+}_{(aq)} + [Cu(H_2O)_6]^{3+}_{(aq)}$

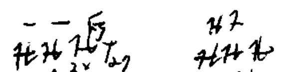
(+3)



Cu^{2+} is substitution labile, so it could lose a ligand to form a bridging species. Co^{3+}, however is substitutaion inert, so the bridging ligand would have to be NH_3, which is very unlikely.

Inner sphere electron transfer unlikely.

$[Ru(NH_3)_5I]^{+}_{(aq)} + [Cu(H_2O)_6]^{2+}_{(aq)} \text{------>} [Ru(NH_3)_5I]^{2+}_{(aq)} + [Cu(H_2O)_6]^{+}_{(aq)}$



Ru^{2+} is substitution inert, but possesses a decent bridging ligand, I^-, Cu^{2+} is substitution labile, so can lose a ligand and form a brigdel intermediate. Inner sphere electron transfer likely.

(+3)

$[(NH_3)_5Ru-I-Cu(H_2O)_5]^{3+}$

(6) Why is the concept of "hardness" and "softness" of acids and bases important? What is the property called "hardness"? How does the hardness of acids and bases relate to bonding?

Hardness & softness allows some quick & easy comparison of likely bond strengths + bonding character. Hardness is the inverse of polarizability. It is the resistance of the species to adding or losing electrons.

(+6)

Hard species don't form covalent bonds well and therefore form ionic bonds. Soft species are polarizable and form covalent bonds.

CHEM432 Take-Home Portion
Name______________________
You may use your class textbook and your notes for this section of the exam. This section is due on Monday, December 3 at 5:00 PM.

(7) $[Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$ ----> $[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+}$ $k = 4.2\ M^{-1}s^{-1}$

$[Ru(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$ ----> $[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+}$ $k = 4.0 \times 10^3\ M^{-1}s^{-1}$

$[Fe(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$ -------> $[Ru(NH_3)_6]^{3+} + [Fe(H_2O)_6]^{2+}$ $k = ?$

If $K_{12} = 2.1 \times 10^{11}$ for the reaction above, what is the value of k?

(+2)

$k_{12} = \sqrt{(4.2)(4.0\times10^3)M^{-2}s^{-2}(1)(2.1\times10^{11})}$

$k_{12} = 5.9 \times 10^7\ M^{-1}s^{-1}$

What would the value of K have to be for k to be $1 \times 10^7\ M^{-1}s^{-1}$

(+2)

$k = 1\times10^7\ M^{-1}s^{-1} = \sqrt{(4.2M)(4.0\times10^3)M^{-2}s^{-2}(1)(K_{12})}$

$1\times10^{14}\ M^{-2}s^{-2} = 1.68\times10^4\ M^{-2}s^{-2}\ K_{12}$

$5.9\times10^9 = K_{12}$

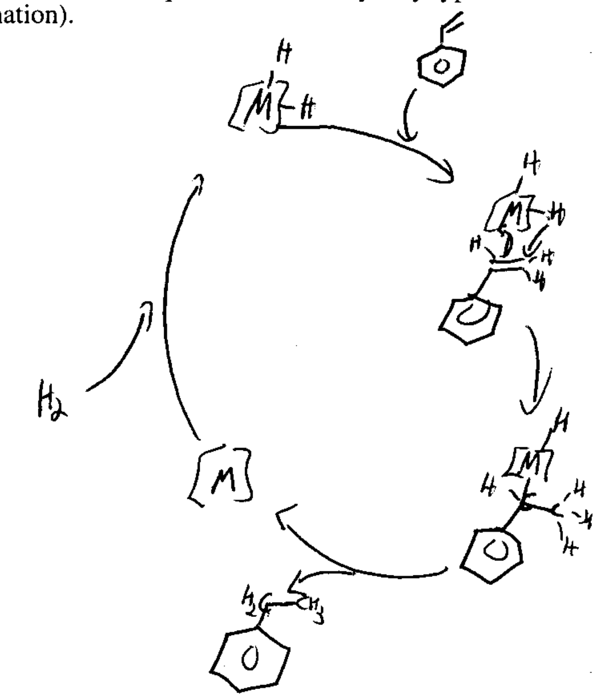
Which is the stronger oxidizing agent, $[Fe(H_2O)_6]^{3+}$ or $[Ru(NH_3)_6]^{3+}$ and why?

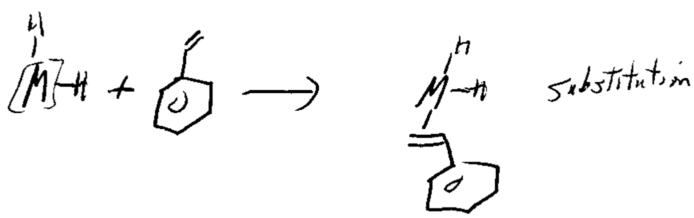
(+2)

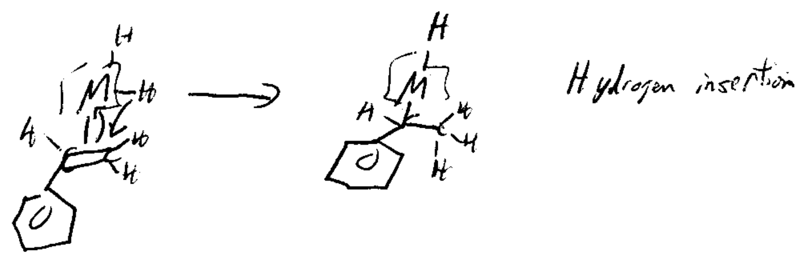
K_{12} is large, which means the equilibrium lies to the right. Therefore $[Fe(H_2O)_6]^{3+}$ is a better oxidizing agent than $[Ru(NH_3)_6]^{3+}$.

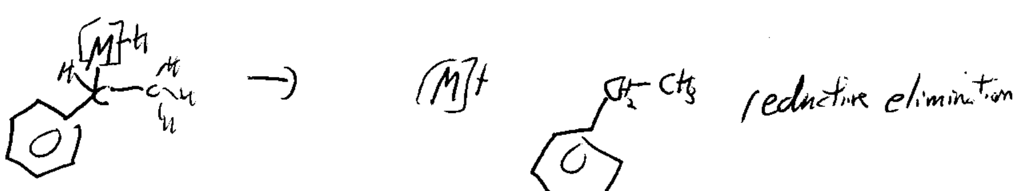
(8) Draw a catalytic cycle for the hydrogenation of styrene by a metal hydride catalyst. For each step in the cycle, write the equation and identfy they type of reaction (i.e. reductive elimination, or beta elimination).

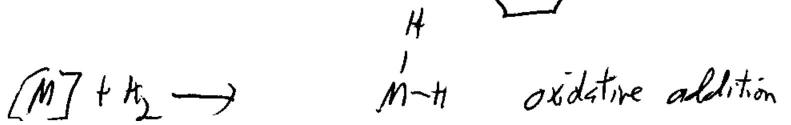
+8





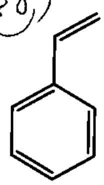






(8) Draw a catalytic process for the formation of a styrene trimer (three styrene units) by olefin polymerization. Start with a catalyst containing a hydride ligand.

+8



styrene