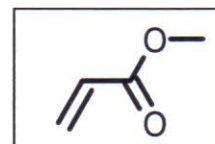


**General:** Provide for every metal compound the electron count, the number of *d*-electrons and the formal oxidation state of the metal. In mechanisms do not perform two steps in one – give each separate step. Name every reaction step. Please write legibly (do not use a pencil), if I can't read it,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

- Oxidative addition and catalytic ether formation.
    - Describe three different mechanisms for oxidative addition, with the appropriate substrate.  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{OTs}$  (HOTs = *p*-toluenesulfonic acid) can be used to discriminate between two of the mechanisms: explain which mechanisms and why.
    - Methanol will not undergo oxidative addition to form  $\text{CH}_3$  and  $\text{OH}$  bound to a metal center: why not? Which co-catalyst is used in the carbonylation of methanol to acetic acid to activate methanol? Show how this works.
    - In contrast, allyl alcohol (2-propene-1ol) *can* give oxidative addition to a metal center: provide an explanation. The oxidative addition of allyl alcohol is facilitated by the addition of a catalytic amount of acid. Explain.
    - Provide the reaction sequence of the oxidative addition of allyl alcohol to the ruthenium compound shown in the figure. Give all intermediate steps with electron count and oxidation states.
    - The final product formed in the previous question can react with nucleophiles such as phenol to give an ether. Provide a mechanism for this reaction. Explain that this must be an equilibrium reaction.
- 
- DuPont employs an industrial process in which ethene and 1,3-butadiene are co-dimerized to form a product that is used as starting material for synthetic rubbers.
    - Can you give another name for this reaction? Draw the possible products that can be formed in this reaction.
    - Discuss the terms regioselectivity and enantioselectivity using these products.
    - Which side-products do you expect in this reaction?
    - Propose a likely catalyst including ligands; how would you prepare this catalyst?
    - Draw a detailed catalytic cycle for this reaction.
  - Hydroformylation is an important industrial process based on homogeneous catalysis.
    - What is hydroformylation?
    - Give a likely mechanism for the hydroformylation of styrene starting from the catalyst precursor  $[\text{RhH}(\text{PR}_3)_2(\text{CO})_2]$ .
    - Which two factors (Tolman) are used to describe the properties of a phosphorus ligand? How can these factors be quantified?
    - Discuss the influence of the ligand  $\text{PR}_3$  or the use of bidentate ligands on product selectivity.
    - The so-called "third generation" hydroformylation catalysts are used in a two-phase system. What does such a two-phase system look like? Discuss advantages and disadvantages of a two-phase process. Which adjustments are necessary to be made to the catalyst?

## Organometallic Chemistry and Homogeneous Catalysis

4. Methyl acrylate (see figure) can be synthesized from ethyne, CO and methanol (hydromethoxycarbonylation) using a palladium catalyst. Methyl acrylate is the monomer for plexiglas.



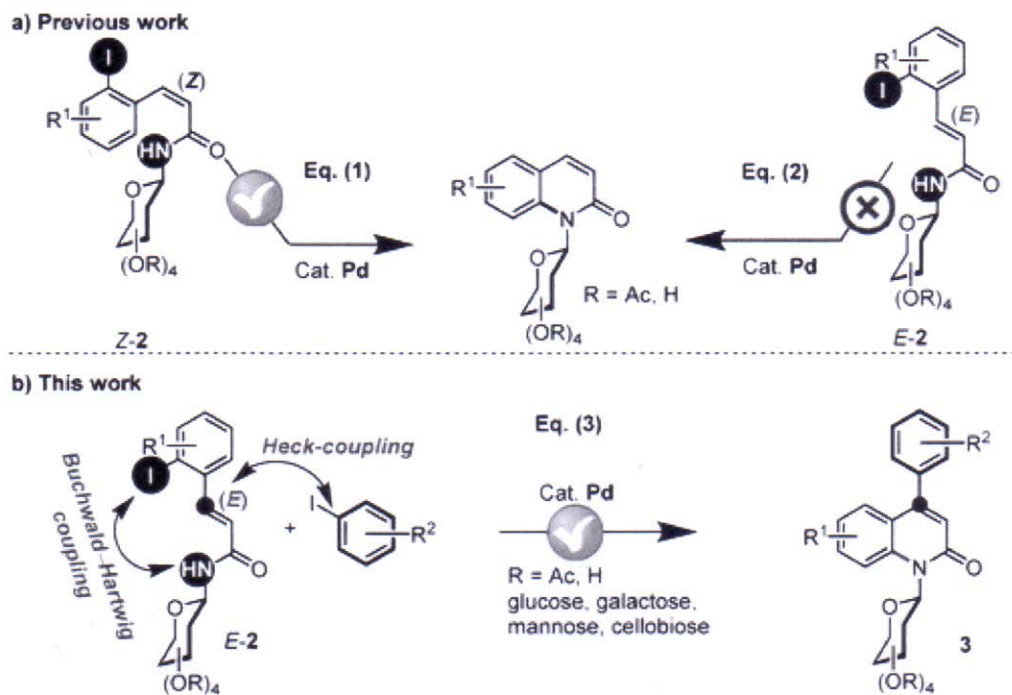
- Propose a mechanistic cycle for the formation of methyl acrylate starting from the precursor catalyst  $[\text{Pd}(\text{PP})\text{Cl}_2]$  (PP = bidentate phosphine ligand). Include a proposal for the formation of the actual catalyst.
  - Which products can be formed after the *first* hydromethoxycarbonylation of 1,3-butadiene? Show how you get to the answer.
  - Draw a global structure for plexiglas. Discuss tacticity, describing the relative orientation of the side groups in this polymer, in relation to the physical properties of the polymer.
  - What types of tacticity are known? Make a schematic drawing of the catalysts that could make the two most important types of polymer.
5. This question is related to the scheme shown on the next page (taken from: *Adv. Synth. & Catal.*, **2017**, 359, 1320-1330). In previous work the authors have described a Buchwald-Hartwig coupling reaction, catalyzed by palladium.
- Propose a catalyst (including oxidation state) for the reaction shown in Scheme 1a. Which additional reagent would you need for this reaction? Which byproduct is formed?
  - Provide a mechanism for the Buchwald-Hartwig coupling shown in Scheme 1a.
  - Why does the reaction shown in Scheme 1a not work for E-2 as starting material? Explain why in contrast the Buchwald-Hartwig coupling is possible in the reaction shown in Scheme 1b.
  - Propose a catalyst and provide a mechanism for the Heck reaction shown in Scheme 1b.
  - What side products could be formed in this cascade reaction? Indicate at which intermediates in the answers provided for 5b or 5d things can go 'wrong'. Consider the overall reaction.

### 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

**Selective Palladium-Catalyzed Domino Heck/Buchwald–Hartwig Arylations of *N*-Glycosylcinnamamides: An Efficient Route to 4-Aryl-*N*-glycosylquinolin-2-ones**

Thi Thanh Huyen Luong, Sabrina Touchet, Mouad Alami, Samir Messaoudi,  
*Adv. Synth. & Catal.*, **2017**, *359*, 1320-1330, DOI: 10.1002/adsc.201601382



Scheme 1: Synthesis of substituted *N*-glycosyl quinolin-2-ones