

Examples of exam questions:

Alkyls

Which of the following compounds do you think are stable, which not and why?

- $[\text{Rh}(\text{CH}_2\text{CHMe}_2)(\text{PPh}_3)_3]$
- $[\text{Ir}(\text{Me})(\text{I})(\text{Cl})\text{CO}(\text{PPh}_3)_2]$
- $[\text{Rh}(\text{Cp})(\text{CH}_2\text{CHMe}_2)(\text{PMe}_3)_2]^+$
- $[\text{Rh}(\text{Cp})(\text{H})(\text{CH}_2\text{CHMe}_2)(\text{PMe}_3)]^+$

Give a detailed reason (qualitative MO theory) why $\text{M}-\text{CF}_3$ species are more stable for late transition metals than for early transition metals.

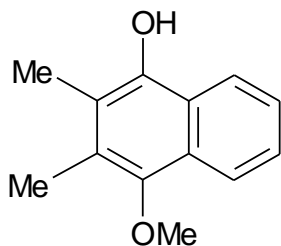
Reactions directly at ligands

Remember that reactions at the metal always remain an alternative: check the 16/18VE counting and sterics! Also think of eventual likely follow-up reactions!

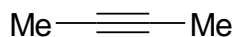
What is the most likely outcome of the following reactions:

- $\text{MeLi} + [\text{Mo}(\eta^4\text{-butadiene})(\eta^3\text{-C}_3\text{H}_5)(\eta^6\text{-benzene})]^+$
- $\text{MeLi} + [\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^6\text{-benzene})]^+$
- $\text{Mn}(\text{CO})_6 + \text{Et}_3\text{NO}$
- $[\text{Ir}(\text{NMe}_3)_5(\text{C}_2\text{H}_4)]^{2+} + \text{O}_2$
- $[\text{Pd}(\text{H}_2\text{O})\text{Cl}_2(\text{C}_2\text{H}_4)] + \text{H}_2\text{O}$

Carbenes



A



B

You want to prepare the substituted naphthol B from 2-butyne (B) via the Dötz reaction. The other reagents you have available are: $\text{Cr}(\text{CO})_6$, PhLi and $[\text{Me}_3\text{O}]\text{BF}_4$.

- The Dötz reaction requires initial formation of a carbene. How would you prepare the carbene? Is it a Fischer or a Schrock carbene?
- Write down the reaction sequence (in detail) via which naphthol B can be synthesized from the carbene and 2-butyne.

General aspects of organometallic chemistry.

- a. Give the electron count of the following compounds and draw their structures, draw possible stereoisomers if relevant:
 $(\text{CH}_3)_2\text{ZrCl}_2$, $(\text{CH}_3)_2\text{PdCl}_2$, $\text{CH}_3\text{Mn}(\text{CO})_3(\text{PPh}_3)_2$.
- b. Which is the order of increasing rate of reaction with water for the following compounds and why is that so? $\text{CH}_3\text{CH}_2\text{Li}$, $(\text{CH}_3)\text{Rh}(\text{PPh}_3)_3$, $(\text{CH}_3)_2\text{TiCl}_2$, $(\text{CH}_3)_2\text{Hg}$, CH_3MgCl . Give the complete equations for the reaction of water with CH_3MgCl and with $(\text{CH}_3)_2\text{TiCl}_2$.
- c. Give reaction equations for the synthesis of (i) tetraethyl lead $\text{Pb}(\text{CH}_2\text{CH}_3)_4$ and (ii) for triethyl aluminum $\text{Al}(\text{CH}_2\text{CH}_3)_3$. You must present two essentially different reactions to obtain these compounds!

Carbonyl and phosphine complexes.

- d. Give the equation for the synthesis of $\text{Ni}(\text{CO})_4$.
- e. Give the routes for the synthesis of compounds *fac*- and *mer*- $\text{Mo}(\text{CO})_3(\text{PMe}_3)_3$ from $\text{Mo}(\text{CO})_6$ and PMe_3 . Discuss the difference in the routes followed and which techniques are used.
- f. Discuss the influence of the cone angle of the phosphine on the rate of reductive elimination of methylbenzene from $[\text{Pd}(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{PR}_3)_2]$.

Substitution reactions.

- g. By which mechanism will $\text{Pt}(\text{PPh}_3)_4$ react with Ph-NC (= phenyl-isonitrile; reaction in the dark, thermal reaction) to give $(\text{PhNC})\text{Pt}(\text{PPh}_3)_3$. Draw the mechanism step by step and draw structure(s) of the intermediate(s).
- h. The same for reaction of $\text{Pt}(\text{CH}_3)\text{Br}(\text{PPh}_3)_2$ with Ph-NC.
- i. Discuss the kinetics of the substitution reaction under h.
- j. Do you expect that the product of reaction b. will undergo a further reaction? If so, how, and what is the product?

Bonding and reactions of unsaturated molecules.

- k. Describe the bonding of CO to a transition metal like Rh^{I} in terms of bonding and back-bonding. Draw sketches to illustrate. Describe how the bond-order in the CO ligand is influenced by the other ligands.
- l. Draw the structures of isomeric Pd compounds (ions) which are formed by migratory insertion involving propene and $\text{cis}[\text{H-Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})]^+$. Draw the mechanism step by step of this reaction. What order do you expect for the rate law?
- m. If styrene (Ph-CH=CH_2) is used instead of propene, one of the regio-isomers can gain additional stability. How? Draw the structure of the complex, showing this extra stabilization.

Butadiene and cyclopentadienyl compounds.

- a. Describe the bonding in a transition metal-(η^4 -1,3-butadiene) complex. Sketch the relevant interactions of the π -type orbitals of the butadiene fragment with the relevant metal orbitals.
- b. How do you think will an iron-(η^4 -1,3-butadiene) complex react with $\text{CH}_3\text{SO}_3\text{H}$? (reacts as H^+ ; the anion is the non-coordinating ion CH_3SO_3^-).
- c. Give an energy level diagram of the frontier orbitals (the five metal-centered orbitals, omit the 6 low-lying ligand-like orbitals) of MnCp_2 , FeCp_2 and CoCp_2 with the electron occupation of these levels. What is the electron count for each of these complexes? Discuss the spin state of the Mn compound.
- d. What is the main difference between the frontier orbitals of Cp_2ZrCl_2 and Cp_2MoCl_2 ? Draw sketches how these orbitals look and how they are occupied.