Organo-lithium compounds

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

• Strongly basic and nucleophilic
  – applications in organic synthesis

• Reducing
  – unwanted side reactions
Organo Na, K compounds

- "Purely" ionic
  - polymeric structures
  - pyrophoric solids
  - mostly insoluble in any solvent they don't react with

- Very strong bases, not that good as nucleophiles
  - few applications
  - organoLi compounds are much easier to handle
Driving force for oligomerization

- ionic interpretation:

Ionic interactions are "soft" but not weak!
Driving force for oligomerization

- covalent interpretation

2e-3c and 2e-4c bonds are not just bonding between Li and C, but also bonding between the Li atoms.
Structure of $[\text{EtLi}]_4$
Structure of \([\text{CyLi}]_6\)
Structure of \([\text{BuLi(THF)}]_4\)
Structure of $[\text{o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li}]_4$
Structure of $[2,6-(\text{MeO})_2\text{C}_6\text{H}_3\text{Li}]_4$
Structure of \([\text{MeLi(sparteine)}]_2\)

not all hydrogen positions well-determined

used for enantioselective deprotonation
Structure of PhLi(pmdta)

pmdta = \[\text{Me}_2\text{N} - \text{N} - \text{Me} - \text{NMe}_2\]
Structure of (Allyl)Li(pmdta)
Structure of $[\text{BzNa(pmdta)}]_\infty$
Structure of $[(\text{Me}_3\text{Si})_3\text{CRb}]_\infty$
Structure of (naphthalene)[Li(tmeda)]₂

tmeda = \begin{array}{c}
\text{Me}_2\text{N} \\
\text{NMe}_2
\end{array}
Synthesis of OrganoLi Compounds

Direct synthesis

\[ RX + Li \rightarrow RLi + LiX \]

- Reactivity: alkyl > aryl, \( Cl < Br < I \) etc
- Commercial synthesis: mostly from chlorides
- In laboratory: usually from alkyl bromides/iodides (easier to start)
- Complication: Li reacts with \( N_2 \), do reaction under Ar!
- Side reaction: Wurtz coupling, especially for \( X = I \)
- In apolar or weakly polar solvents
- Radical mechanism

Transmetallation

\[ RM + Li \rightarrow RLi + M \]

- \( M \) less electropositive than Li
- Infrequently used
Reactions of OrganoLi Compounds

Metallation

\[ \text{RLi} + \text{R'H} \rightarrow \text{R'Li} + \text{RH} \]

- Faster for more basic R⁻
- Faster in polar and/or coordinating solvents
- Works well if product capable of intramolecular coordination

Metal-halogen exchange

\[ \text{RLi} + \text{R'Br} \rightarrow \text{R'Li} + \text{RBr} \]

- Facile for I and Br, usually (too) slow for Cl, F
- Regioselective synthesis of R'Li
- Side reaction: Wurtz coupling
- Usually done at low temperature (-80 to -20°C)
Reactions of OrganoLi Compounds

Metathesis

\[ n \text{RLi} + M X_n \rightarrow n \text{LiCl} + R_n M \]

- Driving force: stability of LiCl (lattice energy!)
- Selective synthesis of $R_i MX_m$ often hard

\[ \text{PhLi} + \text{PhPCl}_2 \ (1:1) \rightarrow \text{PhPCl}_2 + \text{Ph}_2 \text{PCl} + \text{Ph}_3 \text{P} \]

- With excess RLi often "ate" complexes ($R_{n+1} M^-$)
Structure of \([(\text{tmeda})\text{LiMe}_2]\_2\text{Mg}\)