

**Test**

Question 1 \_\_\_\_\_/05 points

Question 2 \_\_\_\_\_/05 points

Question 3 \_\_\_\_\_/06 points

Question 4 \_\_\_\_\_/11 points

Question 5 \_\_\_\_\_/10 points

Question 6 \_\_\_\_\_/10 points

Question 7 \_\_\_\_\_/20 points

Question 8 \_\_\_\_\_/10 points

Question 9 \_\_\_\_\_/15 points

Question 10 \_\_\_\_\_/12 points

Question 11 \_\_\_\_\_/10 points

**TOTAL** \_\_\_\_\_/114 points

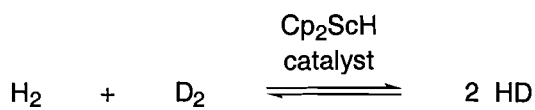
Name \_\_\_\_\_

There are 10 pages of questions (pages 2-11).

(1) (5 points, all or none) Please fill in the remainder of this portion of the periodic table.

Sc									

(2) (5 points) The compound  $\text{Cp}_2\text{ScH}$  catalyzes the reaction illustrated below. Please provide the best mechanism for this process. Name each elementary step (e.g., oxidative addition, reductive elimination...).



(3) (6 points total) The frontier molecular orbitals of carbon monoxide and methyl isocyanide are very similar to one other, and both serve as ligands for transition metals.

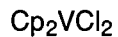


(a) (3 points) Which ligand would you expect to be the better  $\sigma$  donor? Briefly explain your reasoning.

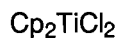
(b) (3 points) Which ligand would you expect to be the better  $\pi$  acceptor? Briefly explain your reasoning.

(4) (11 points total) For the indicated metal complexes, please provide:

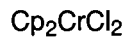
- (a) (2 points) the total electron count
- (b) (2 points) the formal oxidation state of the metal
- (c) (2 points) the  $d^n$  electron count (i.e., give  $n$ )
- (d) (2 points) the  $ML_aX_b$  assignment (i.e., give  $a$  and  $b$ )



- (a)
- (b)
- (c)
- (d)
- (e) Would you expect this metal center to behave as a Lewis acid, a Lewis base, or a radical?  
Succinctly explain your reasoning.

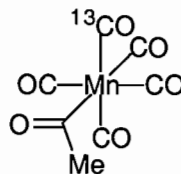
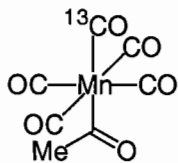


- (a)
- (b)
- (c)
- (d)
- (e) Would you expect this metal center to behave as a Lewis acid, a Lewis base, or a radical?  
Succinctly explain your reasoning.



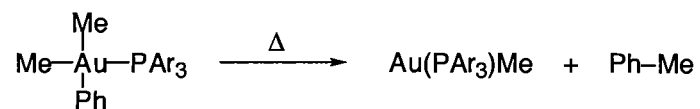
- (a)
- (b)
- (c)
- (d)
- (e) Would you expect this metal center to behave as a Lewis acid, a Lewis base, or a radical?  
Succinctly explain your reasoning.

(5) (10 points) In class, in the context of a mechanistic study of  $\alpha$ -migratory insertion, we discussed IR data for the two compounds illustrated below. For one complex,  $\nu(^{13}\text{CO})$  was  $1976\text{ cm}^{-1}$ , and for the other complex  $\nu(^{13}\text{CO})$  was  $1949\text{ cm}^{-1}$ .



For each structure, please provide the  $\nu(^{13}\text{CO})$  stretching frequency ( $1976$  or  $1949\text{ cm}^{-1}$ ). Briefly explain your reasoning, **with the aid of diagrams that show interactions between Mn d orbitals and ligand orbitals.**

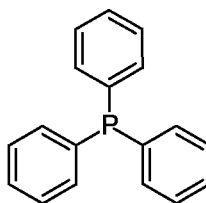
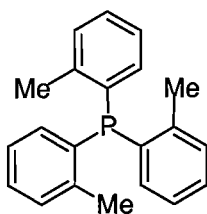
(6) (10 points) The illustrated reaction proceeds more slowly in the presence of added  $\text{PAr}_3$ .



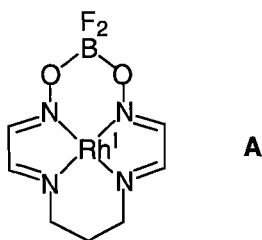
(a) (4 points) Provide the best mechanism for the reaction. Please name each elementary step (e.g., oxidative addition, reductive elimination...).

(b) (3 points) Based on the above observation, is it possible to conclude which step is rate-determining? Please succinctly explain your reasoning.

(c) (3 points) With which phosphine would the reaction proceed more rapidly? Please succinctly explain your reasoning.



(7) (20 points total) For our purposes, the interesting ligand illustrated below is inflexible, occupying a square plane around the Rh(I) metal center.



(a) (4 points) Draw the oxidative addition product of a generic species, X–Y, to complex **A**. Please assume that both X and Y are bound to rhodium. What is the geometry around rhodium (e.g., trigonal, trigonal bipyramidal, tetrahedral...)?

(b) (2 points each, 4 points total)

H<sub>2</sub>: Based on your answer in part (a), would you expect H<sub>2</sub> to oxidatively add to **A**? Please succinctly explain your reasoning.

MeI: Based on your answer in part (a), would you expect MeI to oxidatively add to **A**? Please succinctly explain your reasoning.

(c) (3 points) What are the three common pathways for oxidative addition?

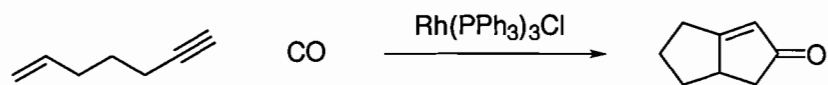
(7) (d) (3 points each, 9 points total) Please suggest three conceptually distinct experiments, each of which would allow you to rule out at least one of the three possible pathways for oxidative addition to **A**. Succinctly explain your reasoning.

Experiment #1:

Experiment #2:

Experiment #3:

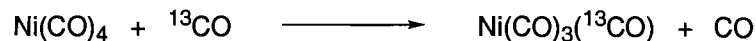
(8) (10 points) Provide the best mechanism for the illustrated reaction. Please name each elementary step (e.g., oxidative addition, reductive elimination...).





(9) (15 points total)

(a) (6 points total) The rate law for CO exchange in  $\text{Ni}(\text{CO})_4$  is:  $\text{rate} = k [\text{Ni}(\text{CO})_4]$ .

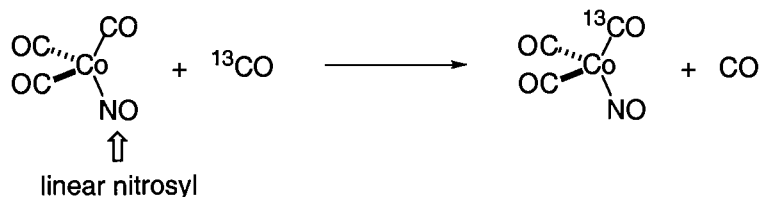


(1 point) Provide the total electron count of  $\text{Ni}(\text{CO})_4$ :

(1 point) Provide the the  $d^n$  electron count of Ni (i.e., give n):

(4 points) Provide the best mechanism for the reaction that is consistent with the rate law. Please name each elementary step (e.g., oxidative addition, reductive elimination...).

(b) (6 points total) The rate law for CO exchange in  $\text{Co}(\text{CO})_3(\text{NO})$  is:  $\text{rate} = k [\text{Co}(\text{CO})_3(\text{NO})] [\text{CO}]$ .



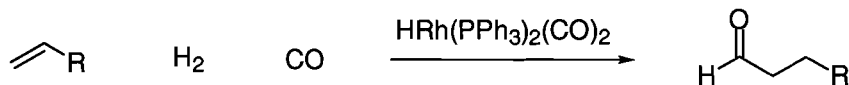
(1 point) Provide the total electron count of  $\text{Co}(\text{CO})_3(\text{NO})$ :

(1 point) Provide the the  $d^n$  electron count of Co (i.e., give n):

(4 points) Provide the best mechanism for the reaction that is consistent with the rate law. Please name each elementary step (e.g., oxidative addition, reductive elimination...).

(c) (3 points) Please provide a succinct explanation for why the nickel and cobalt complexes proceed through different pathways.

(10) (12 points total) Hydroformylation of olefins is a very important industrial process.



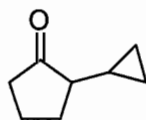
(a) (8 points) Using elementary steps that we have discussed in class, suggest a mechanism for this transformation. Please name each elementary step (e.g., oxidative addition, reductive elimination...).

(b) (4 points) If a  $\text{PEt}_3$  complex is used instead of a  $\text{PPh}_3$  complex, the reaction rate slows down. Based on the mechanism that you provided in part (a), provide a rationale for this observation.

(11) (10 points total) Provide the best mechanism for the formation of the illustrated products. Please show each elementary step.



(a) (5 points)



(b) (5 points)

