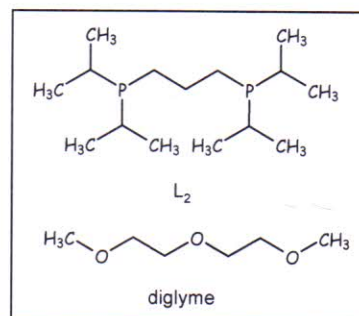


**General:** Provide for every metal compound the electron counting, the number of d-electrons and the formal oxidation state of the metal. In mechanisms do not perform two steps in one – give each separate step. Name every reaction step. Please write legibly (do not use pencil), if I can't read it,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

- In the catalytic cycle of many catalytic reactions a metal-bound alkene or alkyl is essential.
  - Describe the binding interactions between an alkene and a transition metal.
  - Which factors are important for the binding strength of an alkene to a metal, and the orientation of the alkene in the complex?
  - Metal-alkyl compounds are generally difficult to isolate, because of  $\beta$ -hydrogen elimination. Which factors are important for  $\beta$ -hydrogen elimination to occur? How can  $\beta$ -hydrogen elimination be prevented?
  - Discuss the various binding modes and fluxionality for the allyl (propenyl) group.
- Adiponitrile (1,6-hexanedinitrile) can be synthesized from butadiene and HCN using a nickel catalyst. Adiponitrile is a precursor for Nylon-6,6.
  - Propose a mechanistic cycle for the formation of the *first* hydrocyanation product from butadiene with the precursor catalyst  $[\text{Ni}(\text{PP})_2]$  (PP = bidentate phosphite –  $(\text{RO})_2\text{P}$ -bridge- $\text{P}(\text{OR})_2$  ligand). Which two products can be formed?
  - Discuss which additional steps are necessary to form the desired adiponitrile from the products formed after the first reaction.
  - A co-catalyst is necessary for the second hydrocyanation step. What type of co-catalyst and what is its role?
  - Which two factors (Tolman) are used to describe the properties of a phosphorus ligand? How can these factors be quantified? Explain why for the hydrocyanation catalyst the use of phosphite ligands is essential.
- Acetic acid is produced by the carbonylation of methanol.
  - Which co-catalyst is necessary and why? Draw the organic cycle.
  - Provide a mechanism for the carbonylation of methanol with the catalyst  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ .

- (This question was provided by prof. Drent). Palladium compound  $\text{L}_2\text{PdX}_2$  catalyses the hydroformylation of propene in diglyme (See Figure for  $\text{L}_2$  and diglyme;  $\text{X} = \text{methane sulfonate} = \text{CH}_3\text{SO}_3^-$ ), forming two aldehydes in 95% selectivity.
  - Propose a structure for the first catalyst species; how can it be formed from  $\text{L}_2\text{PdX}_2$ ?
  - Construct a complete catalytic cycle for the hydroformylation of propene; which two aldehydes are formed?
  - Which property (properties) of the catalyst determine the relative ratio of the two aldehydes formed?



When the reaction is performed in methanol as the solvent instead of diglyme (using the same catalytic system and reactants) aldehydes are not formed, but *seven* different ketone-type products (partly due to different termination mechanisms) are formed in 95% selectivity.

- Try to think of 6 potential products and draw their structures.
- Construct a potential mechanism for the formation of these products.
- The major product is 2-methyl-3-hexanone, how can you explain this? How could the selectivity to this product be increased?
- Give a likely explanation for the difference in product formation in the two solvents.

## Organometallic Chemistry and Homogeneous Catalysis

5. Provided is the paper entitled "Tandem catalytic asymmetric ring-opening metathesis/cross metathesis" by D.S. La et al., *J. Am. Chem. Soc.*, **1999**, *121*, 11603. Answer the following questions (only one page is provided, remainder of the article is not necessary to be able to answer the questions).
- Metal-carbene complexes can be described with a Fischer or a Schrock model. Describe/discuss these models.
  - Provide electron count, formal oxidation state and number of d-electrons for the two molybdenum compounds **1a** and **2**. Which carbene model do you think is valid for these compounds? **BEWARE** of the nitrogen donor ligand!
  - Use the molybdenum catalyst **1a**, let this precursor react with styrene; show which two products can form. Then use one of the products to propose a catalytic mechanism to convert substrate **3** to product **5a** given in Scheme 1.
  - Discuss the activity of the catalysts (in terms of TON and TOF) using the information given in Scheme 1 and Table 1.
  - Metathesis catalysts can be used for ROMP (ring opening metathesis polymerisation), ADMET (acyclic diene metathesis) and RCM (ring closing metathesis). Explain these reactions; make use of one of the substrates cyclopentene or 1,5-hexadiene to show which product is formed.

**Periodic Table** (relevant part)

| <b>4</b> | <b>5</b> | <b>6</b> | <b>7</b> | <b>8</b> | <b>9</b> | <b>10</b> | <b>11</b> | <b>12</b> |
|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|
| Ti       | V        | Cr       | Mn       | Fe       | Co       | Ni        | Cu        | Zn        |
| Zr       | Nb       | Mo       | Tc       | Ru       | Rh       | Pd        | Ag        | Cd        |

