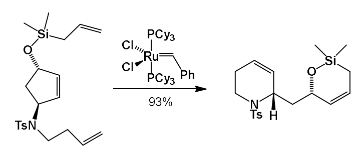
Metal organic chemistry

What and why?

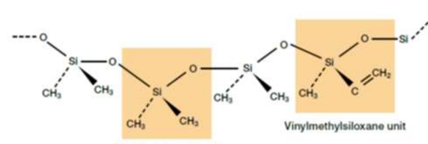
Why should we be interested?

- **Homogeneous catalysis**
  - based on organometallic chemistry
  - synthesis of fine chemicals, pharmaceuticals and many larger-scale chemicals
  - Example: many plastics (polythene, polypropene, butadiene rubber, ...)



- **Understanding heterogeneous catalysis**
  - organometallic chemistry – the basis for understanding the important catalytic steps
  - Example: olefin hydrogenation

- **Materials**
  - most organometallics reactive (rather intermediates than the products)
  - Silicone rubbers – and example of a organometallic compound used as the final product



Example: Acetic Acid synthesis

- Acetic acid is an important industrial chemical.
- The traditional synthesis uses bio-oxidation of ethanol obtained via fermentation:

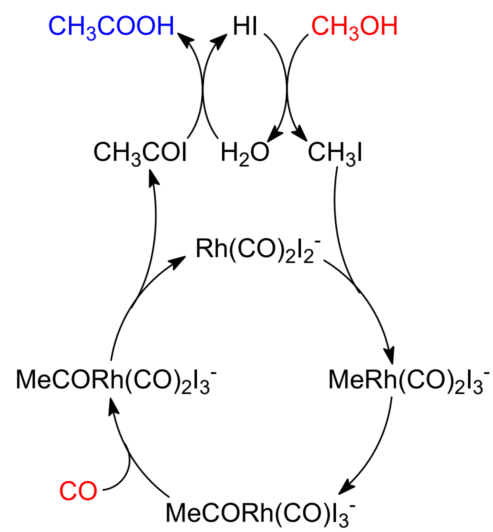
  $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$

  $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$

  This is not a clean and efficient process!
- Industrial acetic acid synthesis:

  $CH_3OH + CO \rightarrow CH_3COOH$

  Catalyzed by a rhodium complex



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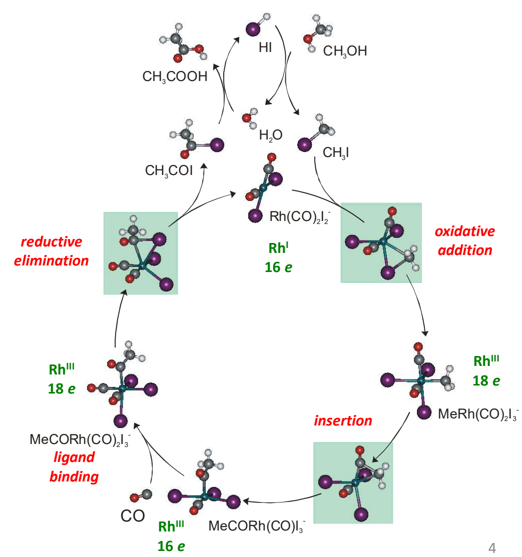
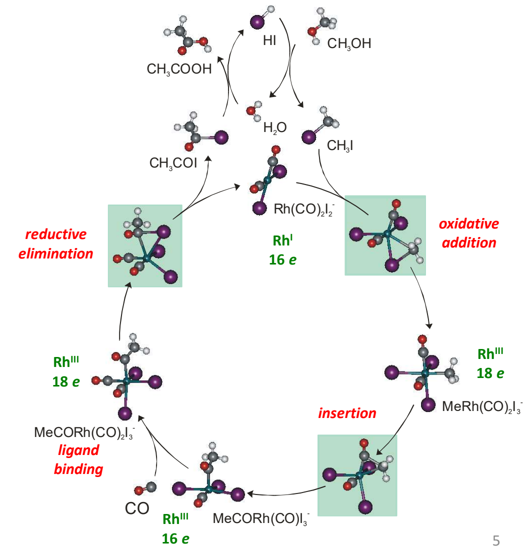


Metal organic chemistry course

Course

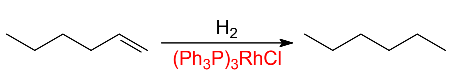
1. Introduction
2. Main group organometallics
3. Transition metal organometallics
4. Reactivity of ligands
5. Insertion/Elimination
6. Oxidative addition/Reductive elimination
7. Carbenes, Metathesis

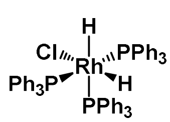


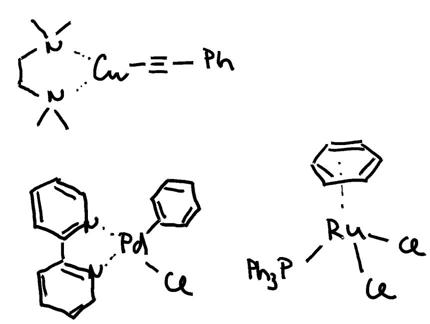
5

What is organometallic chemistry ?

- Metal organic chemistry - compounds containing metals and organic molecules/species
- Organometallics – compounds contain at least one metal-carbon bond
  - Metal hydrides are often included, H being considered as the "smallest organic group" (as in propyl, ethyl, methyl, hydride).

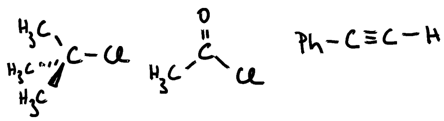




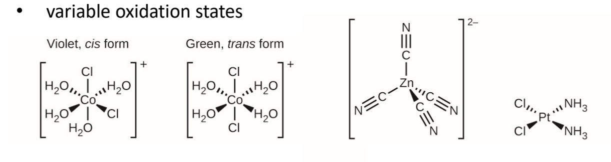


Between organic and inorganic…

Organic chemistry:
- more or less covalent C-X bonds
- rigid element environments
- fixed oxidation states (better: valencies)



Inorganic chemistry:
- primarily ionic M-X bonds, dative M-L bonds
- variable and often fluxional environments
- variable oxidation states



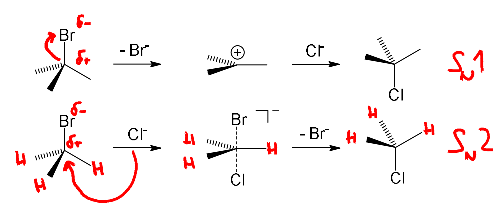
Organometallic chemistry

- Organometallics are **more covalent** and often **less symmetric** than coordination compounds, so orbital symmetry arguments are not as important
- Knowledge of inorganic and coordination chemistry is useful to understand geometries, electron counts and oxidation states of organometallic compounds
- Organometallic chemistry is concerned with *all* metals, in combination with *all* "organic" elements. There are *many* metals… → **Generalization is important**
  - the chemistry of e.g. Fe is not much more complicated than that of C, but after that there are *80 more* metals…
  - we divide reactions in broader categories than organic chemists do
- We concentrate on the M side of the M-C bond, and on how to tune its reactivity

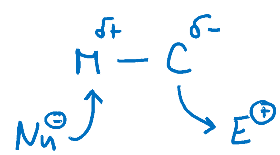
7

Organic vs organometallic reactivity

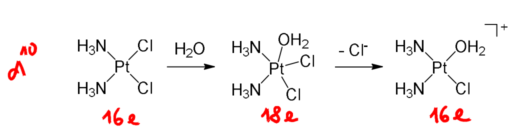
- Organic chemistry:
  - C-C / C-H : covalent, (almost) not polar
  - $C^{\delta+}$-$X^{\delta-}$: polar (partly ionic)
  - reactivity dominated by nucleophilic attack at C
  - S_{N2} and S_{N1} like reactivity



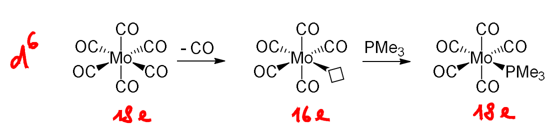
- Organometallic chemistry:
  - C is the negative end of the M-C bond ("umpolung")
  - reactivity dominated by electrophilic attack at C or nucleophilic attack at M
  - associative and dissociative substitution at M



ASSOCIATIVE



DISSOCIATIVE



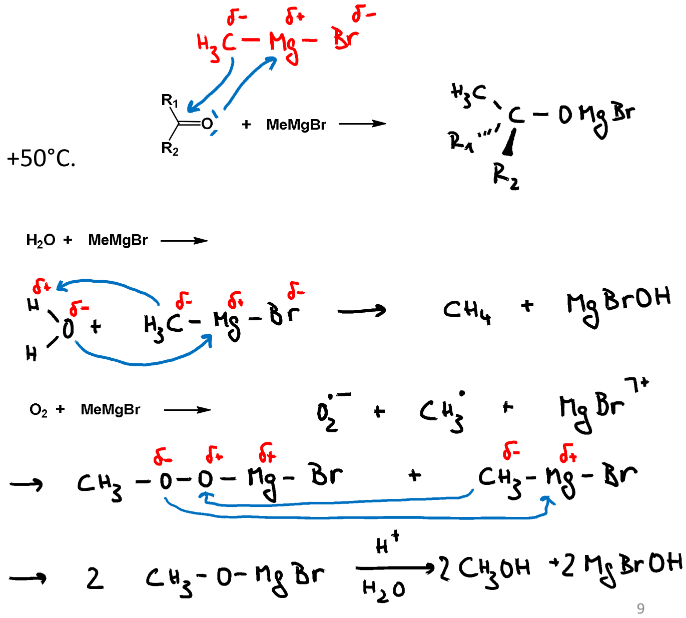
8

Reactivity of the M-C bond

- Metal is the "δ+" side of the M-C bond
- Nucleophilic attack of $C^{\delta-}$ at electrophiles
  - Carbonyl groups:
  - MeLi adds at -80°C, Me_3Sb not even at +50°C.
- Polar → reactive towards for example:
  - Water:

    Me_3Al explodes with water
    Me_4Sn does not react.
  - Oxygen:

    Me_2Zn inflames in air
    Me_4Ge does not react.



Synthesis and reactivity studies in inert atmosphere!:
- Glove box
- Schlenk line, specialized glassware

9

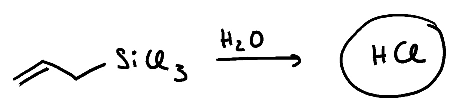
Trends in reactivity of organometallic compounds

- Factors influencing reactivity
  - M-C, M-X bond strengths
  - Electronegativity of M (i.e., polarity of M-C bonds)
  - Number of (d) electrons
  - Coordination number
  - Steric hindrance

Oxidation and hydrolysis: large driving force

Bond strengths in kcal/mol:

Al-C	65	As-C	55	Si-C	74
Al-O	119	As-O	72	Si-O	108
Al-Cl	100			Si-Cl	91



Electronegativities

C
2.55

Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65
Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69
La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9

10

Course Objectives

- By the end of this course, you should be able to:
- Make an educated guess about stability and reactivity of a given compound, based on e.g. electron counting rules
- Propose reasonable mechanisms, based on "standard" organometallic reaction steps, for many metal-catalyzed reactions
- Use steric and electronic arguments to predict how changes in reactants, metal or ligands affect the outcome of reactions
- Read a current research literature paper, understand and explain its content and significance

Useful Background Knowledge

- Organic chemistry: reaction mechanisms, primarily nucleophilic and electrophilic attack
- Inorganic Chemistry: electronegativity; electron counting and stability; properties of (transition) metals
- Physical chemistry: orbitals and MO theory; free energy, enthalpy and entropy

11