Skills to Develop

In this lecture you will learn the following

- How to synthesize and handle sodium, lithium compounds.
- Structural features.

Organometallic compounds of alkaline metals

Organic compounds such as terminal alkynes which contain relatively acidic hydrogen atoms form salts with the alkali metals.

NaCp is pyrophoric in air, but air-sensitivity can be lessened by complexing the Na⁺ with dme. In the solid state, [Na(dme)][Cp] is polymeric

*Pyrophoric material: is one that burns spontaneously when exposed to air.*

Organolithium compounds are of particular importance among the group 1 organometallics.
Many of them are commercially available as solutions in hydrocarbon solvents.

Solvent choices for reactions involving organometallics of the alkali metals are critical. For example, $^n$BuLi is decomposed by Et$_2$O to give $^n$BuH, C$_2$H$_4$ and LiOEt.

Alkali metal organometallics are extremely reactive and must be handled in air- and moisture-free environments; NaMe, for example, burns explosively in air.

Lithium alkyls are polymeric both in solution and in the solid state.

NMR is very useful in understanding the solution structures; $^6$Li (I = 1), $^7$Li (I = $\frac{1}{2}$), $^{13}$C (I = $\frac{1}{2}$)

The structures of ($^t$BuLi)$_4$ and (MeLi)$_4$ are similar. $^n$BuLi when mixed with TMEDA, gives a polymeric chain. TMEDA link cubane units together through the formation of Li-N bonds.

Alkyl lithium compounds are soluble in organic solvents whereas Na and K salts are insoluble, but are solubilized by the chelating ligand TMEDA. Addition of TMEDA may break down the aggregates of lithium alkyls to give lower nuclearity complexes. E.g. [$^n$BuLi.TMEDA]$_2$

However, detailed studies have revealed that the system is far from simple, and it is possible to isolate crystals of either [$^n$BuLi.TMEDA]$_2$ or [$^n$BuLi]$_4$.TMEDA$.\infty$.

In the case of (MeLi)$_4$, the addition of TMEDA does not lead to cluster breakdown, and the X-ray structure confirms the composition (MeLi)$_{4.2}$TMEDA, the presence of both tetramers and the amine molecules in the crystal lattice.


Lithium alkyls and aryls are very useful reagents in organic synthesis and also in making corresponding carbon compounds of main group elements. Lithium alkyls are important catalysts in the synthetic rubber industry for the stereospecific polymerization of alkenes.
Transmetallation:

Organolithium compounds:

Some typical examples include:
- MeLi and nBuLi which depending on solvent may exist as tetramers or hexamers.
- (cyclohexyl)Li which exists as a hexamer.
- t-BuLi exists as a tetramer and can coordinate diethylether to form a dimer or a bulky diamine like tetraethylethylenediamine (TEEDA) to give a monomer.

n-butyllithium

Sodium forms ionic salts with terminal alkynes and cyclopentadiene:

\[ 2\text{Na}^+ + 2 \text{HC≡CEt} \rightarrow 2 \text{Na}^+[\text{C≡CEt}]^- + \text{H}_2 \]

(in THF) \(\text{Cp} + \text{NaH} \rightarrow \text{Na}^+ \text{Cp}^- + \text{H}_2\)

This salt is pyrophoric but it has been found that when 1,2-dimethoxyethane is added as complexing agent the product is less air-sensitive. Both the Na and K salts have been isolated and their structures determined.

The nomenclature used to denote the idea that the 5-carbons of the cp ring are equally attached is by the use of $\eta^5$. For the case where only 1-carbon is attached then the designation would be $\eta^1$. Here the Greek letter "eta" is used and the term is generally called "hapticity".

Sodium and potassium form intensely coloured salts with aromatic compounds. The alkali metal is oxidised and transfers one electron to the aromatic system and this becomes a paramagnetic radical anion:

$$\text{Na + naphthalene} \rightarrow \text{Na}^+\text{[C}_8\text{H}_{10}]^-$$

In the case of naphthalene, the salt is deep blue.

References


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