

Module 4 : Organoelement compounds of Group 15

Lecture 2 : Organometallic compounds of As(III) and Sb(III)

Objectives

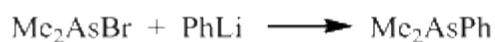
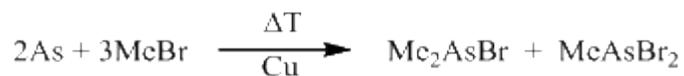
In this lecture you will learn the following

- Preparation of trivalent compounds.
- Mono and bis derivatives.
- Reaction of organo arsenic and antimony compounds.
- Structural features of organolead compounds.

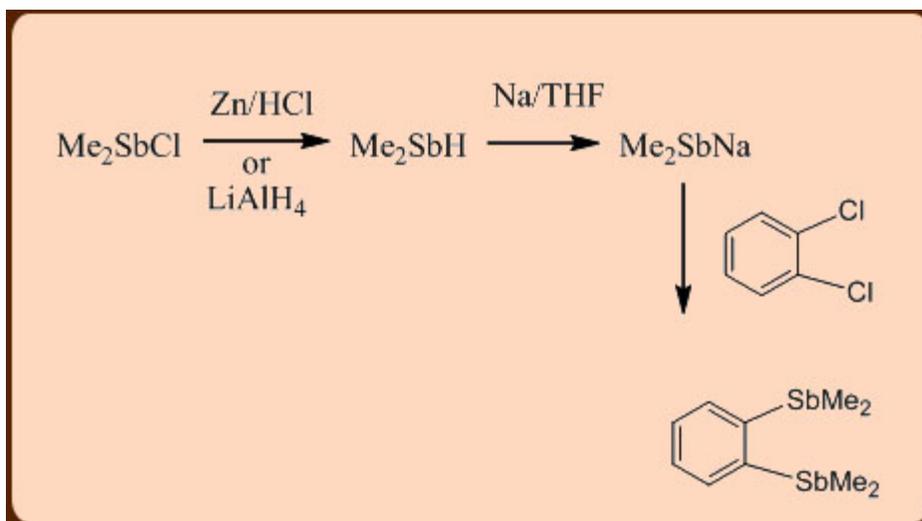
Organometallic compound of As(III) and Sb(III).

Direct synthesis

Mono- derivatives

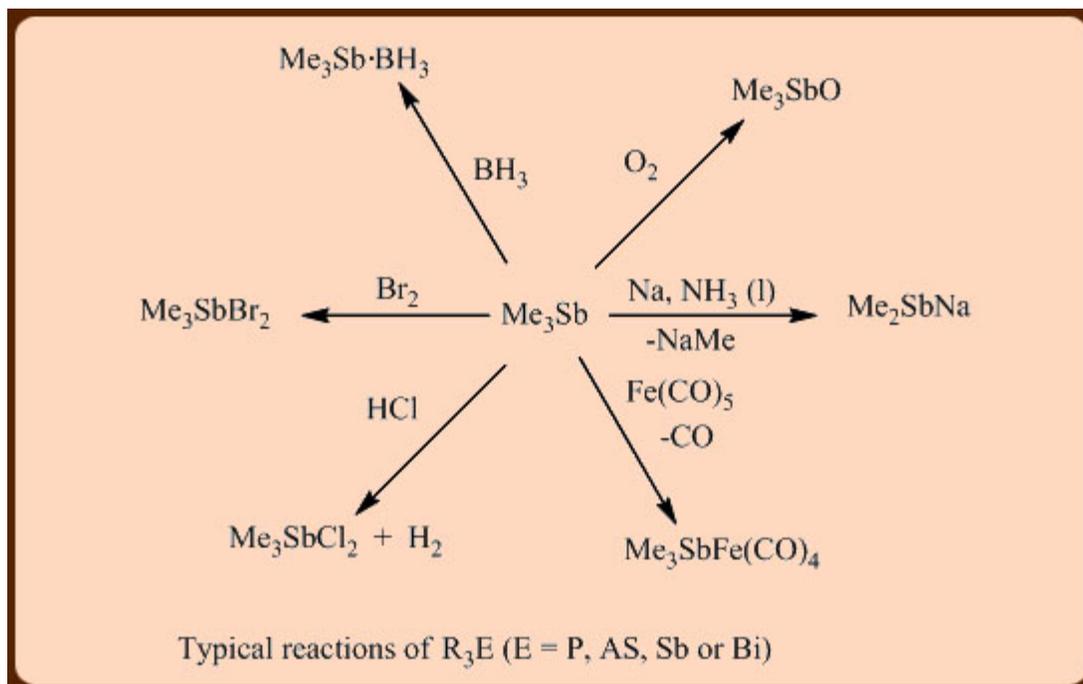


Bis derivatives:



In a similar way, a variety of bisphosphines and arsines can be generated.

Reactions of trialkyl derivatives, R_3E



The transition metal chemistry of R_3E , phosphines, arsines or stibines has been extensively studied because of their distinct donor and acceptor properties. Among them, the phosphines or tertiary phosphines (R_3P) are the most valuable ligands in metal mediated homogeneous catalysis. Interestingly, the steric and electronic properties can be readily tuned by changing the substituents on phosphorus atoms. Chapter 16 is fully dedicated to the chemistry of phosphines.

Properties

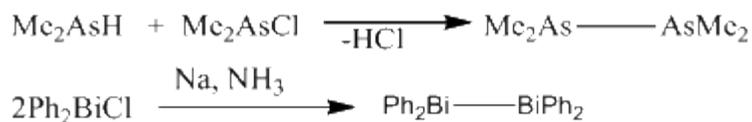
Trialkyl derivatives are highly air-sensitive liquids with low boiling points and some of them are even **pyrophoric**. Triphenyl derivatives are solids at room temperature and are moderately stable and oxidizing agents such as $KMnO_4$, H_2O_2 or $TMNO$ are needed for oxidation to form $Ph_3E=O$.

Cyclic and acyclic derivatives containing $E-E$ bonds

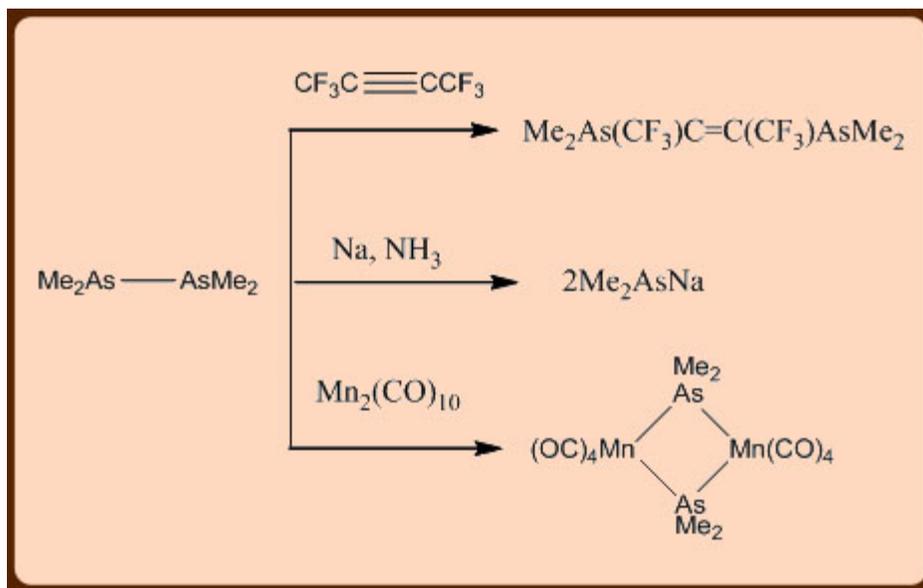
$E-E$ single bonds:

The $E-E$ bond energies suggest that they do not have greater stability and the stability decreases down the group.

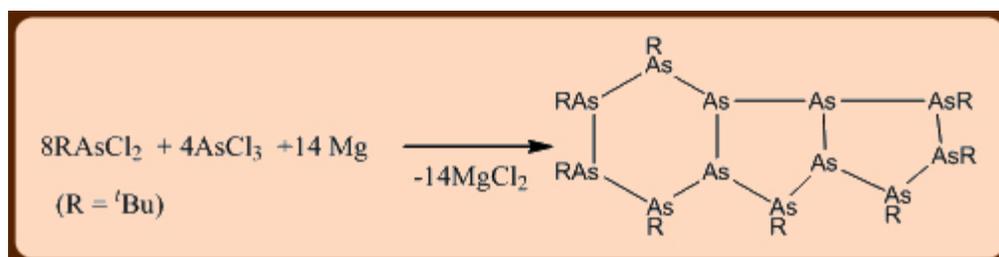
The simplest molecules include Ph_2P-PPh_2 , $Me_2As-AsMe_2$ prepared by coupling reactions:



The weakness of $E-E$ bonds accounts for many interesting reactions and a few of such reactions are listed below:



Cyclic and polycyclic derivatives can be prepared by employing any of the following methods:



Problems:

1. Confirm that the octahedral structure of $[\text{Ph}_6\text{Bi}]^-$ is consistent with VSEPR theory.

Solution:

Octahedral similar to PF_6^-

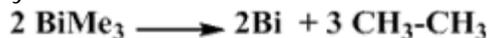
5 (Bi valence electrons) + 6 (each Ph) + 1 (-ve charge) = 12 electrons

i.e. six pairs, octahedral geometry

2. Comment on the stability of BiMe_3 and $\text{Al}_2(\textit{i}\text{Bu})_6$ with respect to their thermal decomposition and give chemical equations for their decomposition.

Solution:

Similar to other heavy p-block elements, Bi—C bonds are weak and readily undergo homolytic cleavage. The resulting methyl radicals will react with other radicals or form ethane



The $\text{Al}_2(\textit{i}\text{Bu})_6$ dimer readily dissociates. At elevated temperature dissociation is followed by β -hydrogen elimination. This type of elimination is common for organometallic compounds that have alkyl groups with β -hydrogens, can form stable M—H bonds, and can provide a coordination site on the central metal.

The decomposition reaction is:

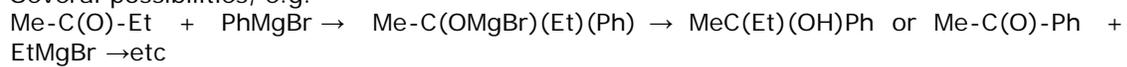


3. Using a suitable Grignard reagent, how would you prepare (i) $\text{MeC}(\text{Et})(\text{OH})\text{Ph}$; (ii) AsPh_3 .

Solution:

- i. Add a Grignard reagent to a C=O bond, then acidify.

Several possibilities, e.g.



- ii. $\text{AsCl}_3 + 3\text{PhMgBr} \rightarrow \text{AsPh}_3 + 3\text{MgBrCl}$.