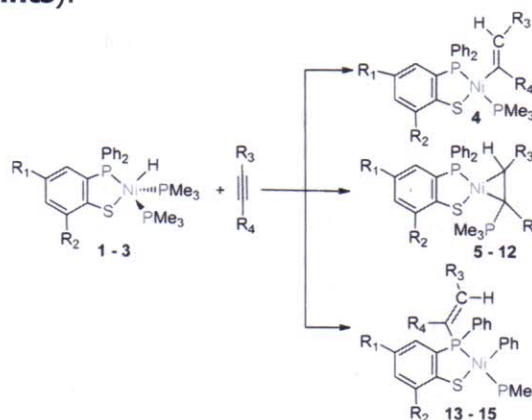


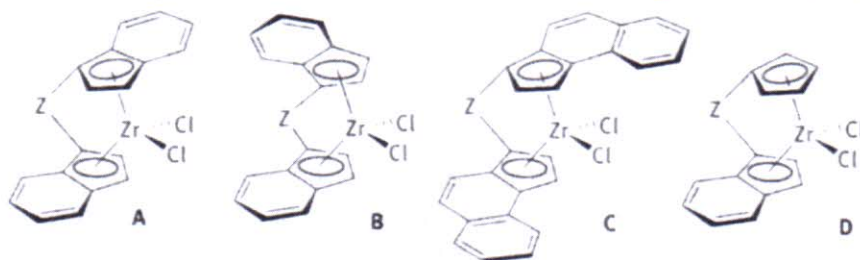
General: Provide for every metal compound the electron count, the number of *d*-electrons and the formal oxidation state of the metal. In mechanisms do not perform two steps in one – give each separate step. Name every reaction step. Please write legibly (do not use a pencil), if I can't read it, it's considered to be wrong.

1. Shown in the figure is the graphical abstract of the paper "Vinyl/Phenyl Exchange Reaction within Vinyl Nickel Complexes Bearing Chelate [P, S]-Ligands" by Xue et al. (*Organometallics* 2017, 36, 4246–4255 DOI:10.1021/acs.organomet.7b00671) (**6 points**).
- a. Compound **1** is prepared from the bidentate phosphane-thiol aromatic ligand and $[\text{Ni}(\text{PMe}_3)_4]$. Give the full reaction equation, describe what happens, and give the electron count, oxidation state and number of *d*-electrons of this compound (**1p**)
- b. Provide a mechanism for the formation of compound **4**. Provide the electron count, oxidation state and number of *d*-electrons of this compound. (**1p**)
- c. Provide a mechanism for the formation of compound **5**. (**1p**)
- d. Describe the interactions of an alkene with a transition metal center. Discuss the two extremes of the binding model. Relate this discussion to the structure drawn for compound **5**. Provide the electron count, oxidation state and number of *d*-electrons of this compound. Beware of the charges! (**2p**)
- e. Describe what happens in the formation of compound **13**. Provide the electron count, oxidation state and number of *d*-electrons of this compound. (**1p**)
2. The reaction of an alkene with a silane can be catalysed with a homogeneous platinum catalyst (**6 points**).
- a. What is the 'systematic' name for this reaction? Draw the possible products that can be formed in the reaction of styrene (=vinylbenzene) with Et_3SiH . (**1p**)
- b. Discuss the terms regioselectivity and enantioselectivity using these products. How is the enantioselectivity of a reaction expressed? (**1p**)
- c. Propose a likely catalyst including ligands; how would you prepare this catalyst? (**1p**)
- d. Propose a catalytic cycle for this reaction. (**2p**)
- e. What are the requirements for the catalyst and the substrate to give good enantioselectivity? (**1p**)
3. Acetic anhydride is prepared from methanol via a carbonylation, esterification and a second carbonylation reaction (Tennessee Eastman process) (**4 points**).
- a. Give the equations of the three reactions leading to acetic anhydride starting from methanol. (**1p**)
- b. Which co-catalyst(s) is (are) necessary for the two carbonylations, and why? Draw the organic cycle(s). (**1p**)
- c. Provide a mechanism for the carbonylation of methanol, using the catalyst $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. (**2p**)



Organometallic Chemistry and Homogeneous Catalysis

4. Given the structures of four *ansa*-metallocenes **A-D** in the figure below. (5 points)



- Provide electron count, formal oxidation state and number of d-electrons of titanium in the catalyst precursor **A**. (1p)
 - Rank the compounds from highest to lowest stereoselectivity. Explain your ranking. (1p)
 - Draw the Fischer projections for the following polypropene pentad structures: i) *mmmm*, ii) *mrrm*, iii) *rrrr*, iv) *mrmm*. With which technique can these pentads be discriminated? What mechanistic information can be obtained from the observation of *mrrm* or *mrmm* pentads? (2p)
 - The *ansa*-metallocene catalysts give rise to highly linear ethene polymers, whereas late-transition metal catalyst generally give highly branched polymers. Describe the reasons for this difference. (1p)
5. This question is related to the provided article (Vogelsang et al, *Chem. Eur. J.*, **2018**, *24*, 2264). Telomerisation of butadiene (bottom reaction in Scheme 1) was discussed in class; the paper advances on this reaction. It is NOT necessary to read the whole paper, you will not find answers. The questions below guide you through the important parts (8 points).
- In Scheme 5, the second reaction concerns a hydromethoxycarbonylation of an alkene. Note that the reaction needs acid. Propose which catalyst (including oxidation state) is necessary for this reaction How would you make this catalyst? (1p)
 - Provide a mechanism for the hydromethoxycarbonylation reaction of compound **2** using a palladium catalyst with a bidentate phosphane ligand. (2p)
 - Note that the reaction conditions for the carboxytelomerisation of butadiene (Scheme 5) are basic. What does this tell you about the catalyst? (1p)
 - Provide a mechanism for the carboxytelomerisation reaction using a palladium catalyst precursor combined with monodentate phosphane ligands. (3p).
 - Explain why the bidentate ligand needed for the hydromethoxycarbonylation reaction does not work well for the carboxytelomerisation reaction in a tandem reaction (Table 1, entry 3). (1p)

Periodic Table (relevant part)

4	5	6	7	8	9	10	11	12
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

