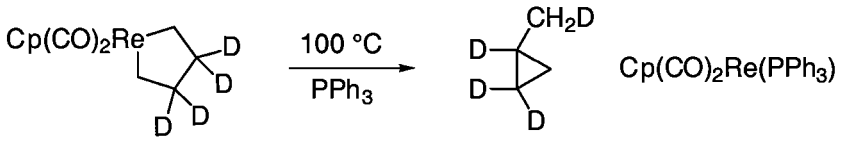
Massachusetts Institute of Technology

5.44: Organometallic Chemistry *Problem Set 2*

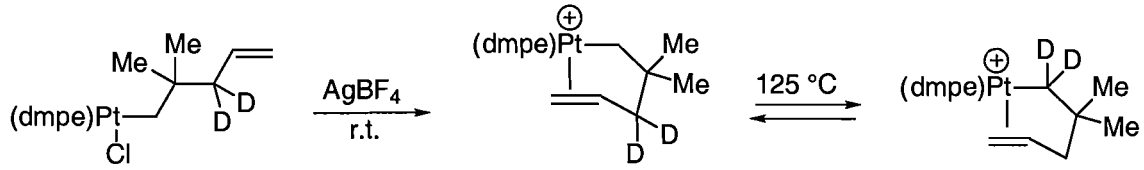
Due: Thursday, November 18, 2004

(1) Propose a mechanism for the illustrated reaction that is consistent with the following observations:

- The reaction is first-order in the starting material
- The reaction is zero-order in phosphine
- CO dissociation does NOT occur during the reaction

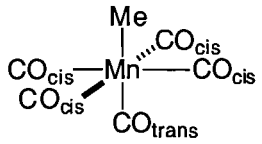


(2) When **A** is treated with Ag^+, **B** is formed. If **B** is heated, a 1:1 mixture of **B** and **C** is generated. Propose a mechanism for the conversion of **B** to **C**.

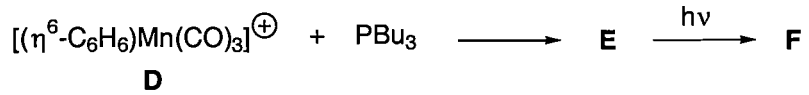


A **B** **C**

(3) Do you expect π-backbonding to CO_{trans} or CO_{cis} to be stronger? Briefly explain your reasoning, with the aid of diagrams that show the overlap between Mn d orbitals and CO π* orbitals. Note that Mn(+1) is a d^6 metal with filled d_{xy}, d_{xz}, and d_{yz} orbitals.

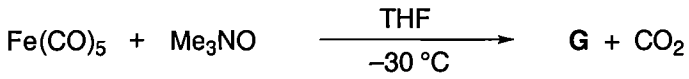


(4) Identify **E** and **F**.



	IR (cm^{-1})	^{1}H NMR (δ)
D	2080, 2026	6.90
E	2028, 1950	6.30 (1H) 5.50 (2H) 4.40 (1H) 3.40 (2H) plus resonances due to PBu_3
F	1997, 1950	6.42 plus resonances due to PBu_3

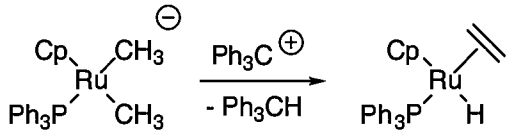
(5) Identify **G** and propose a mechanism for its formation.

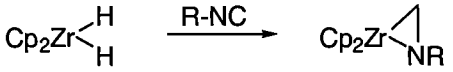


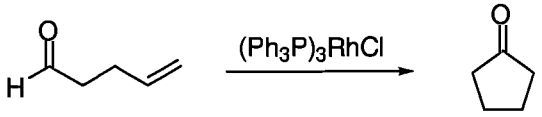
Data for compound **G**: M/e (M^+) = 227
IR (cm^{-1}): 2050, 1960, 1940-1920
^1H NMR (δ): 1.87 (s)
^{13}C NMR (δ): 217.5, 61.4

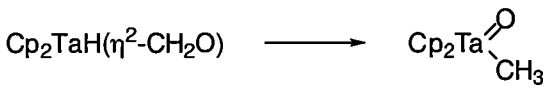
(6) Dissociation from NiL_4 is only very slight for L = $P(OMe)_3$, but almost complete for L = PMe_3. Given that the two ligands have very similar cone angles, discuss the factors that might be responsible for this behavior.

(7) Provide a mechanism. Please name each elementary step (e.g., ligand dissociation or β-migratory insertion).

(a)


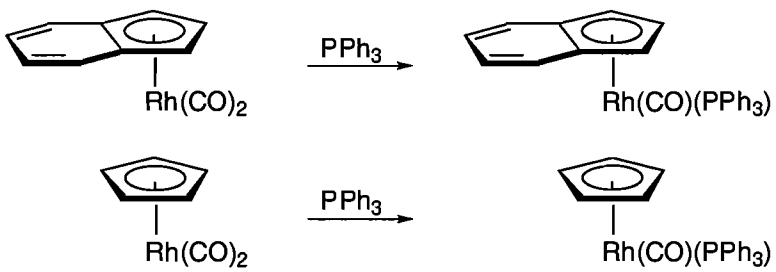
(b)


(c)


(d)


(8) $Na[Mn(CO)_5]$ reacts with allyl chloride to give **A** and **B**. The ^1H NMR spectrum of compound **A**, an 18-electron complex, shows proton resonances in three distinct magnetic environments. When heated, **A** gives off a gas (**C**) and converts to **D**, which has protons in two distinct magnetic environments. Identify compounds **A**, **B**, **C**, and **D**.

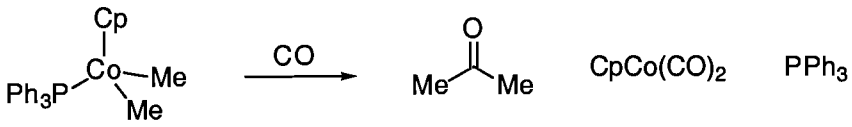
(9) (η^5-Cp)$Rh(CO)_2$ and (η^5-indenyl)$Rh(CO)_2$ undergo substitution by an associative pathway. The rate for the indenyl complex is ~10^8 times greater than for the Cp complex. Provide a succinct explanation for this difference in reactivity.



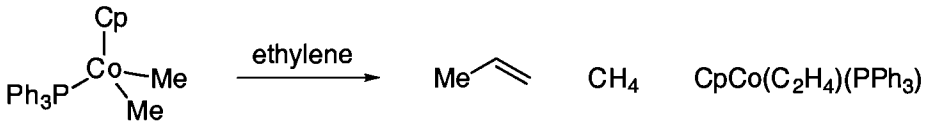
10^8 times faster

(10) Suggest a plausible mechanism for each of the following reactions. Name each elementary step (e.g., oxidative addition, reductive elimination...)

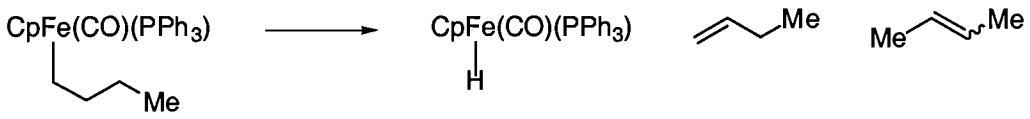
(a)



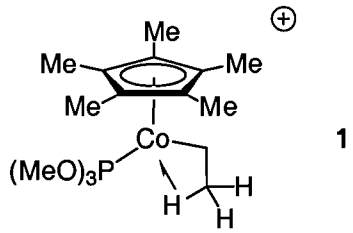
(b)



(11) Provide mechanisms for the formation of 1-butene and of 2-butene. Please name each elementary step (e.g., ligand dissociation or β-migratory insertion).



(12)



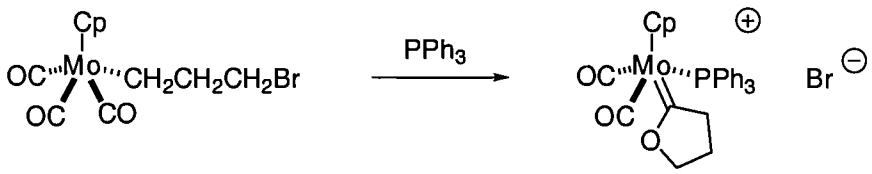
1

(a) In the ^{1}H NMR spectrum of cobalt complex **1** at very low temperature, three types of protons for the ethyl group are observed, with relative integrations of 1H, 2H, and 2H. Explain this observation.

(b) As the temperature increases, instead of three types of protons, only two types of protons (relative integrations of 2H and 3H) for the ethyl group of **1** are observed in the ^{1}H NMR spectrum. Provide a mechanism that accounts for this observation. Briefly explain your rationale. Note: Sixteen-electron complexes derived from **1** may be transiently accessible, but they are unstable relative to **1**.

(c) As the temperature further increases, to room temperature, a singlet for these five protons, integrating to 5H, is observed in the ^{1}H NMR spectrum of **1**. Provide a mechanism that accounts for this observation. Briefly explain your rationale.

(13) Please propose the best mechanism for the illustrated transformation. Name each elementary step.



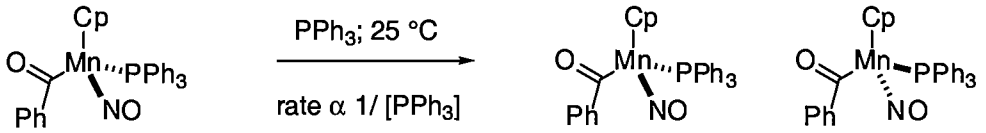
(14) $Fe(CO)_5$ loses CO very slowly, but the addition of aqueous acid greatly accelerates the loss of a CO ligand. Suggest the best explanation for this observation.

(15) NO serves as a useful ligand in organometallic chemistry. It is electronically flexible–able to serve as an X-type ligand or as an LX-type ligand. It adopts a bent geometry when it is an X-type ligand, and it adopts a linear geometry when it is an LX-type ligand.

(a) Draw the orbital interactions for a metal–NO complex wherein the NO is serving as an X-type ligand. *Hint:* The analysis for parts (a) and (b) may be easier when thinking in terms of the covalent model, rather than the ionic model.

(b) Draw the orbital interactions for a metal–NO complex wherein the NO is serving as an LX-type ligand.

(c) The enantiopure Mn complex illustrated below undergoes racemization:



enantiopure racemic

Propose a mechanism that is consistent with the rate being affected inversely by the concentration of added phosphine. Briefly explain your reasoning.