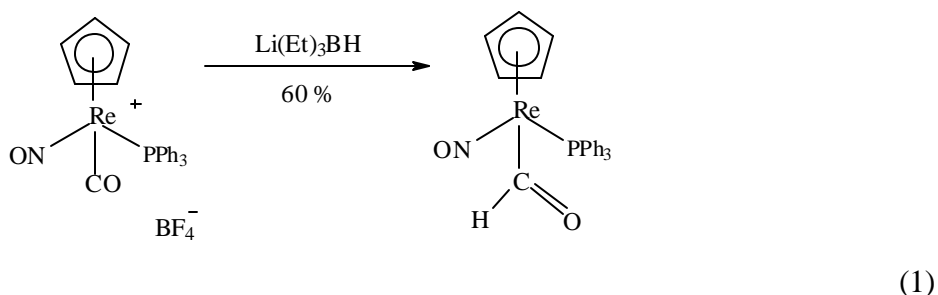


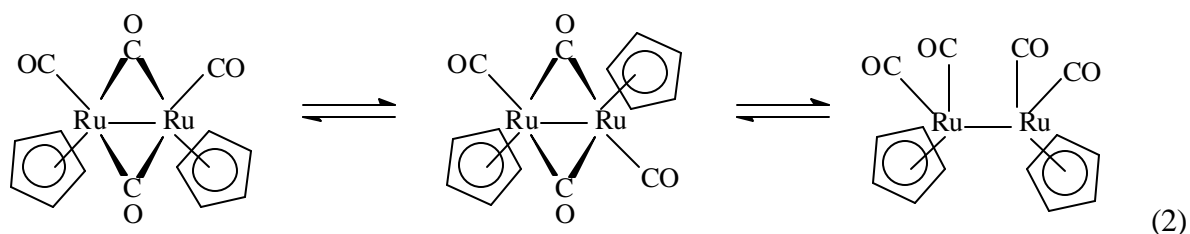
Chem 315, Fall 2001

Answers to Problem Set #9

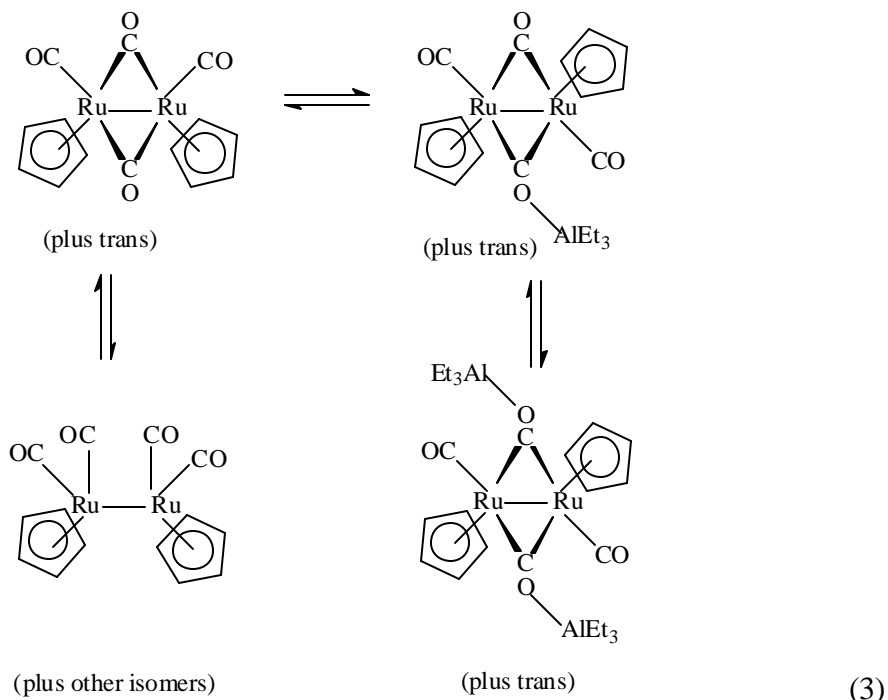
16.1. Oops, there is a typo in a problem: it should read  $\text{Li}(\text{Et})_3\text{BH}$ , and not what the textbook says. Anyway, we deal with a strong nucleophile, which means nucleophilic attack:



16.4. The three existing isomers, present in solution in the fairly comparable amounts are:



The reactions described in the paper are:



As you can expect, upon a reaction there will be a change of the frequency of single bridging-CO species in the *cis*- and *trans*- forms. Two aluminum alkyl groups are attached to the two bridging carbonyls. Three types of concentration bands are observed, but problem deals only with the type III bands, at large  $\text{AlEt}_3$  concentrations (those with a large separation between  $2046\text{ cm}^{-1}$ ,  $2011\text{ cm}^{-1}$ ,  $2006\text{ cm}^{-1}$ , and  $1679\text{ cm}^{-1}$  lines). These bands will dominate the spectrum at large  $\text{AlEt}_3$  concentrations (*think why*). Authors conclude, that the coordination of to the bridging carbonyls

is a driving force for the isomerization of non-bridged isomer to bridged ones (1:1 and 1:2 adducts).

**17.1.**

- a) true;
- b) false
- c) true
- d) true

**Ex. 16.1.**

- a) Iron(0) pentacarbonyl or pentacarbonyliron (0), trigonal bipyramidal structure; 18 electrons;
- b) Nickel(0) tetracarbonyl or tetracarbonylnickel (0), tetrahedral structure, 18 electrons;
- c) Molybdenum(0) hexacarbonyl or hexacarbonylmolybdenum (0), octahedral structure, 18 electrons;
- d) Decacarbonyldimanganese (0),  $D_{4d}$  structure, where each Mn atom has nearly octahedral geometry, 18 electrons;
- e) Vanadium(0) hexacarbonyl or hexacarbonylvandium (0), octahedral structure, 17 electrons. Note: the deviation from 18 electron rule is typical for early transition metals, where you can find really weird electron counts.
- f) Trichloro(ethylene)platinate(-1); square-planar complex, 16 electrons.

**Ex. 16.4.** see Ex. 16.1 for the answers for the first part of exercise.

$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$  has only 17 electrons. This cationic species is called ferrocenium ion, and requires a charge stabilization by a counterion.

$[\text{Fe}(\text{CO})_4]^{2-}$  is isoelectronic with iron(0) pentacarbonyl and has 18 electrons.

$\text{Co}_2(\text{CO})_8$  has 36 electrons total, giving 18 electrons per each Co-part.

**Ex. 17.1.**

- a) typical catalytic hydrogenation reaction, here we deal with heterogeneous catalysis;
- b) not a catalytic reaction: the energy needed is provided by an electric arc;
- c) not a catalytic reaction, also.

**Ex. 17.5.**

This is a bit tricky question: despite the name “Wilkinson catalyst”, it is not a catalyst, but rather a catalytic precursor. In order to generate catalyst, Rh-complex has to undergo intermolecular exchange (phosphine ligand is substituted with a solvent molecule), which is the rate determining step. Increased concentration of phosphine shifts the equilibrium and slows down this step, which leads to slowing down the whole process.