Like Organolithium compounds, but milder:

- Ionic character, electron-deficient
  - oligomeric or polymeric structures

- Basic and nucleophilic
  - Mg: applications in organic synthesis (Grignard reagents !)
  - Be: extremely toxic, not used

- Reducing
  - sometimes unwanted side reactions

Organo Ca, Sr, ... compounds: ionic, insoluble, not used
**Grignard reagents RMgX**

- Direct synthesis ("Grignard reaction"):
  \[ \text{Mg} + \text{RX} \rightarrow \text{RMgX} \]

- Mechanism is **not** simple!
  - almost certainly involves SET (Single Electron Transfer)
  
  \[ \text{RX} + \text{Mg}_s \rightarrow \text{RX}^- + \text{Mg}_s^+ \rightarrow \text{R}^- + \text{X} \text{Mg}_s \rightarrow \text{RMgX}_{solv} \]

  - very sensitive to traces of impurities (Na, K, transition metals) in the Mg
    (vendors sell special "Grignard quality" Mg containing 1-2% Na/K)

  - nature of the Mg surface is important
    (for less reactive halides, surface activation is essential:
     \( I_2, \text{BrCH}_2\text{CH}_2\text{Br}, \text{MeI or HgCl}_2 \))
Grignard reagents RMgX

- Reactivity: I > Br > Cl >> F

- Selectivity: I gives largest amounts of side products

- In ethers:
  - In Et₂O cleaner than in THF, but also slower
  - Also in ether/hydrocarbon mixtures

- Side reactions:
  - Wurtz coupling, especially for allylic halides
    \[ \text{RMgX} + \text{RX} \rightarrow \text{R—R} + \text{MgX}_2 \]
  - Radical rearrangements
Grignard reagents RMgX

- Main application: addition to polar C=X bonds
  - C=O, C=N, C≡N

\[
\begin{align*}
\text{R}^-\text{Mg}^+ & \quad \text{R}^-\text{Mg}^+ \\
& \quad \text{Mg} \\
& \quad \text{Mg}
\end{align*}
\]

- Sometimes radical mechanism (especially for aromatic ketones):
  - same product expected, but possibly different side products

\[
\begin{align*}
\text{R}^-\text{Mg}^+ & \quad \text{R}^-\text{Mg}^+ \\
& \quad \text{R}^-\text{Mg}^+ \\
& \quad \text{Mg} \\
& \quad \text{Mg}
\end{align*}
\]
Grignard reagents RMgX

- Side reaction in C=X addition: reduction through $\beta$-H transfer
  - only for alkyls having a $\beta$-hydrogen...

\[ \text{H} - \text{MgX} \rightarrow \text{H} - \text{O} - \text{MgX} \]
"Barbier reaction":

\[
\text{Mg} + \text{RX} \quad \xrightarrow{1)} \text{R} = \text{O} \quad \xrightarrow{2)} \text{H}^+ \quad \text{OH}
\]

- Selectivity differs from that of Grignard addition
- Probably radical mechanism
- Works even in water!
The Schlenk equilibrium

• Grignard reagents are usually mixtures of many compounds in dynamic equilibrium

• This is often written as the Schlenk equilibrium

\[ \text{R}_2\text{Mg} + \text{MgX}_2 \rightleftharpoons 2 \text{RMgX} \]

but the situation is really more complicated

• Crystal structures may not be representative of species in solution

• The equilibrium can be shifted through addition of ligands:

\[ 2 \text{RMgX} + \text{dioxane} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2(\text{dioxane}) \]
Structure of $[\text{MeMgCl(tmeda)}]_2$
Structure of $\text{MeMgBr(THF)(tmeda)}$
Structure of $\text{Me}_2\text{Mg}_4\text{Cl}_6(\text{THF})_6$
Structure of $[tBu_2Mg]_2$
Structure of $\text{Me}_2\text{Mg(pmdta)}$
Structure of \((\beta\text{-diiminate})\text{MgMe}\)