Solutions to Problems - Section 4

12.7 Remember that Cu^{2+} is a d^9 system, which is susceptible to a Jahn-Teller distortion. Therefore, there is an elongation of the axial positions (so $Cu(H_2O)_6^{2+}$ has D_{4h} symmetry, not O_h), so there are two types of Cu-O bonds, axial and equatorial. Therefore there are two exchange rates.

12.13 Assuming these are all square planar,

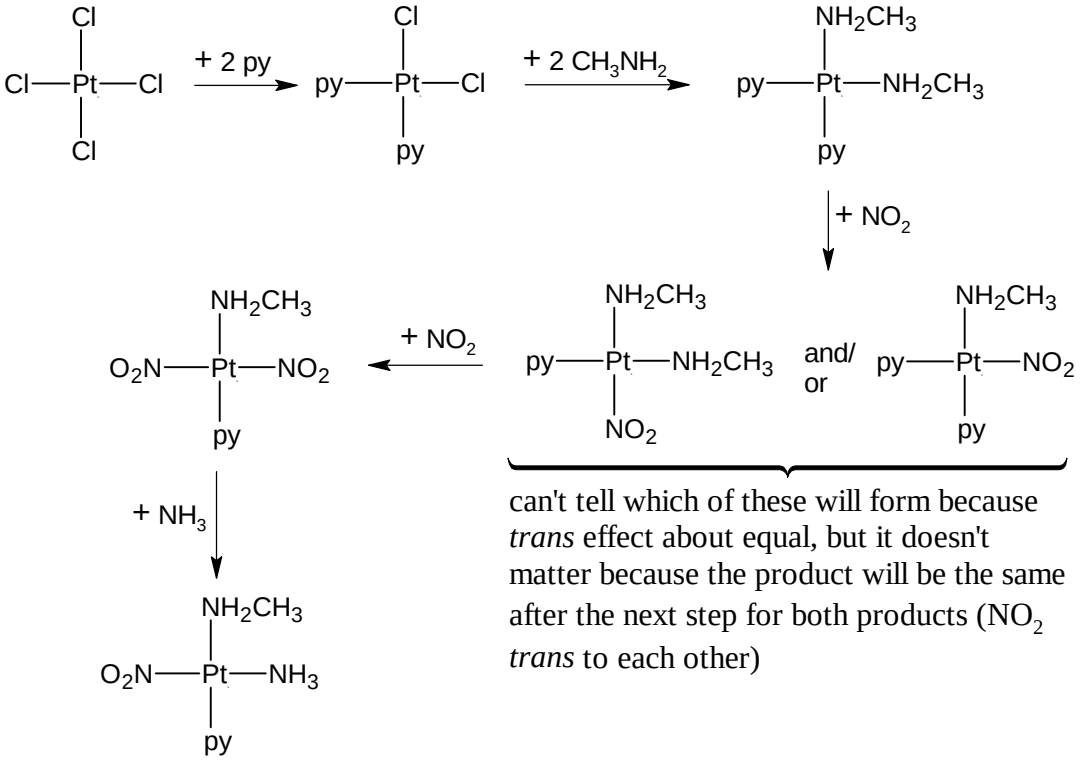
(a) *trans*-$[Pt(CO)(NH_3)Cl_2]^-$ because CO has highest *trans* effect

(b) *cis*-$[Pt(NH_3)_2Br_2]^-$
Br^- has the stronger *trans* effect, and it can either push a Br^- or an NH_3 off the original species. Pushing NH_3 off and replacing with another NH_3 leads to no net change. Pushing off another Br^- gives the *cis* product.

(c) *trans*-$[(C_2H_4)Pt(NH_3)Cl_2]^-$ because ethene has higher *trans* effect

12.14 NOTE: According to the *trans* effect series in the text (p. 440), Cl^- should have a stronger *trans* effect than NH_3 (and py, and CH_3NH_2), but, in fact, it is weaker (see Fig. 12-12 (h)).

(a) Here is one option:



can't tell which of these will form because *trans* effect about equal, but it doesn't matter because the product will be the same after the next step for both products (NO_2 *trans* to each other)

NOTE: because NH_2CH_3, NH_3, and py are all about the same *trans* effect, whatever ligands you use in steps 1 and 2 will give different products (NO_2 must be 3rd step)

14.4 A = $CpFe(CO)_2H$
B = H_2 (colourless gas) and C is a dimer $[CpFe(CO)_2]_2$
D = $CpFe(CO)_2I$
E = $Cp_2Fe(CO)_2$ (one Cp must be η^1 in this structure, which is what the reagent CpTl does)
F = ferrocene, Cp_2Fe

14.8 This is a cone angle question. Cone angle is in the order of $PPh_3 > PBu_3 > P(OPh)_3 > P(OMe)_3$

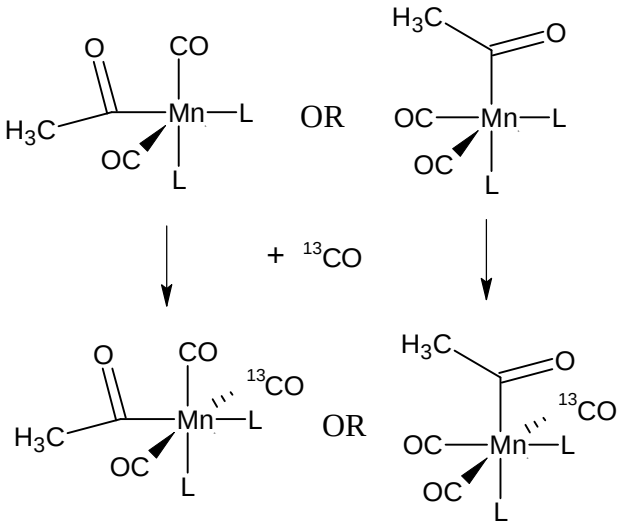
Therefore, PPh_3 comes off easiest, so $Cr(CO)_4(PPh_3)_2$ will react the most quickly with CO.
$P(OMe)_3$ is smallest, so $Cr(CO)_4(PPh_3)(POMe_3)$ will react slowest.

14.9 Another cone angle question.
from largest to smallest cone angle (and therefore *K*), $PPh_3 > PMePh_2 > PEt_3 > PMe_3$

14.10 If the complex can undergo carbonyl exchange (with decarbonylation $^{13}C(=O)\text{-}CH_3$), you would expect a mixture of ^{13}CO and ^{12}CO.

If the complex loses CO *first* and then undergoes cobonyl exchange, all the lost CO would be ^{12}CO. (Which is, in fact, the case in this system.)

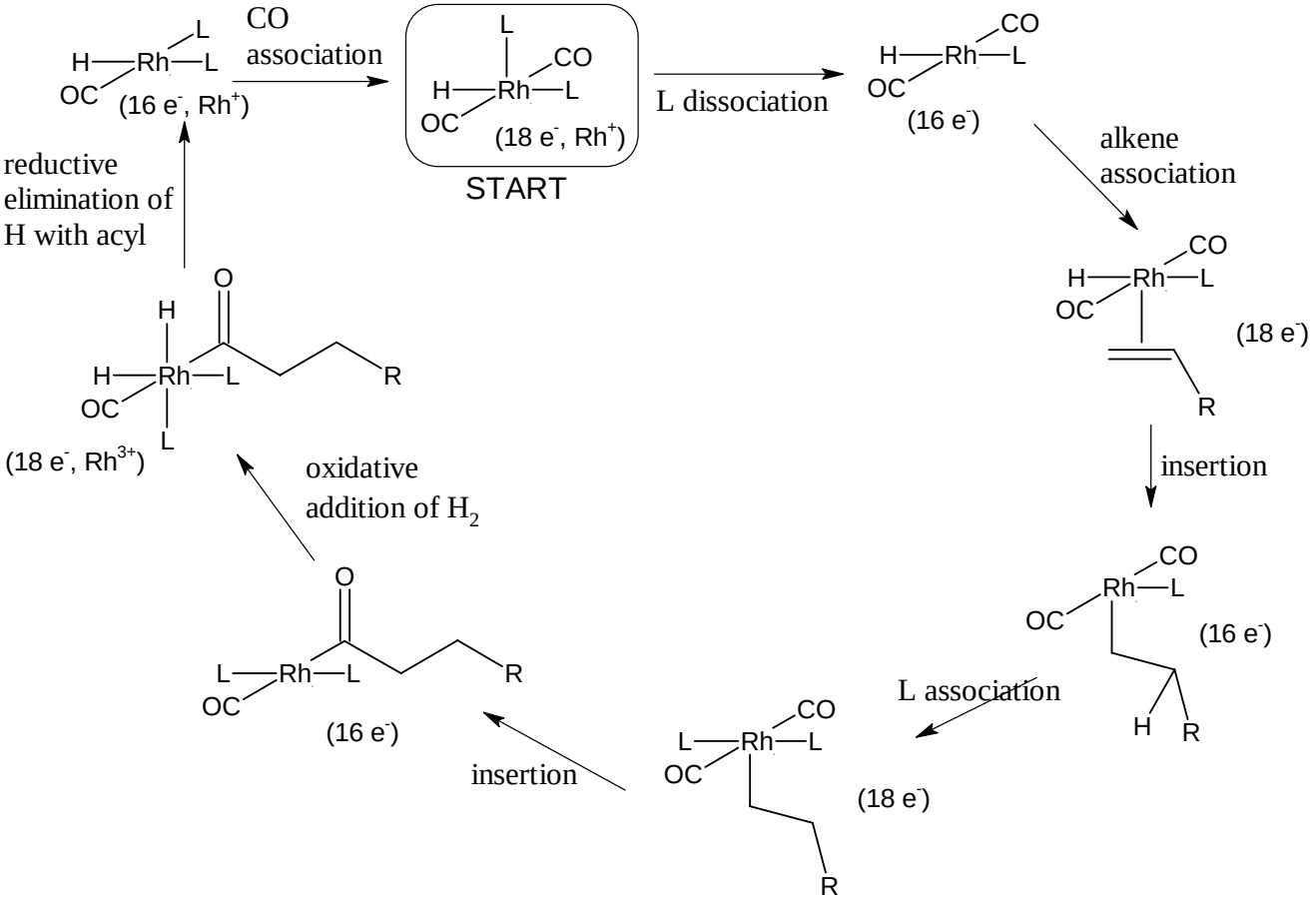
14.11 (a) First step is migration of the CH_3 onto a *cis* CO. There are two choices for the intermediate:



These are optical isomers.

(b) The new peak is an acyl (carbonyl) stretch, which should be around 1630 cm^{-1}.
(according to question 14-5, acyl stretches are at 1630, carbonyl CO's are at 1920)

14.19 The necessary alkene is, therefore, 1-butene. L = PPh_3, R = ethyl. Basically, you just need to follow the diagram 14-15. If I asked this question on the exam, I would specifically mention that H_2 and CO must be continuously added to the reaction mixture to allow the reaction to continue.



14.21

