Selections from Chapter 16
Organometallics

CHEM 462
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Alkene complexes - some of the first organometallics

- Zeise's salt: K[PtCl₃(C₂H₄)] (first made in 1827)
- Alkenes bind side-on as 2e⁻ donors
- π-electrons serve as σ donors (I) to metal, alkene π*
  orbitals can function as π acceptors
  - both interactions tend to weaken the C–C bond
- Organometallic M/alkenes are crucial intermediates in many catalytic cycles for polymerization processes
  (including the famous process invented by K. Ziegler & G. Natta developed catalysts to polymerize ethylene to make polyethylene: (TiCl₄ + Al₂Et₆).

“e⁻ deficient” alkenes bind better

Alkene complexes range from weakly bound to “metallacyclopentanes” with strong binding.
Synthesis of Alkene Complexes

- Substitution of CO or other labile ligands:
  - $\text{Cr(CO)}_6 + \text{cycloheptatriene} \rightarrow \text{Cr(C}_7\text{H}_8)(\text{CO})_3 + 3 \text{CO}$
  - $\text{PdCl}_2(\text{CNR})_2 + \text{COD} \rightarrow \text{Pd(COD)}\text{Cl}_2 + 2 \text{RCN}$

- Reduction of halides or other higher-valent complexes:
  - $\text{Rh}^{II}\text{Cl}_3 + 4 \text{C}_2\text{H}_4 + \text{Zn} \rightarrow (\text{Rh}_2\text{Cl}_2)(\text{C}_2\text{H}_4)_4 + \text{ZnCl}_2$
  - $(\text{EtOH})$
  - $(\text{R}_3\text{P})_2\text{PtCl}_2 + \text{C}_2\text{H}_4 + \text{NaBH}_4 \rightarrow (\text{R}_3\text{P})_2\text{Pt(C}_2\text{H}_4)_2 + 2 \text{NaCl} + \text{H}_2 + \text{B}_2\text{H}_6$

More than one double bond…

- Fe(CO)$_3$(norbornadiene)
- Fe(CO)$_3$(butadiene) – all C–C bonds about equal
- (Rh$_2$Cl$_2$)(COD)$_2$
- Co(CO)$_3$(allyl)
Ferrocene; binding of aromatics

- Wilkinson (1951):
  \[
  \text{FeCl}_2 + \text{Na}(\text{C}_5\text{H}_5) \rightarrow \text{Fe} + 2 \text{NaCl}
  \]

- Fischer & Wilkinson: 1973 Nobel prize

Cyclopentadienyl (Cp) Compounds

- Cp is the most important carbocyclic
  \[
  \text{C}_5\text{H}_6 + \text{Na (or NaH)} \rightarrow \text{Na}^+\text{Cp}^- + \text{H}_2
  \]
  \[\text{TlOH} \]
  \[
  \text{Tl}^+\text{Cp}^- (s) + \text{FeCl}_2 \rightarrow \text{FeCp}_2
  \]

- Cp can replace 3 carbonyls:
  \[
  \text{Na}^+\text{Cp}^- + \text{W(CO)}_6 + 3 \text{CO} \rightarrow \text{W(CO)}_3\text{CpH}
  \]

Reactivity of Ferrocene
Other carbocyclic ligand complexes

- Cr(η⁶-C₆H₆)₂, much more air-sensitive than FeCp₂
- Mn(η⁴-C₅H₅)(C₆H₆)
- Mn(η⁴-C₅H₅)(CO)₃ (cymantrene) - quite stable, survives electrophilic aromatic substitution
- Anions and cations, e.g., CoCp₂⁺, FeCp(CO)₂⁻, ("Fp⁻", organometallic nucleophile)
- Many Cp derivatives, e.g., Cp⁸ = C₅Me₅

What About Metal Alkyls?

- For a long time it was assumed that M–C bonds were too weak to yield stable metal alkyl complexes. However, a few early examples were known (e.g., "CH₃Pt", Pope and Peachy, 1907).
- Compounds like TiEt₄ are very reactive (decomposes above -50°C).
- Some stable compounds: Ti(CH₂Ph)₄, Mn(1-norbornyl)₄, W(CH₃)₆, Os(Ph)₄, Os[η-(CH₂)₂C₆H₄]₃
- Why are these stable and others aren’t?

Carbene Complexes

- Fischer-type carbenes: :CR₂, :CRR’, :CR(OR’) groups bound to low-oxidation state metals:
  - e.g., synthesis of (CO)₅Cr=CR(OR’) from Cr(CO)₆
  - e.g., synthesis of (CO)₅Mo=C{N(Ph)(CH₂)₂(Ph)N} by splitting an electron-rich double bond
- These carbenes are electrophilic:
  - e.g., rxn of methyl isocyanide w/ (CO)₅Cr=CMe(OMe) to form side-on complex of (OMe)(Me)C≡C=NMe
Carbene Complexes

- **Schrock-type carbenes (alkylidenes)**: CRR groups on high-oxidation state metals:
  - e.g., synthesis of Cp₂MeTa=CH₂ from Cp₂Ta(CH₃)₃
- These carbenes are **electron-rich**.
- **Alkyldynes** can be made by deprotonation of alkylidenes:
  - e.g., rxn of (Me₃CCH₂)₃Ta=CH(CMe₃) w/BuLi to make Li[(Me₃CCH₂)₃Ta≡CCMe₃]

Olefin Metathesis

- Extremely important process for scrambling of CR₂ groups between ‘carbene’-complexes and olefins.
- Ring-opening metathesis reactions are involved in one of the most important and promising routes to controlling polymer synthesis and properties (ROMP).