Organoelement compounds of group 15

Organic chemistry of non-metal phosphorus, metalloids such as arsine and antimony along with metallic element bismuth is termed as organoelement chemistry. The importance given to organoarsenic compounds earlier due to their medicinal values was waded out after antibiotics were discovered and also their carcinogenic and toxic properties were revealed. Also, the synthetically important organometallic compounds of group 13 and 14 masked the growth of group 15 elements. However, the organoelement compounds of phosphorus, arsenic and antimony find usefulness as ligands in transition metal chemistry due to their σ-donor and π-acceptor abilities which can be readily tuned by simply changing the substituents. These donor properties are very useful in tuning them as ligands to make suitable metal complexes for metal mediated homogeneous catalysis. Although organoelement compounds can be formed in both +3 (trivalent and tricoordinated) and +5(pentavalent and tetra or pentacoordinated) oxidation states, trivalent compounds are important in coordination chemistry.

For organoelement compounds of group 15, the energy of E—C bond decreases in the order, E = P > As > Sb > Bi, and in the same sequence E—C bond polarity increases.

Organometallic compounds of As(V) and Sb(V)

Due to the strong oxidizing nature of pentahalides, the direct alkylation or arylation to generate ER₅ is not feasible, but can be prepared in two steps.

A few representative methods of preparation are given below:
Structures and properties

Pentaalkyl or pentaaryl derivatives are moderately thermally stable. On heating above 100°C, they form trivalent compounds as shown below:

Reaction with water,

Pentavalent compounds readily form "tetrahedral onium" cations and "octahedral and hexacoordinatged ate" anions.

In solid state, Ph$_5$As adopts trigonal bipyramidal geometry, whereas Ph$_5$Sb prefers square based pyramidal geometry although the energy difference between the two is marginal.

The salts of the type [R$_4$E]$^+$ adopt tetrahedral geometry, whereas hexacoordinated anions [R$_6$E]$^-$ assume octahedral geometry.

Mixed organo-halo compounds of the type R$_n$EX$_{5-n}$ adopt often dimeric structures due to the presence of lone pairs of electrons on X which can readily coordinate to the second molecule. The following structural types can be anticipated.
The thermal stability of $R_nEX_{5-n}$ decreases with decreasing 'n'. Thermal reactions are essentially the reverse reactions of addition reactions used in the preparation of $R_5E$.

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:

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$_2$O$_2$ 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$_2$As—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 $\text{PF}_6^-$
   5 (Bi valence electrons) + 6 (each Ph ) + 1 (-ve charge) = 12 electrons
   i.e. six pairs, octahedral geometry

2. Comment on the stability of $\text{BiMe}_3$ and $\text{Al}_2\text{(iBu)}_6$ 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 $\text{Al}_2(\text{Bu})_6$ dimer readily dissociates. At elevated temperature dissociation is followed by $\beta$-hydrogen elimination. This type of elimination is common for organometallic compounds that have alkyl groups with $\beta$-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) $\text{AsPh}_3$.

Solution:

1. Add a Grignard reagent to a $\text{C}=\text{O}$ bond, then acidify.

   Several possibilities, e.g.
   $\text{Me-C(O)-Et} + \text{PhMgBr} \rightarrow \text{Me-C(OMgBr)(Et)(Ph)} \rightarrow \text{MeC(Et)(OH)Ph}$ or $\text{Me-C(O)-Ph} + \text{EtMgBr} \rightarrow \text{etc}$

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

Contributors

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