TDC Part I
Paper I, Group B
Inorganic Chemistry

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TOPIC:- ORGANOSODIUM
ORGANOBERYLIUM
ORGANOCALCIUM

Organosodium Compounds

Organosodium chemistry is the chemistry of organometallic compounds containing a carbon to sodium chemical bond.The application of organosodium compounds in chemistry is limited in part due to competition from organolithium compounds, which are commercially available and exhibit more convenient reactivity.

The principal organosodium compound of commercial importance is sodium cyclopentadienide.Sodium tetraphenylborate is also an organosodium compound

Organometal bonds in group 1 are characterised by high polarity with corresponding high nucleophilicity on carbon.The carbanionic nature of organosodium compounds can be minimized by resonance stabilizationOne consequence of the highly polarized Na-C bond is that simple organosodium compounds tend to aggregate and are often poorly soluble.

Synthesis and structure:

The usual method for preparing organosodium compounds involves deprotonation. Sodium cyclopentadienide is thus prepared by treating sodium metal and cyclopentadiene:

$2\ Na + 2\ C_5H_6 \rightarrow 2\ NaC_5H_5 + H_2$

Trityl sodium can be prepared by metal-halogen exchange. This method is used in preparing trityl sodium:

$Ph_3CCl + 2\ Na \rightarrow Ph_3CNa + NaCl$

Sodium also reacts with polycyclic aromatic hydrocarbons via one-electron reduction. With solutions of naphthalene, it forms the deeply coloured radical sodium naphthalenide, which is used as a soluble reducing agent:

In the original work the alkylsodium compound was accessed from the dialkylmercury compound by transmetallation.

Simple organosodium compounds such as the alkyl and aryl derivatives are generally insoluble polymers.

Reactions:

Organosodium compounds are traditionally used as strong bases

The higher alkali metals are known to metalate even some unactivated hydrocarbons and are known to self-metalate

In the **Wanklyn reaction** organosodium compounds react with carbon dioxide to give carboxylates:

$C_2H_5Na + CO_2 \rightarrow C_2H_5CO_2Na$

Grignard reagents undergo a similar reaction.

Some organosodium compounds degrade by beta-elimination

Industrial applications

Although organosodium chemistry has been described to be of "little industrial importance", it once was central to the production oftetraethyllead.

A similar Wurtz coupling-like reaction is the basis of the industrial route to triphenylphosphine:

$3 PhCl + PCl_3 + 6 Na \rightarrow PPh_3 + 6 NaCl$

The higher alkali metals, organopotassium, organorubidium and organocaesium, are even more reactive than organosodium compounds and of limited utility.

The higher alkali metals also favor the sterically congested conformation.

Organoberyllium compounds

Organoberyllium chemistry is limited to academic research due to the cost and toxicity of beryllium, beryllium derivatives and reagents required for the introduction of beryllium, such as beryllium chloride. Examples of known organoberyllium compounds are dineopentylberyllium, beryllocene (Cp_2Be), diallylberyllium (by exchange reaction of diethyl beryllium with triallyl boron) and bis(1,3-trimethylsilylallyl)beryllium. Ligands can also be aryls and alkynyls.

organocalcium chemistry should be quite extensive; however, advances in this chemistry have been hindered by the lack of an easy preparation for organocalcium products. Reacting the calcium metal with organic substrates results in reduced activity due to surface poisoning factors, which restrict the oxidative addition.

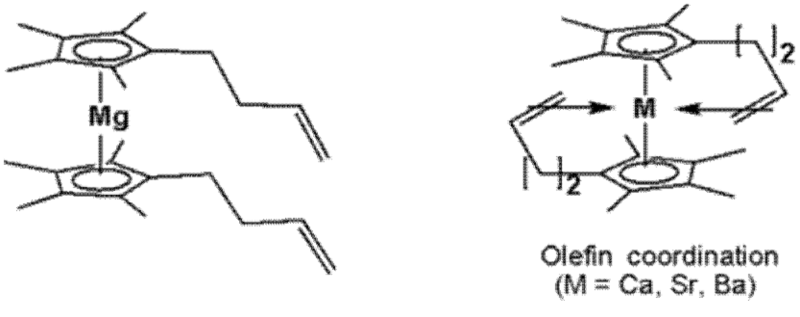
A well known organocalcium compound is (Cp)calcium(I). Bis(allyl)calcium was described in 2009.[14] It forms in a metathesis reaction of allylpotassium and calcium iodide as a stable non-pyrophoric off-white powder:

2 KC3H5 + CaI2 → (C3H5)2Ca + 2 KI (THF 25 °C)

The bonding mode is η3. This compound is also reported to give access to an η1 polymeric (CaCH2CHCH2)n compound.[15]

The compound [(thf)3Ca{μ-C6H3-1,3,5-Ph3}Ca(thf)3] also described in 2009[16][17] is an inverse sandwich compound with two calcium atoms at either side of an arene.

Olefins tethered to cyclopentadienyl ligands have been shown to coordinate to calcium(II), strontium(II), and barium(II):



Olefin complexes of calcium, strontium and barium

Summary

The unit summarized as :-The term "metalorganics" usually refers to metal-containing compounds lacking direct metal-carbon bonds but which contain organic ligands.Metal beta-diketonates, alkoxides, and dialkylamides are representative members of this class. In addition to the traditional metals, lanthanides, actinides, and semimetals, elements such as boron, silicon, arsenic,and selenium are considered to form organometallic compounds, e.g. organoborane compounds such as triethylborane (Et_3B). Organometallics find practical uses in stoichiometric and catalytic processes, especially processes involving carbon monoxide and alkene-derived polymers. All the world's polyethylene and polypropylene are produced via organometallic catalysts, usually heterogeneously via Ziegler-Natta catalysis. Acetic acid is produced via metal carbonyl catalysts inthe Monsanto process and Cativa process. Most synthetic aldehydes are produced via hydroformylation. The bulk of the synthetic alcohols, at least those larger than ethanol, are produced by hydrogenation of hydroformylation derived aldehydes.

Similarly, the Wacker process is used in the oxidation of ethylene to acetaldehyde. Organolithium, organomagnesium, and organoaluminium compounds are highly basic and highly reducing. They catalyze many polymerization reactions, but are also useful stoichiometrically. III-V semiconductors are produced from trimethylgallium, trimethylindium, trimethylaluminium and related nitrogen / phosphorus / arsenic / antimony compounds. These volatile compounds are decomposed along with ammonia, arsine, phosphine and related hydrides on a heated substrate via metalorganic vapor phase epitaxy (MOVPE) process for applications such as light emitting diodes (LEDs) fabrication. Organometallic compounds may be found in the environment and some, such as organolead and organomercury compounds are a toxic hazard.

Review Questions

1. What are organometallic compouns?
2. Give method of preparation of organosodium compouns.
3. What is Grignard Reagent, discuss its structure.
4. Discuss Organolithium compounds.
5. Define organoberillium and organocalcium compouns.