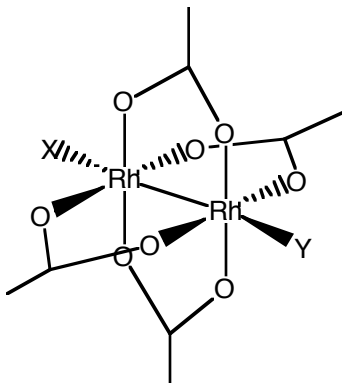


## Chem 450 Practice Exam

(1) In the following molecule, the rate of substitution of Y was studied. It was found to be independent of the entering group. The dependence on the leaving group, Y, and the ligand trans to the leaving group, X, is shown below. What is the mechanism for this reaction and why did you choose that one?

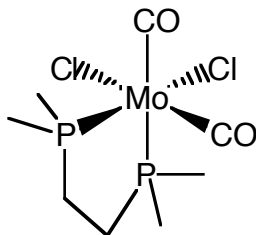


X	Y	$k/(\text{L mol}^{-1} \text{s}^{-1})$
H <sub>2</sub> O	H <sub>2</sub> O	$10^5-10^7$
CH <sub>3</sub> OH	CH <sub>3</sub> OH	$2 \times 10^6$
CH <sub>3</sub> CN	CH <sub>3</sub> CN	$1.1 \times 10^5$
PPh <sub>3</sub>	PPh <sub>3</sub>	$1.5 \times 10^5$
CH <sub>3</sub> CN	PR <sub>3</sub>	$10^7-10^9$
PR <sub>3</sub>	CH <sub>3</sub> CN	$10^{-1}-10^2$
N-donor	H <sub>2</sub> O	$10^2-10^3$

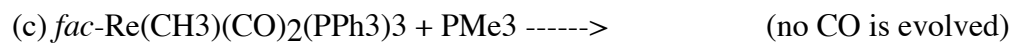
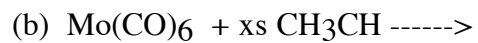
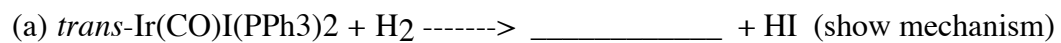
Note that the complex has a  $d^7$  configuration at each Rh and a single Rh—Rh bond.

from Shriver and Atkins, *Inorganic Chemistry* third ed.

(2) Draw a mechanism that would make the CO ligands in the following molecule equivalent in NMR.



(3)(25 pts) Predict the product(s) of the following reactions and write the type of reaction it is (substitution, etc).



(d) *trans*-CrI<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> + 2PPh<sub>3</sub> ----->  
(draw correct isomer)

(e) (□<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(Et)(CO)<sub>2</sub> -----> \_\_\_\_\_ + CH<sub>2</sub>CH<sub>2</sub> (show mechanism)

(4) Count the electrons in the following species

(a) Re(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>

(b) Mn(CO)<sub>6</sub><sup>+</sup>

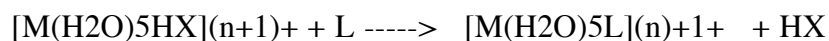
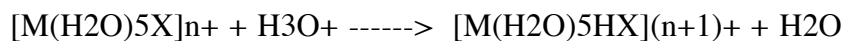
(c) (□<sup>3</sup>-C<sub>5</sub>H<sub>5</sub>)Ir(PPh<sub>3</sub>)<sub>3</sub>

(5)(15 pts) For the reaction below, the following kinetic data was found.  
 $ML_6 + Y \rightarrow ML_5Y + L$

L for (Y=CO)	Relative Rate	$\Delta S^\ddagger$
NMe <sub>3</sub>	110	75
NH <sub>3</sub>	20	55
PPh <sub>3</sub>	2	40
Cl <sup>-</sup>	199	-30
NO <sub>2</sub> <sup>-</sup>	203	-35
OH <sup>-</sup>	209	-10

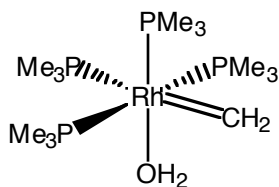
Explain the following data with respect to possible mechanisms.

(6)(15 pts) Some substitutions can be accelerated by acid in solution. The acid protonates the outgoing ligand, decreasing the metal-ligand bond strength.

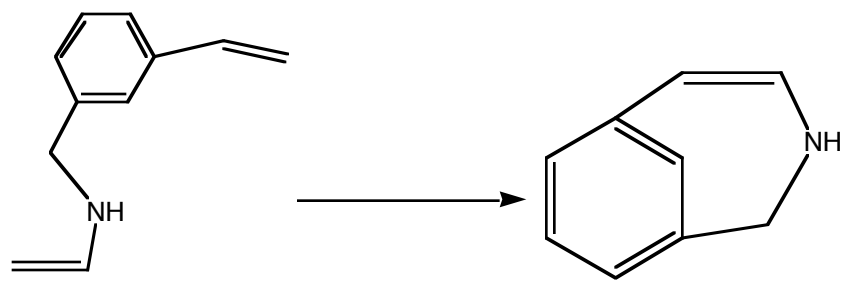


For which of the following ligands, decide which one should show the greatest acceleration of substitution rate by the addition of acid and explain why.

X	K <sub>b</sub>
F <sup>-</sup>	1.4 x 10 <sup>-11</sup>
S <sup>2-</sup>	0.083
CN <sup>-</sup>	1.7 x 10 <sup>-5</sup>



(7) The molecule catalyzes the following reaction.



Write a mechanism for the reaction.