Chemistry 652

Organometallic Chemistry

Final Examination, May 26, 2015

Please write your answers directly in the spaces provided.

Name: Key

1) ____

2) ____

3) ____

4) ____

5) ____

6) ____

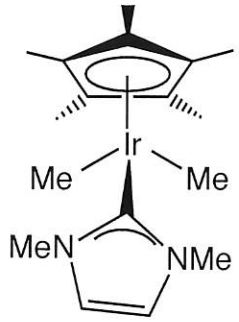
7) ____

8) ____

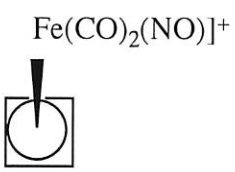
Total: ____

Have a productive summer!

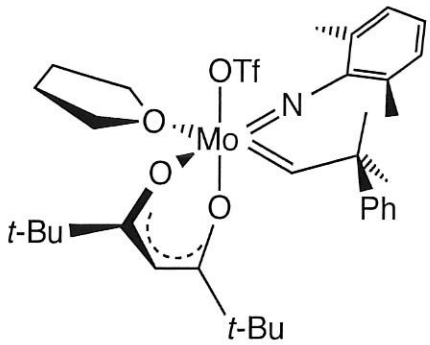
1) (20 points) For each of the following organometallic compounds, give the electron count, the formal oxidation state of the metal, and the d^n configuration.



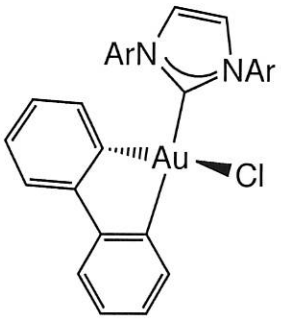
18e
+III
d^6



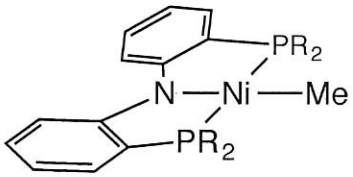
18e
+II
d^6



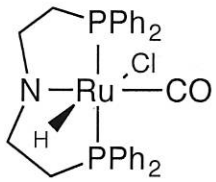
16e
+VI
d^0



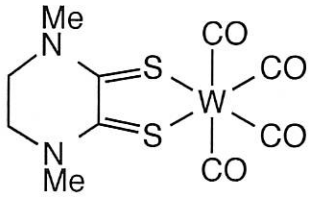
16e
+II
d^8



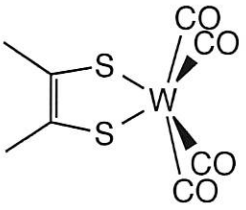
16e
+II
d^8



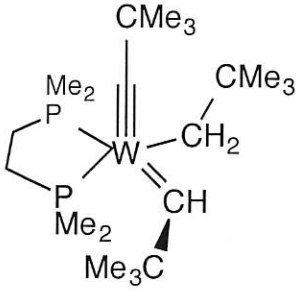
17e
+III
d^5



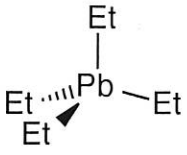
18e
0
d^6



16e
+II
d^4



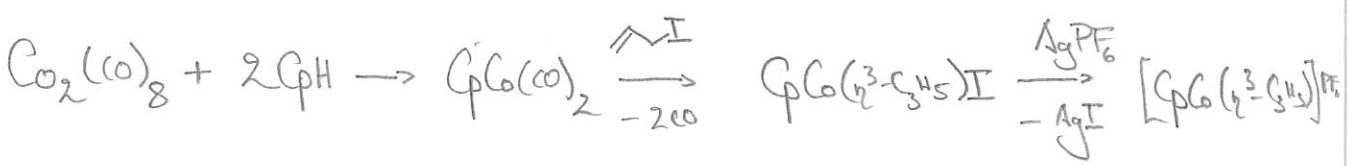
16e
+VI
d^0



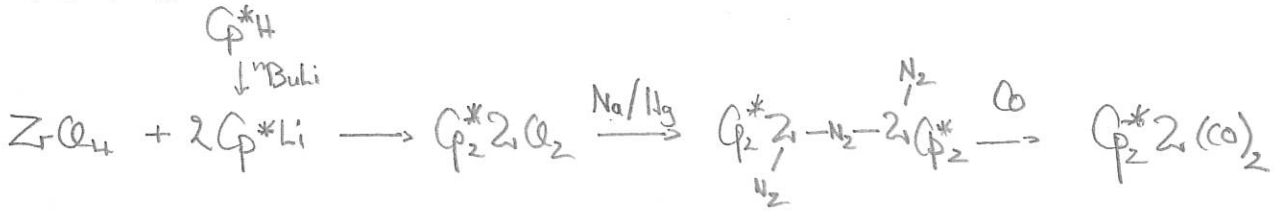
18e
+IV
d^{10}

2) (15 pts). Using only <u>simple starting materials</u> (i.e. metals, stable metal halides, homoleptic metal carbonyls, and commercially available organic reagents), design and outline synthetic procedures for the synthesis of the following compounds:

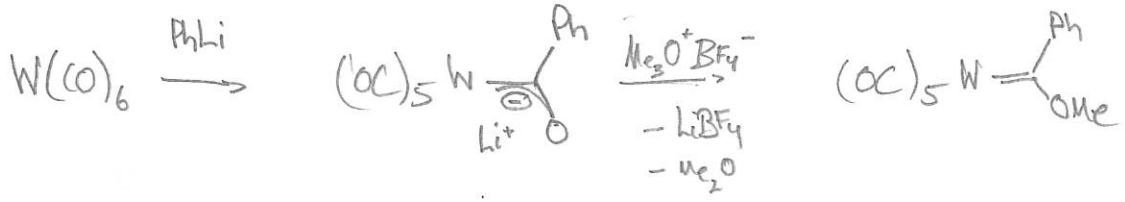
a) $[CpCo(\eta^3\text{-}C_3H_5)]PF_6$



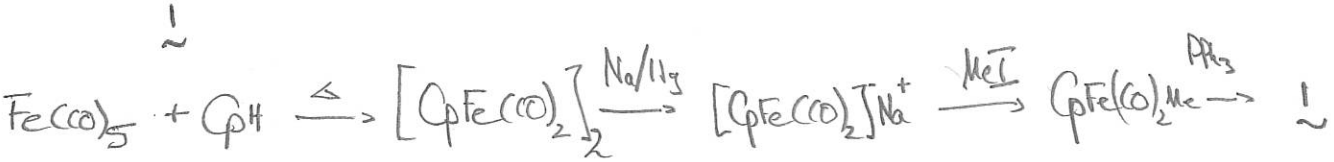
b) $Cp^*_2Zr(CO)_2$



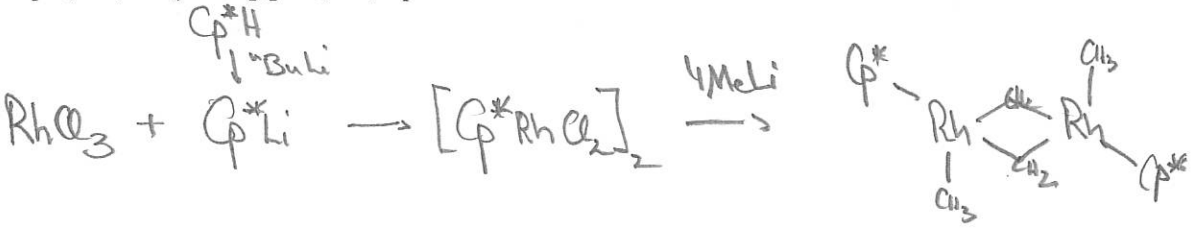
c) $(OC)_5W{=}C(OMe)Ph$



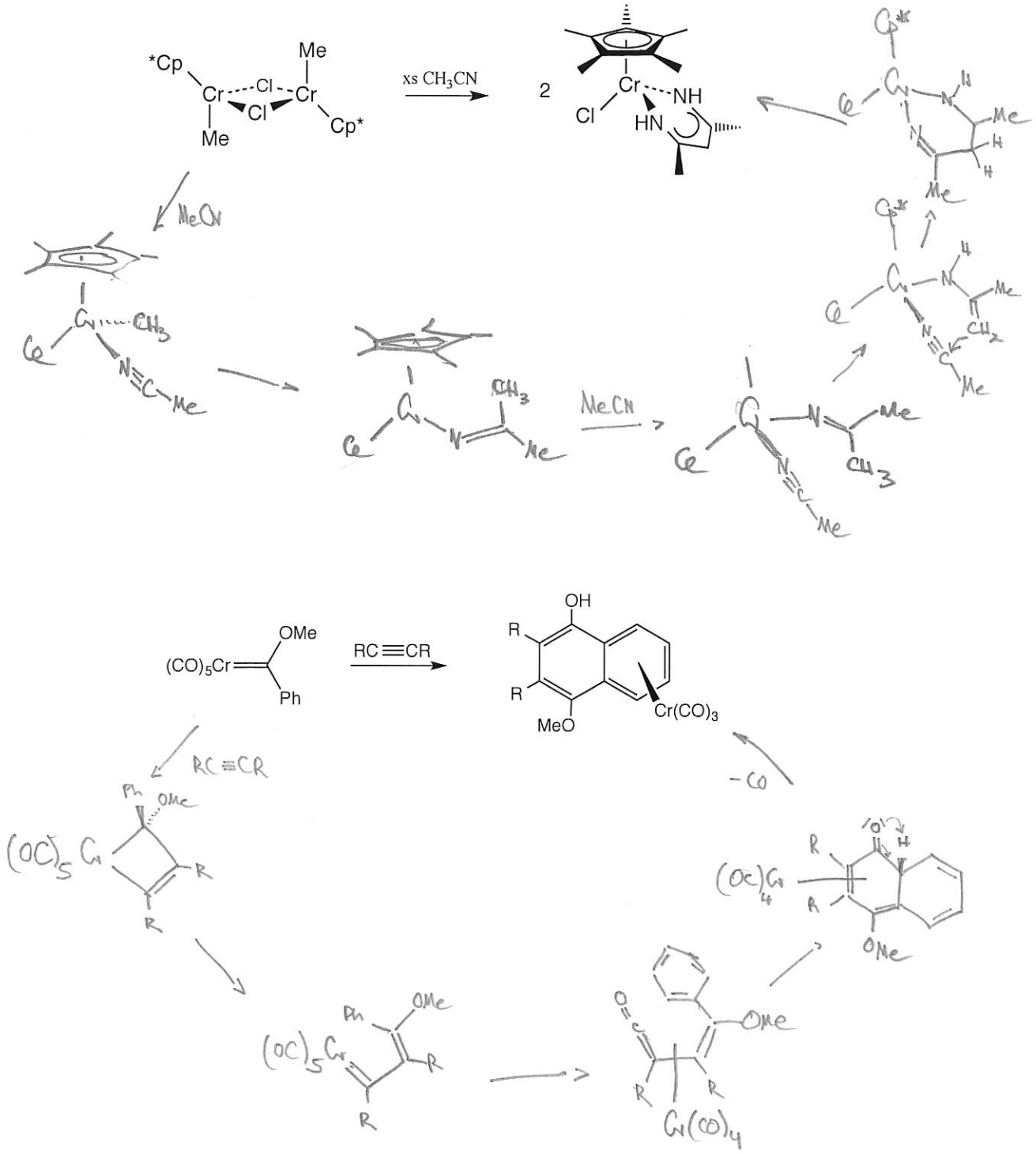
d) $CpFe(PPh_3)(CO)(C(O)Me)$



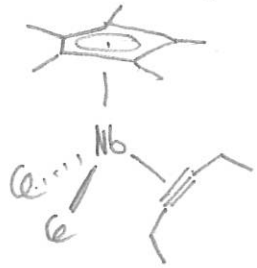
e) $Cp^*(Me)Rh(\mu\text{-}CH_2)_2Rh(Me)Cp^*$



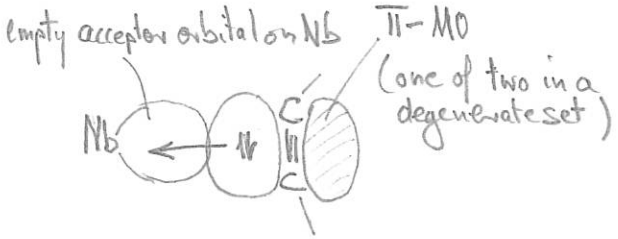
3) (10 points) Draw reaction mechanisms for the two transformation shown below. Show structures of proposed intermediates Keep track of unusual charges, oxidation states and electron counts, to avoid mistakes.



4) (10 points) The compound Cp*Nb(η^2-3-hexyne)Cl_2 is an example of an electron deficient early metal organometallic. The alkyne in this complex is best considered to be a 4-electron donor. Discuss – and draw pictures of the relevant orbitals – of all interactions between niobium and 3-hexyne that contribute to the chemical bonding.



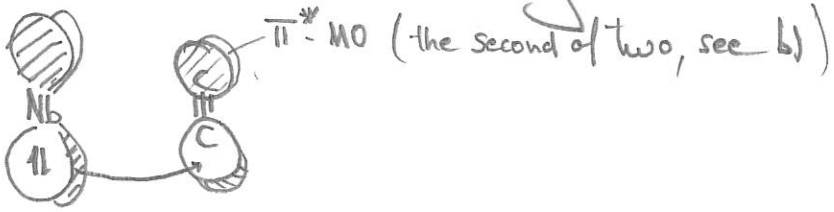
a) σ-donation



b) π-backbonding

c) π-donation

d)



5) (15 points) Consider the mechanism of the reductive elimination of mercury dialkyls, RHgR'. The following observations provide relevant information:

i) "When a solution of isobutyl(neopentyl)mercury in CCl_4 is heated, metallic mercury is formed as a shiny globule along with equimolar amounts of chloroform and neopentylchloride (NpCl). In addition, isobutene is observed

ii) Only traces of isobutylchloride are formed and neither isobutyl- nor neopentyl-mercuric chloride is found.

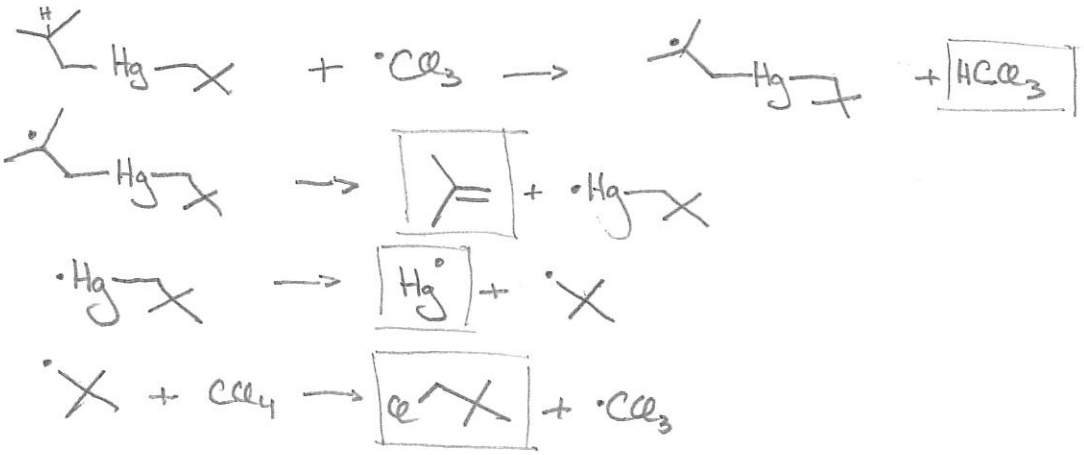
iii) Decomposition of mercuracycloheptane yields discrete amounts of cyclopentylmethylchloride.

iv) The reaction is markedly accelerated by the addition of small amounts of AIBN (i.e., azobisisobutyronitrile), and it is inhibited by galvinoxyl or *o,o'*-di-*tert*-butyl-*p*-cresol.

Identify the mechanism of this reductive elimination. Write a series of reaction steps rationalizing the observed products, and explain how observations i) – iv) support your mechanistic assignment.

This reductive elimination proceeds by a 'free radical chain mechanism'

i.e.:



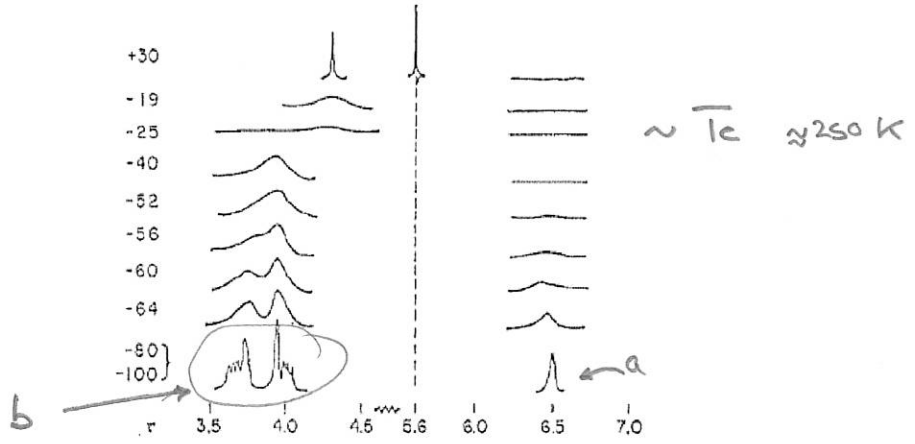
This mechanism explains the formation of all products listed in i) - see boxes

The tertiary C-H of ^{i}Bu is the weakest C-H bond in the molecule, leading to elimination

The mercuracycloheptane forms hexenyl radical, which rearranges to 

The effect of known radical initiators and radical traps indicates the occurrence of a radical chain rxn.

6) (10 points) Shown below are the ^{1}H NMR spectra (note: shifts given on the τ scale) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ (**1**) in CS_2 at various temperatures. The position and width of the $(\eta^5\text{-}C_5H_5)$-resonance at t ~ 5.6 are essentially invariant.

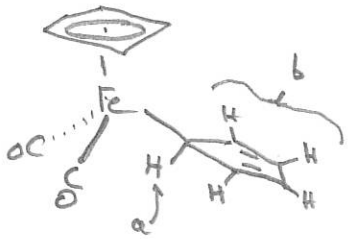


i) Draw the structure of **1**, and assign the resonances observed in the low temperature spectrum.

ii) What process is responsible for the temperature dependence of the spectra?

iii) Estimate the free energy of activation for this process.

i)



ii) The process is a series of 1,5-shifts of the Fe around the η^1-bound Cp which eventually equilibrates all its H-atoms on the NMR time scale
=> a fluxional process, thus a coalescence phenomenon

iii)

$$\Delta G^{\ddagger} = 50 \cdot T_c$$

$$= 50 \cdot 250 = 12.500$$

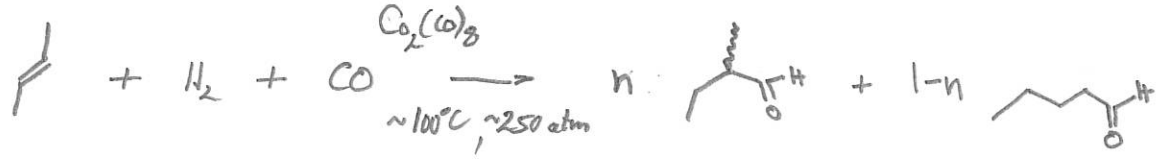
$$\Delta G^{\ddagger} \cong 12.5 \text{ kcal/mol}$$

7) (10 points) One of the largest scale homogeneous catalytic processes in the chemical industry is the 'hydroformylation' of olefins.

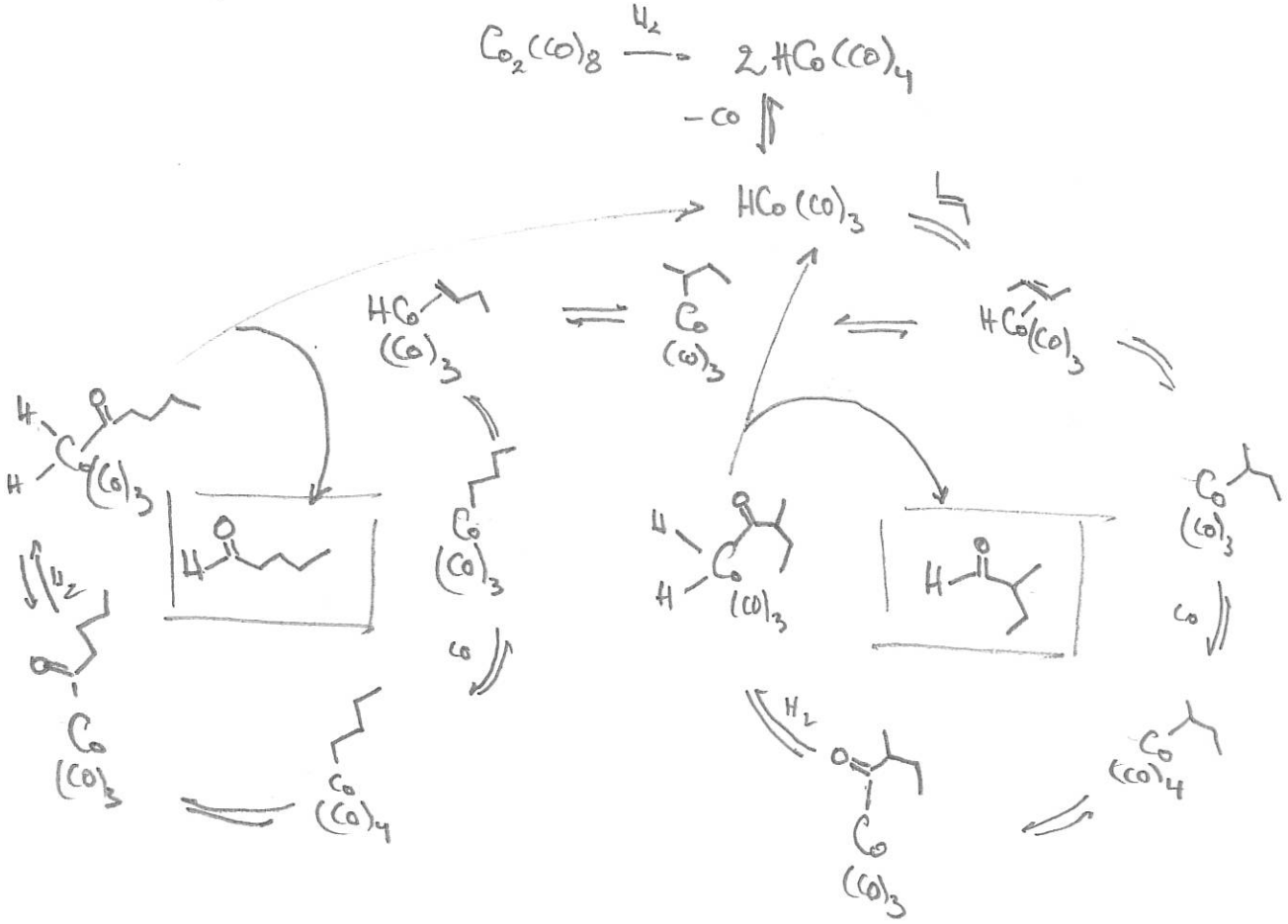
i) Write a balanced reaction equation for the hydroformylation of 2-butene, showing all possible products. Over the reaction arrow indicate the catalyst (or catalyst precursor) and typical reaction conditions.

ii) Draw a catalytic cycle showing the elementary reaction steps and structures of intermediates, which – in aggregate – explain the formation of all products you listed in i).

i)



ii)



8) (10 pts) Yves Chauvin received 1/3 of the 2005 Nobel Prize in Chemistry for his proposal regarding the mechanism of the olefin metathesis reaction. Using the example of the 'ring opening metathesis polymerization' (ROMP) of norbornene, show how his mechanism yields a polymer, and what its structure is. Draw critical intermediates, using either a Grubbs- or Schrock-type catalyst.