

Test Exam Answers

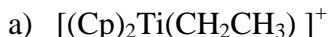
For all answers, provide a satisfactory explanation.

Where appropriate and supportive of your answer, provide the correct oxidation state and valence electron counting of the complexes.

Question 1

Which of the following TM-alkyls do you think are stable, and which are not?

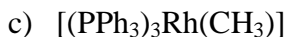
Explain your answer. Provide the most logical decomposition pathway for the instable ones.



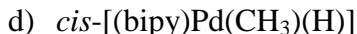
Ti^{IV} , no d electrons, first row TM so 18 VE not a strict requirement. This species should be relatively stable, because the absence of d-electrons makes a beta-hydrogen elimination very difficult (not impossible). Other possible decomposition pathways: reaction with solvent, water (air), binuclear reductive elimination etc.



This species is not stable. It is a 16 VE d^8 species, ideal for beta-elimination to form $[(\text{PPh}_3)_3\text{Rh}(\text{H})(\text{ethene})]$. (Rh^{I} , d^8 , 18 VE)



This species should be relatively stable. It has no beta-hydrogen atoms, and it is a 16 VE d^8 species, a relatively stable configuration.



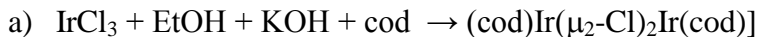
This species cannot be very stable. It has a hydride and an alkyl in *cis* position. These are very likely to undergo reductive elimination to form methane and $(\text{PPh}_3)_3\text{Pd}^0$ (the latter often decomposes to form colloidal Pd^0 clusters, also called “palladium black”).



This species should be relatively stable. It has beta-hydrogen atoms, but the Ru atom is coordinatively and electronically saturated (Ru^{II} , d^6 , 18 VE), and Ru^{II} is not labile (strong metal-ligand bonds). The species cannot easily create a *cis* vacant site required for beta hydrogen elimination. Reductive elimination of EtOMe is perhaps possible, but in general reductive eliminations involving hetero-atoms are extremely difficult (the filled p-orbital of the oxygen-atom is “in the way”).

Question 2

Suggest a plausible mechanism for the following two reactions:

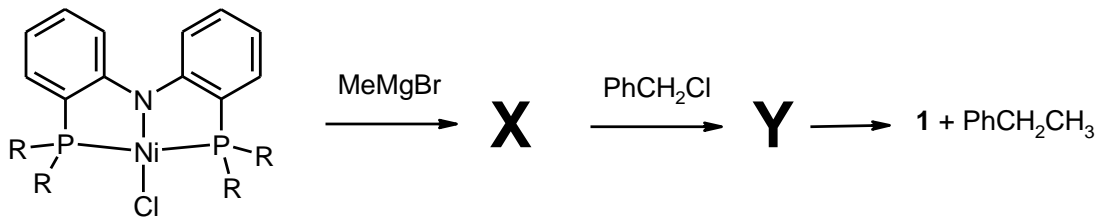


Formation of $\text{Ir}^{\text{III}}\text{-O-CH}_2\text{CH}_3$ is followed by beta-elimination and dissociation of acetaldehyde (ethanal, $\text{CH}_3\text{C(O)H}$) to form an $\text{Ir}^{\text{III}}\text{-H}$ species. This one is deprotonated by KOH to produce an Ir^{I} species. The “soft” Ir^{I} has a much higher affinity for cod and a lower affinity for Cl^- (compared to the “hard” Ir^{III}). This d^8 metal has a preference for forming a four-coordinate 16 VE complex. It will thus bind cod and form a 16 VE four-coordinate complex. It could have formed $[\text{Ir}(\text{cod})(\text{Cl})_2]$, but it prefers to form a neutral bis-chloride bridged complex. The driving force for that is the precipitation of the neutral complex from the polar solvent.



Binding of formiate to Rh , followed by beta-hydrogen elimination. This produces the hydride and CO_2 (which escapes the reaction mixture as a gas).

Complex **1** (below) can be used for two-step C-C bond formation:

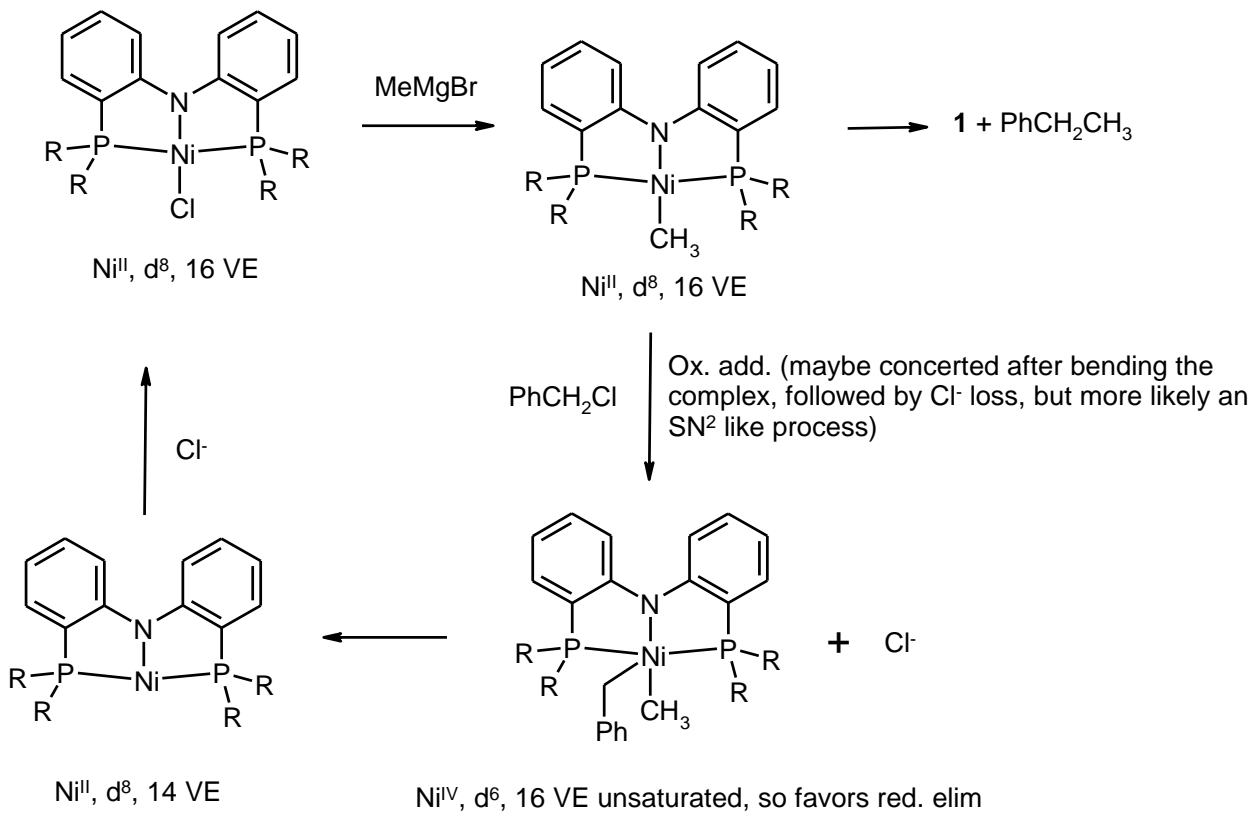


1

c) What is **X**?

X is most likely the complex in which the Cl^- ligand is replaced by a CH_3^- ligand (the Grignard reagent is a source of CH_3^-).

d) Provide a plausible mechanism for this C-C bond forming reaction

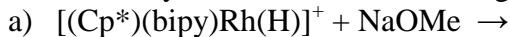


- e) What would be the effect on the reaction rates of all steps if we replace the two PPh_2 groups in **1** by the more electron donating P^iPr groups?

It would make the alkylation to form **X** slower, it would make the ox. add. reaction step faster, and it would make the red. elim. step slower. Perhaps it would allow the detection or isolation of intermediate **Y**.

Question 3

Predict the likely outcome of the following two reactions:

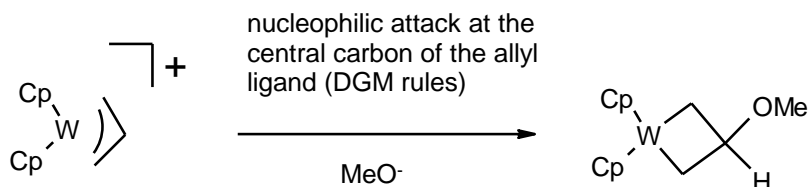
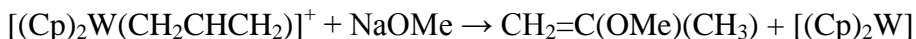


Deprotonation of the hydride to form the Rh^{I} compound $[(\text{Cp}^*)(\text{bipy})\text{Rh}]$. This 16 VE complex cannot become square planar, so it is unsaturated and will likely bind solvent or MeO^- to become 18 VE.



Nucleophilic attack of Ph^- at a CO ligand forms the $[(\text{CO})_5\text{W}=\text{C}(\text{Ph})(\text{O}^-)]^-$ intermediate, which is attacked by the “ Et^+ ” electrophile to form the stable Fischer carbene complex $[(\text{CO})_5\text{W}=\text{C}(\text{OEt})(\text{Ph})]$.

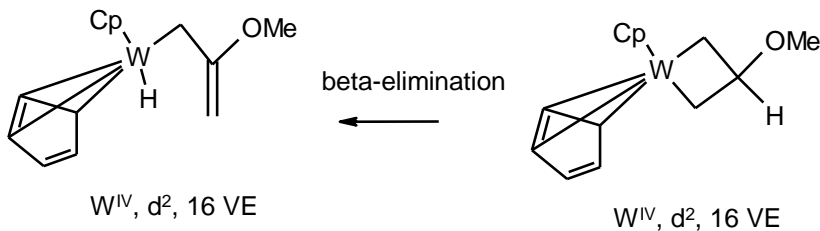
c) Provide a plausible mechanistic explanation for the following reaction:



$\text{W}^{\text{IV}}, d^2, 18 \text{ VE}$
(W is not very EN, so electron donating)

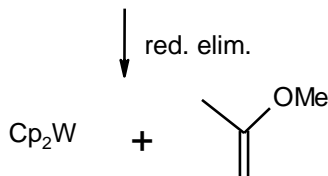
$\text{W}^{\text{IV}}, d^2, 18 \text{ VE}$

ring slippage
to a $\eta^3 \text{ Cp}$



$\text{W}^{\text{IV}}, d^2, 16 \text{ VE}$

$\text{W}^{\text{IV}}, d^2, 16 \text{ VE}$



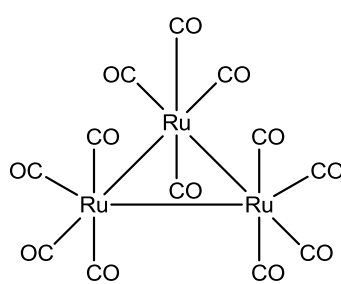
$\text{W}^{\text{II}}, d^4, 16 \text{ VE}$

Cp_2W may bind solvent or the alkene product.

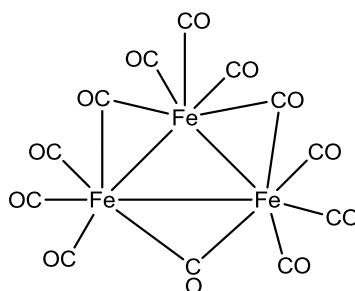
Question 4

Carbonyl compounds and substitution reactions.

Draw plausible structures for $\text{Ru}_3(\text{CO})_{12}$ and of $\text{Fe}_3(\text{CO})_{12}$, given that the first has none and the second contains three μ_2 -CO ligands. Explain how and why the wave numbers in the IR change going from free to terminal to a bridging CO ligand.



18 VE



18 VE

More pi-back donation, lower C-O bond order, lower wave numbers.

- Give a detailed account of the substitution of one CO in $\text{W}(\text{CO})_6$ by a phosphine. What type of substitution occurs, what is the mechanism (draw this, stepwise). Give the rate law, assuming that the 'back' reaction is not important (slow).

Dissociative process (W is low spin, d^6 and 6-coordinate; no empty orbitals to bind PR_3 via σ -bonding). So first CO dissociates, then PR_3 associates. Rate law: $v = k[\text{W}(\text{CO})_6]$

- What is the stereochemistry (or geometry) of the intermediate that occurs?

5 coordinate compound, so tbp or sqpy, probably these are in rapid equilibrium.

- Discuss the effect of the cone angle and the basicity of the phosphine on the rate of substitution of CO in $\text{W}(\text{CO})_5(\text{PR}_3)$.

Larger cone angle, more sterics, CO dissociates faster, so faster reaction.

- d. Several metallocenes violate the 18e rule but are nevertheless relatively stable compounds. Explain this for: MnCp_2 , CoCp_2 , NiCp_2 .

First of all, these compounds do not need to fulfill the 18VE rule. The σ^* metal d-orbitals are not very high in energy, so easily accessible (violation of 18 VE rule with higher VE countings are thus no problem). The compounds do not have pi-acceptor ligands, so VE counting numbers than 18 are also not a problem.

Furthermore, the following additional arguments can be mentioned:

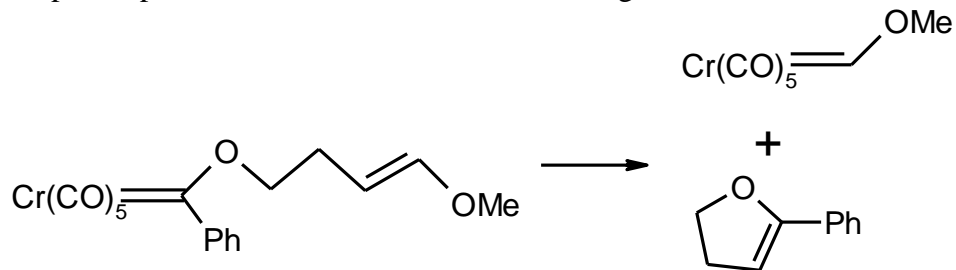
MnCp_2 : 17 VE. Additional ligand makes it 19VE (unfavorable).

CoCp_2 : 19 VE. Additional ligand makes it 21VE (unfavorable), and hapto-3 coordination of one Cp ring makes it 17 VE but is not favorable for entropy reasons (chelate effect).

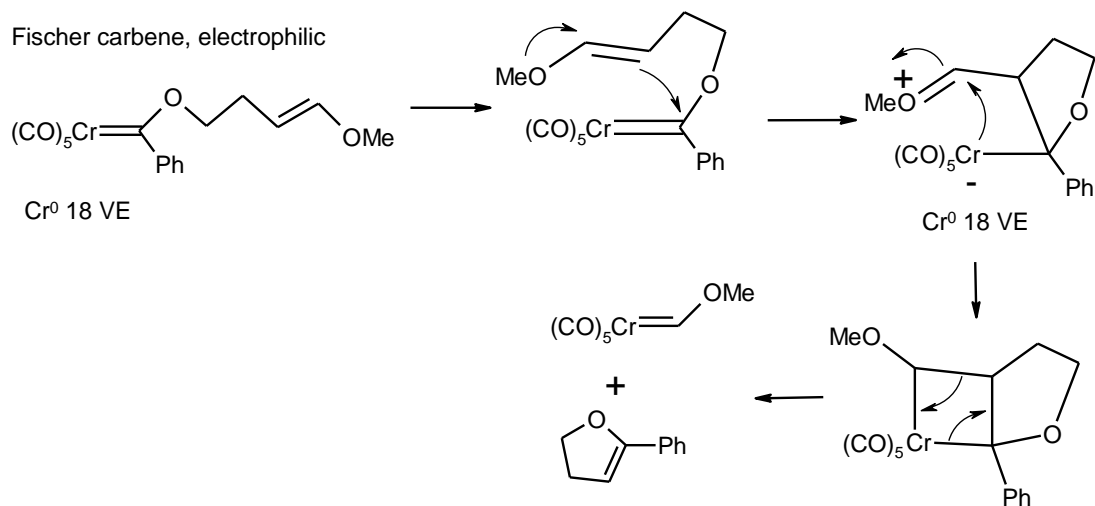
NiCp_2 : 20 VE. Additional ligand makes it 22VE (unfavorable), and hapto-3 coordination of one Cp ring makes it 18 VE but is not favorable for entropy reasons (chelate effect).

Question 5

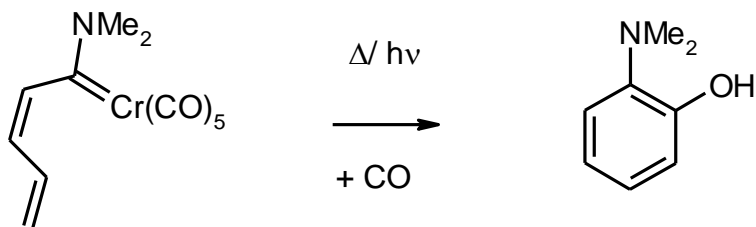
Propose a plausible mechanism for the following reactions:



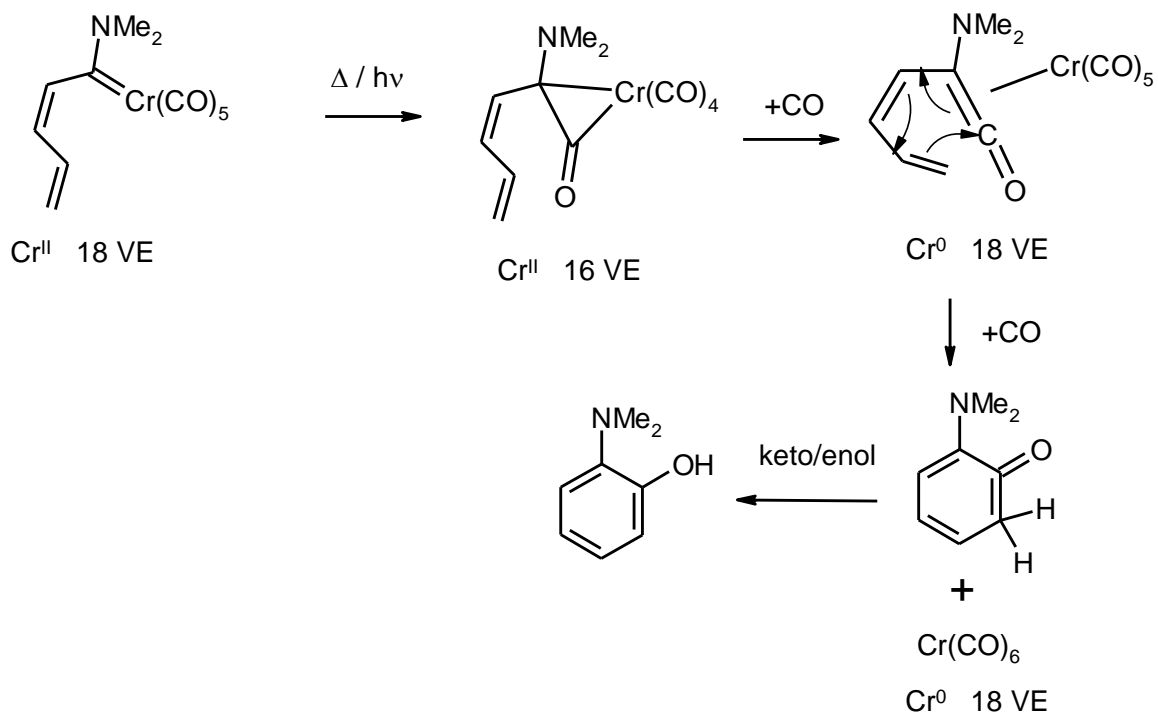
Make sure that the above reaction proceeds without loss of CO !!!



No loss of CO required because the reaction proceeds via two nucleophilic attacks. It is not required to open the coordination sphere to pre-coordinate the olefin.



Explain why the above reaction only proceeds with additional CO !!!



Without additional CO the substrate would coordinate too strongly to any of the unsaturated (16 VE) intermediates, and the product would not be formed.