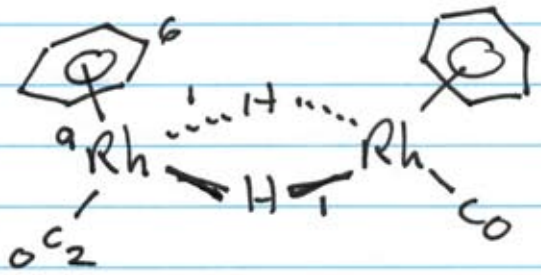
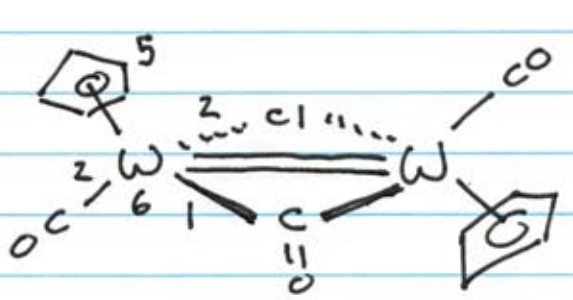
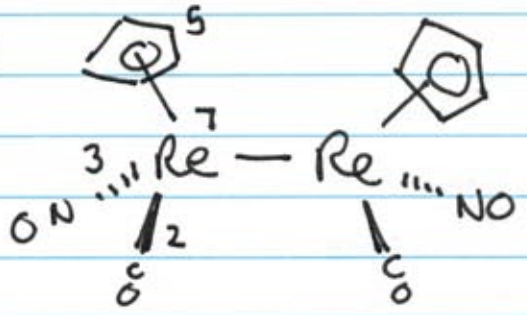
Chem 423/523 Midterm 1 Key

① a) 

Rh^+
18e⁻ without bond

b) 

W^+
16e⁻ without bond

c) 

Re^0
17e⁻ without bond

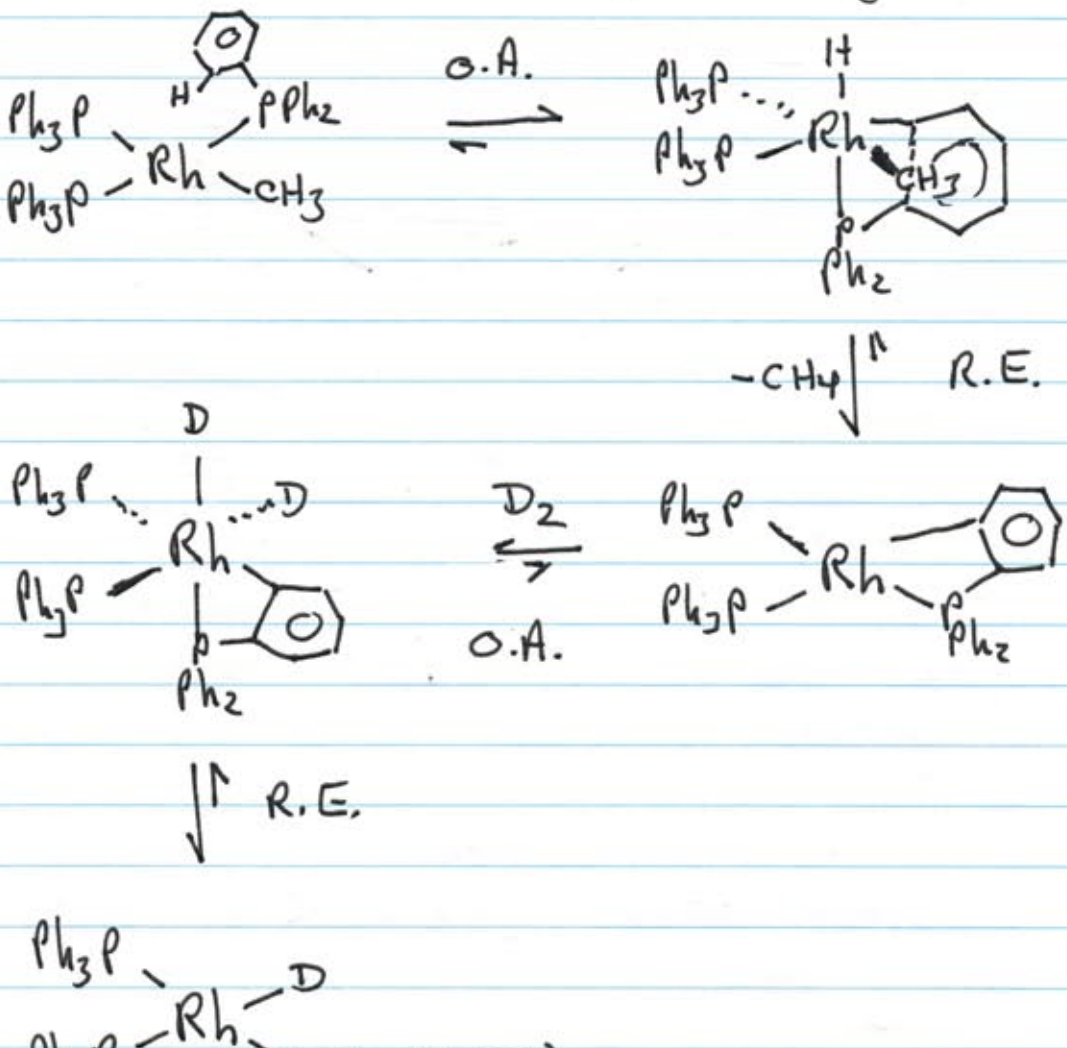
^+NO linear, isoelectronic 2e⁻ with CO so NO neutral is 3e⁻

② a) $W-H > W-CH_3$ better overlap and no nonbonding e⁻ density on H

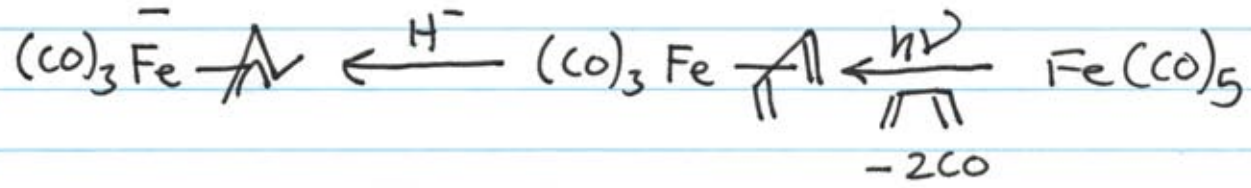
b) $Ta-CH_3 > V-CH_3$ bond strength increases down a triad due to better overlap

c) $Ti-CH_3 > Co-CH_3$ better orbital overlap and less nonbonding e⁻ density on early T.M.

(3) With Rh, this must be a sequence of oxidative-additions / reductive eliminations to explain the observed products. To see CH_4, oxidative-addn. of D_2 cannot happen first and the most logical place to get the required H to eliminate is from the o-hydrogen of one Ph group:



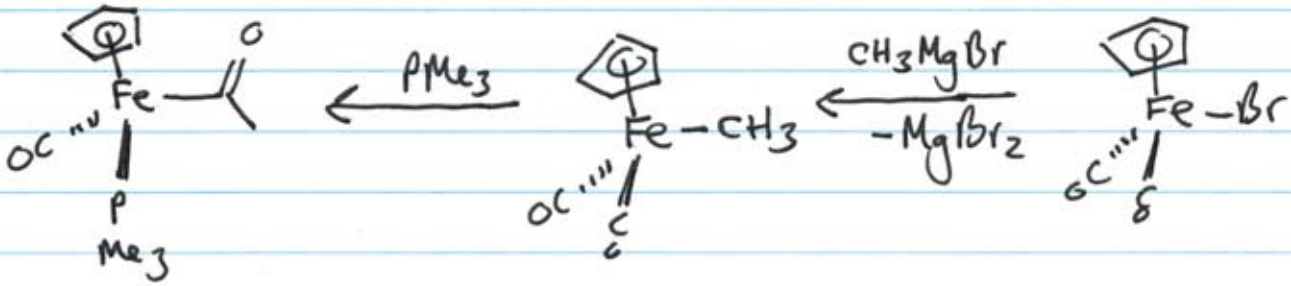
④ a)



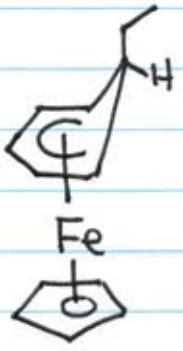
b) $Cr(CO)_6 \xleftarrow[\text{excess CO}]{\text{K metal}} CrCp_2$

$-2K^+Cp^-$

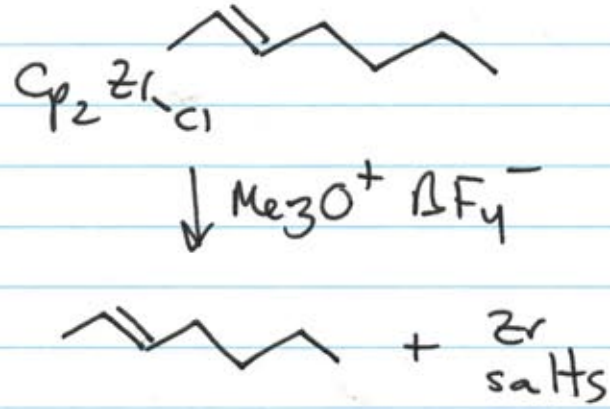
c)



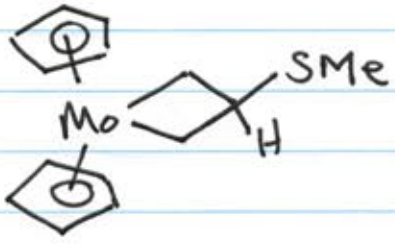
⑤ a)



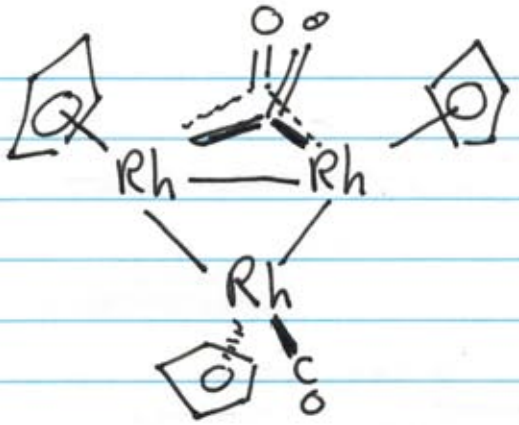
b)



c)

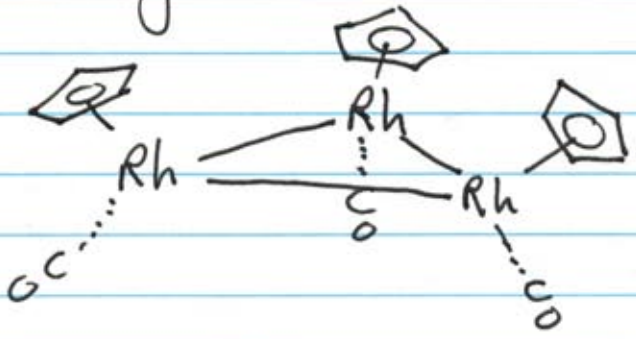


⑥ a)



b) Implies CO does not dissociate during exchange

c) Simplest explanation is that it simply goes through a symmetrical unbridged intermediate:



Any CO can then re-enter the bridge.

d) If you have rate data for each temperature, then you can plot $\ln(k/T)$ vs. $1/T$ and you should get a straight line with an intercept of $\Delta S^{\ddagger} - \ln(h/k_b)$

e) Likely small and positive. Since there is no dissociation involved, $\Delta S^{\ddagger}$ should be small. Probably positive because the lack of bridging CO means more degrees of freedom for bond rotations, bends (less constrained).