

1. Discuss the classification of organometallic compounds on the basis of the position of the metal in the periodic table.

2. Describe briefly the general characteristics of organometallic compounds.

3. Based on the IUPAC rules, name the following organometallic compounds:

- (a)  $\text{Zn}(\text{C}_2\text{H}_5)_2$ ; (b)  $(\text{LiC}_2\text{H}_5)_4$ ; (c)  $\text{CH}_3\text{SiH}_2\text{Cl}$ ;  
 (d)  $\text{K}[\text{PtCl}_5(\text{C}_2\text{H}_4)]$ ; (e)  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ ; (f)  $\text{Mn}(\eta^3\text{-C}_3\text{H}_3)(\text{CO})_4$ ;

4. Define the following:

- (a) Homo- and hetero-leptic organometallic compounds  
 (b) Hapticity  
 (c) Electron deficient organometallic compounds

5. Discuss the factors influencing behaviour of  $\sigma$ -bonded organometallic compounds.

### Supplementary Reading

1. 'Nomenclature of Organic Chemistry', *International Union of Pure and Applied Chemistry* (IUPAC), pp. 360-466, Pergamon Press (1979).
2. 'Organometallic Chemistry' by E.G. Rochow, Reinhold, New York (1964).
3. 'The long search for stable transition metal alkyls', by G. Wilkinson, Noble Lecture (1973).
4. 'The Chemistry of Organometallic Compounds', By J.J. Eisch, Macmillan, New York (1967).
5. 'Principles of Organometallic Chemistry', by G.E. Coates, M.L.H. Green, P. Powell, and K. Wade (First published in 1968 by Methuen & Co. Ltd.) Reprint 1977 published by Chapman and Hall, London.
6. 'Introduction to Organometallic Chemistry', by F.K. Cardidge and H. Gilman, pp. 1-33 in 'Characterization of Organometallic Compounds', edited by M. Trautsl, Interscience Publishers, New York (1969).
7. 'Organometallic Compounds', by Open University Course Team, The Open University Press, Walton Hall, Milton Keynes, U.K. (1977).
8. 'Structures of Main Group Organometallic Compounds Containing Electron-Deficient Bridge Bonds', by J.P. Oliver, in *Advances in Organometallic Chemistry*, edited by F.G.A. Stone, and R. West, Vol. 15, pp. 235-267, Academic Press, New York (1977).

## Organometallic Compounds of Main Group Elements

### 3.1 INTRODUCTION

Although the first organoarsenic derivative was synthesised in 1769 by L.C. Cadet de Gassicourt, yet it was only in mid-19th century that the nature of the compound was established as  $(\text{H}_3\text{C})_2\text{As}^+\text{As}^-(\text{CH}_3)_2$ . The real beginnings of the non-transition (main group) metal organometallic chemistry can, however, be traced to the synthesis of zinc alkyls by Frankland in 1848 which was followed a few decades later by Grignard's synthesis and exploitation of organomagnesium halides (Grignard received Nobel Prize for this work in 1912) in organic synthesis.

Besides structural and other features, a wide and in fact fastly growing interest in organometallic compounds of main group elements is sustained by their established and potential applications as reagents (e.g. organometallics of lithium, magnesium, zinc, cadmium, mercury, boron, aluminium, thallium, silicon, and tin) in organic and organometallic synthesis (see Chapter 6).

This chapter provides with the aid of a few illustrative examples, a general account of the salient (synthetic, structural and bonding) characteristics of this class (main group organometallics) of compounds, beginning with a few selected chronological developments:

1760 L.C. Cadet de Gassicourt's accidental preparation methylarsenical liquid ("cacodyl").

1840 R.W. Bunsen characterizes cacodyl as  $\text{As}_2(\text{CH}_3)_4$ .

1849 E. Frankland (generally regarded as founder of organometallic chemistry) discovers alkylzinc compounds.

1852 E. Frankland describes the preparation of methylmercury iodide from mercury and iodomethane in sunlight.

1863 C. Friedel and J.M. Crafts prepare tetramethylsilane (the first organosilane).

1898 O. Dimroth studies mercuration of aromatic compounds

1900 V. Grignard describes direct preparation of organomagnesium halides now known as Grignard reagents.

- 1901 F.S. Kipping lays the foundation of organosilicon chemistry and prepares  $[(C_4H_9)_2SiO]_n$  (diphenylsilicone).
- 1909 P. Ehrlich (Nobel Prize, 1908) introduced Salvarsan for treatment of syphilis and laid the foundation of chemotherapy.
- 1912 V. Grignard and P. Sabatier share the Nobel Prize in chemistry for discovery of the Grignard reagent, and for developing method of hydrogenating organic compounds in the presence of finely disintegrated metals respectively.
- 1914 W. Schlenk and coworkers investigate organoalkali compounds.
- 1922 T. Midgley and T.A. Boyd describe the anti-knocking behaviour of Pb  $(C_2H_5)_4$ .
- 1929 T.A. Paneth generates alkyl radicals through pyrolysis of  $PbR_4$ .
- 1930 K. Ziegler and H. Colonius describe direct preparation of lithium alkyls.
- 1934 H. Gilman and coworkers describe metallation of aromatic hydrocarbons with organolithium reagents.
- 1938 H. Gilman as well as G. Wittig prepare aryllithium reagents independently from aryl halides and butyllithium (halogen-lithium exchange reaction).
- 1943 E. G. Rochow describes the 'direct synthesis' of chlorosilanes, extensively used for preparation of silicones (which have become industrially very important).
- 1955 K. Ziegler and coworkers prepare aluminium alkyls by the direct combination of aluminium hydrogen, and alkenes.
- 1956 H.C. Brown and B.C. Subba Rao discover hydroboration.
- 1956 G. Wittig describes methylenation of carbonyl compounds with methylenetriphenylphosphoranes.
- 1960 M.F. Hawthorne and coworkers discover carboranes.
- 1976 M.F. Lappert and coworkers laid the foundation of subvalent Group 14 metal alkyls and stable organometal (III) free radicals  $MR_3$ .
- 1979 Nobel Prize to H.C. Brown and G. Wittig for their contributions on the applications of organoboranes and methylenephosphoranes, respectively, in organic synthesis.
- 1981 R. West and coworkers isolate the first stable compound  $Si_2(C_6H_5Me_3-1,3,5)_4$  with Si = Si double bond.
- 1981 A.G. Brook, et al. report a stable compound containing Si = C bond,  $(Me_3Si)_2Si = C(OSiMe_3)_2C_6H_5$ .
- 1981-90 The synthesis of  $Ar^+P^- = PAr^+$  ( $Ar^+ = C_6H_5Bu_3-2,4,6$ ) in M. Yoshifuji's group, followed by isolation of  $-P = As-$ ,  $-P = Sb-$ , and  $-As = As-$  derivatives by A.H. Cowley, et al. and further extension to material chemistry.

### 3.2 GENERAL CHARACTERISTICS

Most organometallic compounds (simple alkyls and aryls) of main group elements (where the organic group is bonded to the element by a normal 2-electron 2-centre

### ORGANOMETALLIC COMPOUNDS OF MAIN GROUP ELEMENTS

bond, with few exceptions such as alkyls of lithium, beryllium, magnesium, aluminium and zinc, which in view of their electron deficient character and association through two-electron three-centre bonds depict properties characteristic of organic rather than inorganic compounds. The majority of these discrete molecular structure (Fig. 3.1).

These, therefore, exist at ambient temperatures either as low-melting crystalline solids or as volatile liquids, which are soluble (miscible) in weakly polar solvents like THF, etc.) or non-polar (e.g. PhH, PhMe, etc.) organic solvents.

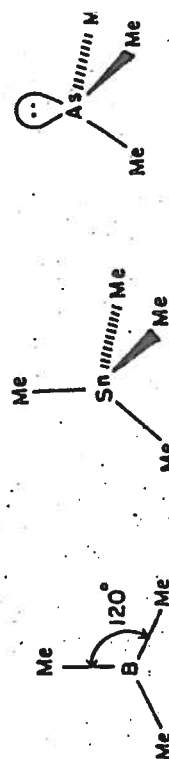


Fig. 3.1 Some simple metal alkyls

The lower alkyls, particularly the methyls tend to be amongst the most volatile derivatives of the metal concerned.

Table 3.1 Boiling Points of Methyl Derivatives  $M(CH_3)_n$  of Some Main Group Elements

GROUP I		GROUP II		GROUP III		GROUP IV		GROUP V		GROUP VI	
$M(CH_3)_2$	b.p. (°C)	$M(CH_3)_3$	b.p. (°C)	$M(CH_3)_4$	b.p. (°C)	$M(CH_3)_5$	b.p. (°C)	$M(CH_3)_6$	b.p. (°C)	$M(CH_3)_7$	b.p. (°C)
Be	217 <sup>a</sup>	B	-22	C	10	N	3	O	-		
Mg	—	Al	226 <sup>a*</sup>	Si	27	P	40	S	—		
Zn	44	Ga	56	Ge	43	As	52	Se	—		
Cd	106	In	136	Sn	77	Sb	79	Te	—		
Hg	93	Tl	147 <sup>a</sup>	Pb	110	Bi	110	Po	—		

\* Extrapolated boiling point. Unlike their group congeners, which have discrete molecular structures,  $Be(CH_3)_2$  and  $Mg(CH_3)_2$  have associated polymeric structures and hence, these are compared non-volatile.

\*\* Trimethylaluminium vaporises as dimeric  $Al_2(CH_3)_6$ .

A perusal of the data in Table 3.1 shows that with the exception of the associated methyls of beryllium and magnesium and to a lesser extent of dimethylaluminium, the values of boiling points of the metal methyls show expected decrease in volatility with increasing relative molecular mass for members of a group of elements in the Periodic Table.

The chemical properties of these organometallic compounds vary widely and can be correlated with the difference in electronegativity (i.e. % ionic character) between the metal and carbon, and by the donor characteristics of the central atom. At the one extreme, alkyls of more electropositive metals (e.g. Li, Na, K) including aluminium, zinc and even boron are spontaneously inflammable in

59 by L.C. Cadet of the compound he non-transition be traced to the ed a few decades um halides (Grignard thesis. ly growing interest ned by their establishment of lithium, um, silicon, and tin) examples, a general characteristics of this class with a few selected

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and react violently with water (except that of boron, which requires a higher temperature); at the other end, the tetra-alkyls of group IVB elements are relatively unreactive species.

### 3.3 STABILITY OF ORGANOMETALLIC COMPOUNDS

In dealing with the stability of a compound, one should be clear about the type of stability under consideration. In general terms, the stability of an organometallic compound may refer to either its thermal stability, or resistance to chemical attack (particularly by air and moisture). Obviously, these different types of stabilities would depend both on thermodynamic as well as kinetic factors. Most metal alkyls and aryls,  $MR_n$ , are thermodynamically (though not necessarily from a kinetic view point) unstable to oxidation and hydrolysis and, therefore, need protection (all manipulations in such cases should be carried out in an inert atmosphere of pure and anhydrous nitrogen/argon or under vacuum) from the atmosphere during their synthesis, isolation, and storage. There are few other examples of organometallic compounds like tetramethyllead which are thermodynamically unstable with respect to oxidation and hydrolysis, yet they survive exposure to air or/and moisture possibly because of kinetic factors.

#### 3.3.1 Thermal Stability

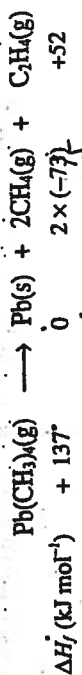
The thermodynamic stability of a compound relative to its constituent elements (or for practical purposes, relative to the products of decomposition) would obviously depend upon the standard free energies of formation,  $\Delta G_f^\circ$  of the different species concerned. In view of the non-availability of accurate data on  $\Delta G_f^\circ$  values for organometallic compounds, one has to rely on the known standard enthalpies of formation,  $\Delta H_f^\circ$ , making due allowance for plausible estimates for the contributions of the entropy terms  $T\Delta S$ , in the well-known relationship:

$$\Delta G = \Delta H - T\Delta S$$

In Table 3.2 are listed the standard values of molar enthalpies of formation ( $\Delta H_f^\circ$  / kJ mol<sup>-1</sup> as well as of metal-carbon average bond enthalpies  $E_m(M-C)$  of some volatile metal methyls,  $M(CH_3)_n$ .

The decomposition of the metal methyls into the component elements, i.e., metal, carbon and hydrogen could be expected to be an exothermic process in the case of heavier metal alkyls, e.g.,  $MgMe_2$ ,  $CdMe_2$ ,  $InMe_3$ ,  $PbMe_4$  and  $BiMe_3$ , for which  $\Delta H_f^\circ$ , i.e., the enthalpy of formation is positive. Conversely for methyls of lighter elements such as B, Al, Si, Ge and P, it should be an endothermic process.

In an actual decomposition process; however, the metal alkyls yield the metal, hydrogen and mixtures of hydrocarbons rather than simple elementary carbon. In such situations, therefore, we would have to take into account the enthalpies of formation of the hydrocarbons involved. For example, let us for the purpose of simplicity consider that tetramethyllead decomposes into lead, methane and ethene only, i.e.,



The standard enthalpy change  $\Delta H_m^\circ$  for this reaction would be given by the difference between the standard enthalpies of formation,  $\Delta H_f^\circ$ , of the products and the reactants, i.e.,

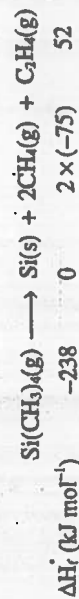
$$\Delta H_m^\circ = -150 + 52 - 137 = -235 \text{ kJ mol}^{-1}$$

Table 3.2 Standard Molar Enthalpies of Formation ( $\Delta H_f^\circ$  in kJ mol<sup>-1</sup>) and Metal Carbon Average Bond Enthalpies  $E_m(M-C)$  in kJ mol<sup>-1</sup> of some Metal Methyls,  $M(CH_3)_n$ .

Compound	$\Delta H_f^\circ$	$E_m$
<b>Group IIB (12)</b>		
ZnMe <sub>2</sub>	+55	176
CdMe <sub>2</sub>	+110	138
HgMe <sub>2</sub>	-93	121
<b>Group IIIB (13)</b>		
BMe <sub>3</sub>	-122	364
AlMe <sub>3</sub>	-88	276
GaMe <sub>3</sub>	-39	247
InMe <sub>3</sub>	+172	163
TlMe <sub>3</sub>	...	...
<b>Group IVB (14)</b>		
CMe <sub>4</sub>	-167	347
SiMe <sub>4</sub>	-238	293
GeMe <sub>4</sub>	-108	247
SnMe <sub>4</sub>	-19	218
PbMe <sub>4</sub>	+137	155
<b>Group VIB (15)</b>		
NMe <sub>3</sub>	-24	314
PMe <sub>3</sub>	-96	276
AsMe <sub>3</sub>	+15	230
SbMe <sub>3</sub>	+31	218
BiMe <sub>3</sub>	+192	114

The reaction, therefore, is highly exothermic. Moreover, the reaction should involve an increase of entropy as three gaseous product molecules are formed for every reagent molecule decomposed. The term,  $T\Delta S$  in the relationship,  $\Delta G = \Delta H - T\Delta S$  would, therefore, be negative and enhance the overall negative value of  $\Delta G^\circ$ . This clearly indicates a higher stability for the products than the reactant molecules.

Similarly for the reaction:



From the above data,  $\Delta H_m$  for  $\text{Si}(\text{CH}_3)_4$  works out to be equal to  $-150 + 52 + 238 = +140 \text{ kJ mol}^{-1}$ . The value of  $\Delta G^\circ$  for  $\text{Si}(\text{CH}_3)_4$  also can be estimated from the relationship,  $\Delta G = \Delta H - T\Delta S$ . For reason stated in the case of  $\text{Pb}(\text{CH}_3)_4$ , the value of  $-T\Delta S$  would be negative in this case also. The value of  $\Delta G^\circ$  for  $\text{Si}(\text{CH}_3)_4$ , therefore, would be lower than  $+140 \text{ kJ mol}^{-1}$ , but it would become negative (indicating the thermodynamic instability of tetramethylsilicon also on these simple considerations), only if the absolute value of  $T\Delta S$  is greater than  $140$  (which is rather improbable).

The question naturally arises as to how species like tetramethyllead with such a high negative value of  $\Delta G^\circ$  (indicating thermodynamic instability) can be actually isolated.

For resolving such anomalies, one would have to take into consideration whether a suitable reaction path is available for the decomposition process to occur. The kinetic stability factor, therefore, appears to play a more predominant role. Although thermodynamically unstable, there appears to be no route in such cases with sufficiently low activation energy by which decomposition could occur at ordinary (and sometimes even at elevated) temperatures with a noticeable rate. The point is illustrated schematically in Figure 3.2, which represents the decomposition of a metal alkyl by homolytic dissociation of its metal carbon bonds.

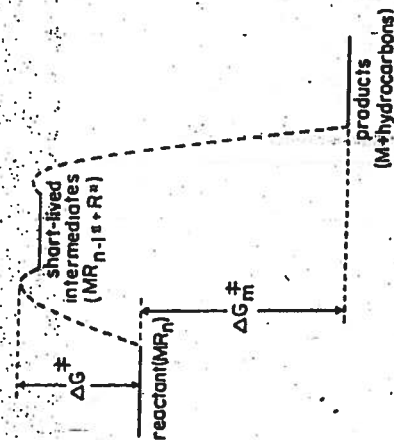
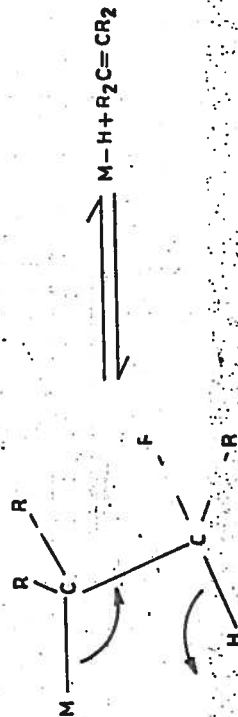


Fig. 3.2 Schematic representation of the thermal decomposition of a metal alkyl  $\text{MR}_n$  by unimolecular homolytic dissociation ( $\Delta G^\ddagger$ , the free energy of activation of the first stage of the reaction is a measure of the kinetic stability of  $\text{MR}_n$ , whereas  $\Delta G_m$ , the free energy of the overall decomposition indicates the thermodynamic instability of  $\text{MR}_n$ ).

The value of activation energy,  $\Delta G^\ddagger$  will depend largely on the metal-carbon bond strength, i.e., on  $E_m(\text{M}-\text{C})$ . As the data in Table 3.2 shows, the value of  $E_m(\text{M}-\text{C})$  decreases, making the thermal decomposition of the metal alkyls more facile as the atomic weight increases for members of the same group of the periodic table. In homolytic dissociation processes of this type, radicals like  $\text{MR}_{n-1}^\cdot$  and  $\text{R}^\cdot$ ,

once formed, are highly reactive and undergo rapid irreversible changes further with the formation of stable products, e.g., formation of  $\text{R}-\text{R}$  by association of  $\text{R}^\cdot$  or of alkane  $\text{RH}$  by abstraction of hydrogen. The thermodynamic stability of these stable final products provides the driving force for the reaction, once it is initiated. By contrast, dissociation of  $\text{MX}_n$ , say  $\text{M}(\text{CO})_n$  into  $\text{M}(\text{CO})_{n-1}$  and  $\text{CO}$  could be reversible, as the  $\text{CO}$  molecules, even after being dissociated from the parent metal carbonyl, remain available for recombination with  $\text{M}(\text{CO})_{n-1}$ .

Homolytic dissociation of metal-carbon bond is not the only way by which organometallic compounds may decompose thermally. Another important route by which such decompositions often occur is called 'β' elimination, in which the hydrogen atom on a β-carbon atom can migrate to the metal atom, allowing elimination of alkene and the formation of a metal hydride:



Such β-elimination reactions will be more facile if the metal atom is coordinatively unsaturated (and possesses a low-lying vacant orbital to accommodate the metal-hydrogen bonding electrons). Naturally one would expect that derivatives of Group II and III metal atoms can be stabilised by adduct formation with Lewis bases. Thus the adduct  $\text{MR}_2\text{L}$  ( $\text{M} = \text{Be}, \text{Mg}, \text{or Zn}$ ) and  $\text{MR}_3\text{L}$  ( $\text{M}' = \text{B}, \text{Al}, \text{Ga}, \text{In}$  or  $\text{Tl}$ ) where  $\text{L}$  is a Lewis base, are thermally more stable than the parent alkyls. The metal carbon bond cleavage reactions can also be facilitated by the presence of low-lying vacant orbitals on the metal or ligand, even in the absence of a β-hydrogen atom, by accommodating electrons promoted from metal carbon bonding orbitals with consequent weakening of metal-carbon bonds. This is generally the predominant factor for the thermal instability (cf. Section 4.2.1) of some transition metal alkyls; e.g. tetramethyltitanium,  $\text{TiMe}_4$ , decomposes above  $-78^\circ\text{C}$ .

### 3.3.2 Stability to Oxidation

The thermodynamic instability of organometallic compounds may be ascribed to the large value of free energies of formation of the metal oxides, carbon dioxide and water. Actually the combustion of organometallic compounds is a highly exothermic process, e.g.,



$$\Delta H_m^\circ = -1918 \text{ kJ mol}^{-1}$$



$$\Delta H_m^\circ = -3591 \text{ kJ mol}^{-1}$$

It is worth noting that dimethylzinc is a spontaneously inflammable compound whereas tetramethyltin is air stable. The greater reactivity of dimethylzinc can be easily understood on the basis of its strong Lewis acid character. In addition to ZnMe<sub>2</sub>, the lighter alkyls of Li, Na, Be, Mg, Zn, B, Al, Ga, In, Tl, As, Sb and Bi are also spontaneously inflammable. Thus the presence of empty low-lying orbitals (e.g. 4p orbital of GaMe<sub>3</sub>) or a lone pair of electrons (as in SbMe<sub>3</sub>) appears to be a source for kinetic reactivity to oxidation by air. The Group IVB tetraalkyls such as SnMe<sub>4</sub> possess neither of these characteristics and, therefore, they resist oxidation at ambient temperatures.

### 3.3.3 Stability to Hydrolysis

The organometallic compounds are generally hydrolysed via nucleophilic attack by water, which is facilitated by: (i) the presence of empty low-lying orbitals on the metal, and (ii) the polarity of metal-carbon bonds. As a consequence of these factors, the organoderivatives of alkali and alkaline earth metals as well as of Zn, Cd, Al, Ga and In are readily hydrolyzed. By contrast, the trialkylboranes although coordinatively unsaturated (the empty 2p orbital on the boron atom provides a site for nucleophilic attack) are unaffected by water at ambient temperatures, possibly due to comparatively very low polarity of boron-carbon bonds. The alkyls and aryls of the Group IV and V elements are also kinetically inert to hydrolysis by water.

## 3.4. PREPARATIVE ROUTES FOR METAL-CARBON BOND FORMATION

The types of reactions generally employed for the synthesis of non-transition metal organometallic compounds have been summarized in Table 3.3.

Out of a very large number of preparative methods available now for the synthesis of organometallic compounds (homoleptic or heteroleptic) of non-transition elements, only a few methods of more general applicability are being presented in Sections 3.4.1 to 3.4.8. Under each section, a few illustrative examples of the application of the specific method have been presented, the method of carbanion-halide exchange reaction (Section 3.4.3) is of such wide applicability to organometallics of groups 2 to 16 element that these have been presented in different sub-sections.

### 3.4.1 Oxidative-Addition Reactions

These reactions constitute one of the principal routes for the formation of metal-carbon bonds; these can be formally termed as 'oxidative addition' types, as they involve the oxidation of a metal 'M' by the addition of a group 'RX'. Naturally, such reactions are more prone to occur with metals of high electropositivity (metals with low ionization energy). The following equations represent one- and two-electron oxidative addition reactions respectively:

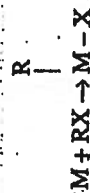


Table 3.3 Preparation of Main Group Organometallics

Types of Reaction (Sub-section)	Preparation
✓ Oxidative-Addition (3.4.1)	$2M + RX \rightarrow MR + MX$ or $M + RX \rightarrow M(R)X$
✓ Metal-Metal Exchange (Transmetalation) (3.4.2)	$M + M'R_n \rightarrow MR_n + M'$ (M' = Mg, Zn, Hg, Al, Sn)
✓ Carbanion-Halide Exchange (3.4.3)	$nM'R_m + mRX_n \rightarrow mMR_n + nM'X_m$ (M' = Li, Mg, Zn, Cd, Hg, Al, Sn)
✓ Metal-Hydrogen Exchange (3.4.4)	$MR' + RH \rightarrow MR + R'H$
Metal-Hydride-Alkene (Addition) (3.4.5)	$M - H + \text{>C} = \text{C} < \rightarrow M - \text{C} - \text{C} - H$
Methylene-Insertion (3.4.6)	$MCl_4 + CH_2N_2 \rightarrow MCl_3(CH_2Cl) + N_2$
Miscellaneous (3.4.7 & 3.4.8)	$As(OEt)_3 + PhN_2X \rightarrow PhAs(OEt)_2 + N_2 + HX$ $M(O_2CMe)_2 \xrightarrow{\text{heat}} MM_2 + 2CO_2$ $M(O_2CMe)_n + CaH_2 \rightarrow M(O_2CMe)_{n-1}(CaH_5) + MeCO_2H$

These reactions involve changes in the formal oxidation states. Some specific examples of these two types of reactions are described in the following pages:



(R = alkyl or aryl; X = Cl; Br (in most cases), or I (in some specific cases); M = Li).

With more electropositive metals, e.g., sodium to caesium, the initially formed metal alkyl has a strong tendency to undergo Wurtz-Fittig reaction (e.g. NaR + RX  $\rightarrow$  R—R + NaX), which can be avoided to some extent by modifications, such as the use of finely divided metals and efficient stirring, which enhance the formation of metal alkyls and also by slow addition of alkyl halides to minimize the side-reaction. The alkyls of less electropositive metals have generally been prepared, by using the metal in the form of an alloy:



\* Ethers are generally prone to attack by organolithium derivatives, but there are wide variations in the reaction rates. For example, more basic tetrahydrofuran reacts faster with an organolithium reagent than diethyl ether. It is, therefore, preferred to keep the temperature of the reaction as low as possible, but sufficiently high to keep it going.





(R = alkyl)



(X = Cl, I)

The main driving force for these reactions appears to be the reaction between a halogen and an electropositive (alkali) metal.

The well known example of two-electron oxidative-addition reaction is the formation of Grignard reagents and related compounds:



(R = alkyl, aryl or fluoroalkyl; X = halogen) (N.B. the reactivity of the alkyl halide increases from chloride to iodide; bromides are generally chosen as the reactions with chlorides may be too slow and the use of iodides is entailed by some side-reactions).

This type of oxidative-addition reactions has been extended to metals other than magnesium.

Reactions with Ca\*, Sr and Ba are generally not as facile as for Mg and special attention to experimental conditions is necessary to obtain satisfactory yields. A slight change in the reaction conditions as illustrated by the following equations gives rise to some potentially useful homoleptic- and heteroleptic-organometallics of metals arranged groupwise.



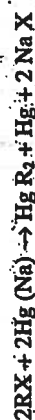
(E = C, Si)



(R = alkyl)



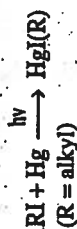
(Zn\* = finally divided zinc prepared from Zn Br<sub>2</sub> and potassium in THF).



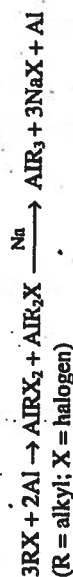
(X = Cl, Br; R = Me, Et, CH<sub>2</sub>Ph; usually Hg R<sub>2</sub>, but unsymmetrical, Hg(R)X may also be formed).



\* For example, successful preparations of calcium compounds require either very pure metal with low sodium content or slightly less pure calcium in the presence of mercury.



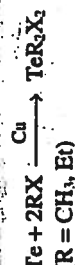
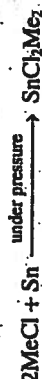
(R = alkyl)



(R = alkyl; X = halogen)



The above reaction produces a mixture of products (SiCl<sub>4</sub>, SiCl<sub>3</sub>(Me), SiCl<sub>2</sub>Me<sub>2</sub>, and SiClMe<sub>3</sub>, with SiCl<sub>2</sub>Me<sub>2</sub> predominating).

(R = CH<sub>3</sub>, Et)

(n = 4 or 5)

### 3.4.2 Metal-Metal Exchange Reactions (Transmetalation)

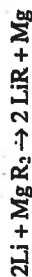
These have been generally represented by the following equation:



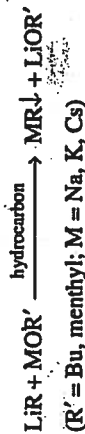
The facility of this route depends upon the difference in the free energies of the formation of the two species MR and M' R. In view of the unavailability of reliable values for  $\Delta G^\circ$  for organometallic compounds in general,  $\Delta H_f^\circ$  (heats of formation) may be used to estimate the thermodynamic feasibility of such reactions. A perusal of thermodynamic data in Table 3.2 indicates that heavier metal alkyls (and aryls) should be more prone to lose organic groups.

There are two ways of estimating the feasibility of the above reactions. Firstly, it may be considered formally as an oxidation-reduction reaction in which the more electropositive metals (main groups I, II and III, except boron) should be more

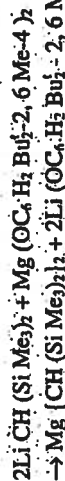
prone to participate in such transformations. Secondly, the reaction of any metal whose metal-carbon (M—C) bond energy is higher than that of M'—C bond energy in M'R used, would tend to occur as:



The reaction of sodium with mercury alkyls has often been used when pure organoalkali metal compounds (including compounds of heavier alkali metals) are required; although free from Wurtz coupling, yet the reaction is slow and inconvenient. Recently (1980) a more versatile method has been developed in which an unfavourable equilibrium is displaced by the solubility of lithium alkoxides and insolubility of organoalkali metal compounds in the solvents employed:



More recently (1990), an opposite type of solubility behaviour of the products has been exploited for the synthesis of some soluble magnesium alkyls:



Additionally, some more reactions of synthetic utility are as shown:



(M = Ga or In; especially for R = alkyl)



(excess)

The last reaction is not applicable for cadmium, because only a mixture of products is obtained:



(R = alkyl, 75%; R = phenyl, 25%)

As the Hg—C bonds are exceptionally weak, such transformation should be feasible for many metals using HgR<sub>2</sub> derivatives. For example, organometallics of main group I, II or III metals, Sn, Bi (using metal-amalgam), and Te may be prepared by this route. However, experimentally there are a large number of exceptions. One of the advantages of the above general reaction is its feasibility in non-etheral solvents resulting thereby in ether-free compounds (that are potentially strong Lewis acids) of Be, Al or Ga.

### 3.4.3 Carbanion-Halide Exchange Reactions

This type of reaction will obviously involve the interchange of the carbanion (alkyl/aryl) and halide groups present on two different metals and can be represented in most general terms by the following type of equation:



This is a general procedure of considerable synthetic value and is probably the most versatile and widely used for all laboratory methods. A perusal of the thermochemical information given in Figure 3.3 leads to the conclusion that such reactions proceed effectively in the direction leading to the bonding of the halogen with more electropositive and of the carbanion with the less electropositive metal.

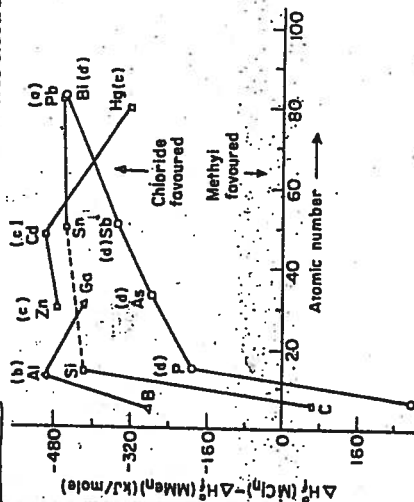


Fig. 3.3 Plot of  $\Delta H_f^\circ [\text{MCl}_n(\text{g})] - \Delta H_f^\circ [\text{M}(\text{CH}_3)_n(\text{g})]$  versus atomic number.

Amongst the halides (MX<sub>n</sub>) employed for such reactions, chlorides have been commonly used. In some cases, metal derivatives like hydrides, alkoxides, etc. have also been employed in place of halides. For the reactants represented by M'R<sub>m</sub>, the Grignard reagents MgRX or the organolithium reagents, LiR are the most common ones, but alkyls (aryls) of other metals like zinc, cadmium, aluminium, tin, and lead have also been used. The versatility of this synthetic route is being indicated in the following sub-sections by its applications to the preparation of organometallics of a few metals arranged groupwise:

#### 3.4.3.1 Synthesis of Organometallics of Beryllium, Magnesium, Zinc, Cadmium and Mercury

A large number of reactions of anionic alkylating (aryllating) agents with halides of the above metals are known, a few of which are indicated by the following equations:



(M' = Li or MgX, X = usually the chloride, R = alkyl or aryl).

(In the above reactions, the products are generally complexed species with ether in view of the strongly Lewis acid character of  $\text{BeR}_2$  and a hydrocarbon medium will have to be employed for obtaining ether-free  $\text{BeR}_2$  species).



(X = Br, I; R = alkyl or aryl).

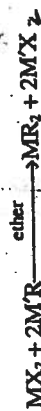
(This reaction may be a route of potential value for Grignard reagents, which are difficult to be prepared by the direct reaction:  $\text{Mg} + \text{RX} \rightarrow \text{Mg(R)X}$ )



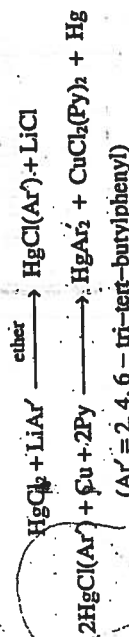
(M' = Li or MgX, X = halogen; R = alkyl or aryl).

(The last two reactions are of such a general nature that these are sometimes used as a means of characterizing the reactive Grignard or organolithium reagents).

Recently some sterically congested organometallics (some of them exhibiting unusual properties) of zinc, cadmium, or mercury have been synthesized using Grignard or organolithium reagents, e.g.,

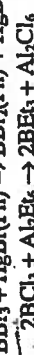
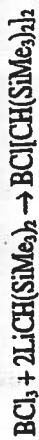
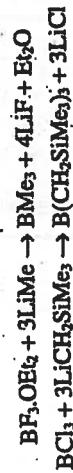


(M = Zn, Cd, or Hg; M' = Li or MgX; X = a halogen, but usually the chloride; R = a highly ramified moiety like  $(\text{Me}_3\text{Si})_2\text{CH}$  or  $(\text{Me}_3\text{Si})_2\text{C}$ ).

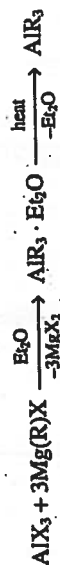


### 3.4.3.2 Organometallics of Main Group III Metals (B, Al, Ga, In and Tl)

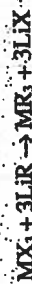
The organometallic compounds (alkyls, aryls, alkenyls or alkynyls) of Li, Na, K, Al, Si, Pb, Sn, Cd, or Hg have proved to be more popular reagents to introduce an organic group in boron compounds,  $\text{BX}_3$  (X = halogens, hydrogen, alkoxy, thioxy, or amido group). Some typical reactions are represented by the following equations:



Synthetic routes to other group III organometallics can be represented by the following typical reactions:

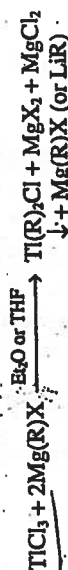


(M = Ga or In; specially applicable for R = phenyl, substituted phenyl or other organic group)

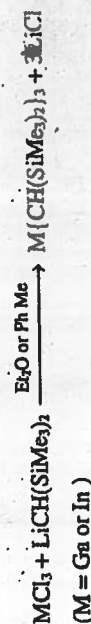
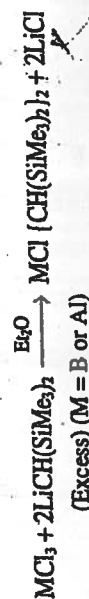


or NaR

(R = alkyl; M = Ga or In; X = a halogen)



The role of the steric demands of the ligands on the course of the reaction of group III metal halides can be demonstrated by the reactions described below. Whereas the reactions of  $\text{LiCH}_2\text{SiMe}_3$  proceed to completion in the cases of chlorides of all the group III metals, i.e., B, Al, Ga and In, the same is able to proceed to the formation of only a bis-product in the case of a more hindered ligand,  $\text{Li[CH(SiMe}_3)_2]$  with the smaller elements of the group, i.e., B and Al:



arbanion  
be repre-

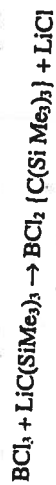
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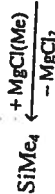


It would, however, be of interest to note that on using even a more ramified ligand, i.e., tris (trimethylsilyl) methyl lithium, only one group can be introduced around the boron atom:

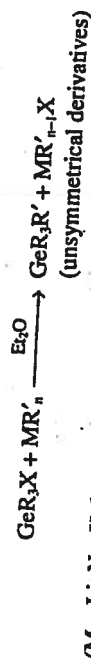


### 3.4.3.3 Organometallics of Main Group IV and V Elements (Si, Ge, Sn, Pb, As, Sb, and Bi)

The synthetic reactions employed for group IV organometallics are also of the same pattern as those described in the preceding sub-section for elements of group II and III and can be exemplified by



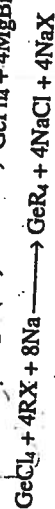
Note: Preparations by Wurtz reactions do not require isolation of the intermediate organometallic reagents.



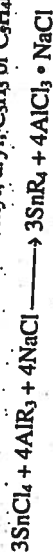
(M = Li, Na, K, Mg, Zn, Hg, or Al; n = valency of the metal).



(M = Li or MgX; X = Cl or Br; R = alkyl, C<sub>2</sub>H<sub>5</sub>, or C<sub>3</sub>H<sub>7</sub>Me)



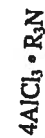
(M = Li, Na, K, MgX, Zn, or Al; R = alkyl, aryl, C<sub>2</sub>H<sub>5</sub>, or C<sub>3</sub>H<sub>7</sub>Me)



or

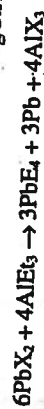
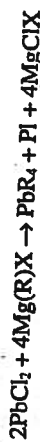


or

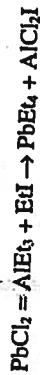
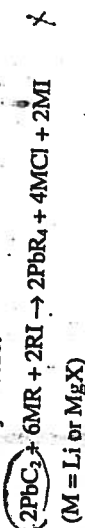


(Unsymmetrical derivatives)

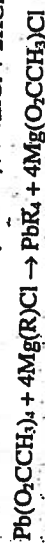
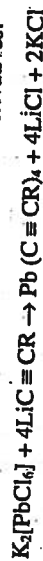
Because of the industrial interest in tetraethyl- and tetramethyllead as antiknock additives for gasoline, the synthesis of these tetraalkyls has been intensively investigated, using lead (II) salts (usually PbCl<sub>2</sub>) as starting materials:



The deposition of the lead metal may be avoided by carrying out the reactions in the presence of an alkyl iodide:

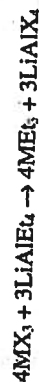
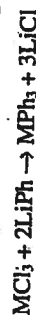
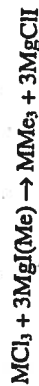


Although the use of lead (IV) salts (such as Pb(O<sub>2</sub>COCH<sub>3</sub>)<sub>4</sub> or K<sub>2</sub>[PbCl<sub>6</sub>]) in place of lead (II) chloride, does not appear to offer any special advantage, yet these continue to be sometimes used in the synthesis of a few derivatives:

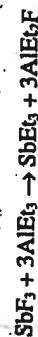
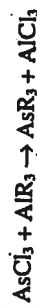


Some preparative routes for the synthesis of important organometallic halide precursors have already been mentioned earlier (Section 3.4) and other methods which utilize either metal-carbon bond cleavage and oxidative addition reactions (cf. Section 3.5.7) or redistribution reactions (Section 3.5.11) will be discussed later in this chapter.

The applications of carbanion-halide exchange method for the synthesis of organometallic derivatives of main group V elements can be exemplified by the following reactions:

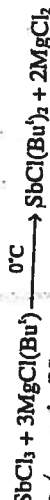
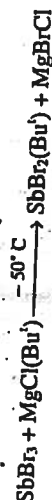
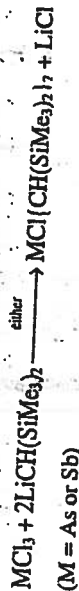


(M = As, Sb, or Bi)

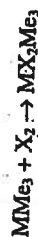


Under controlled conditions and/or with sterically crowded Grignard or lithium reagents, the reaction of MX<sub>3</sub> is generally stopped at partial substitution e.g.,

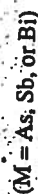
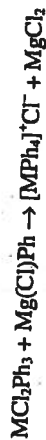
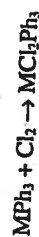
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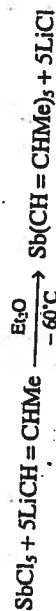
The organo-arsenic (V), -antimony (V), and -bismuth (V) derivatives can be prepared by the following reactions:



(It may be mentioned that amongst these,  $\text{SbMe}_3$  is the most stable and the bismuth analogue is the least stable).

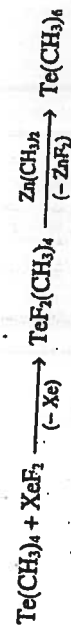
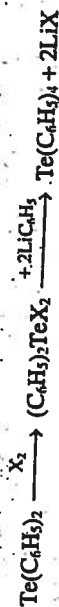
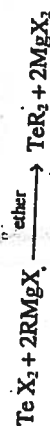


Although pentahalides are not suitable precursors for penta-alkyls or aryls of main Group V elements, yet the vinyl derivative of antimony can be prepared from  $\text{SbCl}_3$ :



### 3.4.3.4 Organo-Derivatives of Main Group VI Elements

The applications of carbanion-halide exchange reactions for the synthesis of the simpler organo-derivatives of tellurium can be illustrated by the following equations:



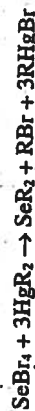
Diphenylselenium can also be synthesized by the following reaction which might involve a carbanion (in situ):

$\text{LiCl}$

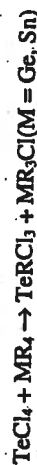
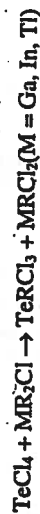
1 Grignard or  
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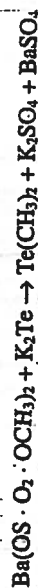
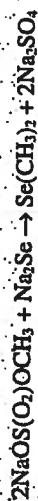
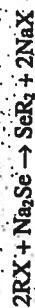
Carbanion-halide reactions accompanied by reduction of selenium/tellurium derivatives from tetra- to di-valent states can be represented by the following equations:



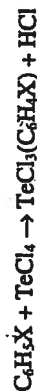
Reactions of tellurium tetrachloride with third and fourth group organometallics appear to proceed without reduction of tellurium (IV):



In view of the electronegative nature of selenium and tellurium, the reverse type of reactions of alkali selenides and tellurides with alkyl (aryl) halides can also be used for the synthesis of organo-selenium and -tellurium derivatives. For example, dialkyls (aryls) or selenium (tellurium) can be prepared by the interaction of sodium (potassium) selenide (telluride) with alkyl halides (or sulphoniates):



Aryl derivatives of tellurium can also be readily prepared by the following types of reactions:



### 3.4.4 Metal-Hydrogen Exchange (Metallation) Reactions

These metallation reactions represented by the following general equation:



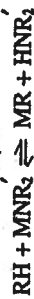
are reversible but in many cases the equilibrium lies far to one side or the reaction can be pushed to one side to make the metallation effectively complete.

The metallation reactions are believed to occur through nucleophilic attack of the hydrocarbon moiety of the organometal reagent on a hydrogen atom of the organic substrate. The natural expectation would, therefore, be that the hydrogen atom undergoing metallation must be quite acidic, and the organic moiety of the metal-containing reagent should have pronounced carbanionic character. Some examples of metallation reactions are represented as follows:





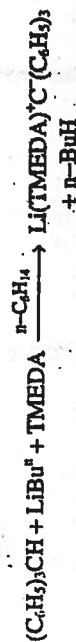
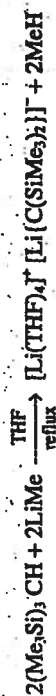
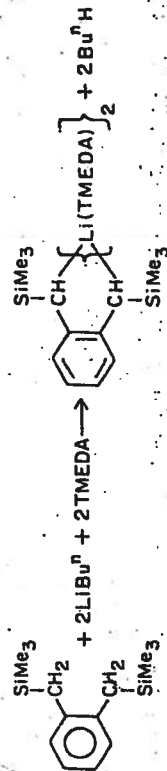
It has been observed that alkali amides are potentially more effective metallating reagents than the thermodynamically more basic alkyl- and aryl-alkali metals:



The increased kinetic basicity of the amido group is a consequence of the use of nitrogen lone pair in the metallation reaction involving a four-centred transition state:



In view of the strong polarization ( $M^{\delta+} - C^{\delta-}$ ) of the alkali metal carbon bond, the carbon atom bound to an alkali metal should be rather a strong base, capable of abstracting protons from more acidic hydrocarbons; consequently many alkali metal organometallics may be used as powerful metallating agents. However, in practice only a few commercially available reagents such as  $LiBu^+$ ,  $LiBu^+$ , and  $LiMe$  find common usage for their synthetic utility. As the organic groups like  $Bu^+$ ,  $Bu^+$ , and  $Me$  have  $pK_a$  values of nearly 40, these common alkyl lithium reagents should be capable of metallating hydrocarbons with  $pK_a < 35$  (cf. Table 2.2). For metallating organic substrates with less acidic proton, some modification in the lithium reagent is essential, which could enhance the effective basicity of the alkyl lithium reagents. Such enhancement of carbanionic character can be achieved by the presence of electron-donating (cation-solvating) solvents or ligands such as THF, TMEDA, PMDT, HMPT, DABCO, etc., leading to metallation of less acidic organic substrates, which could not be metallated by the use of simple alkyl lithium reagents:

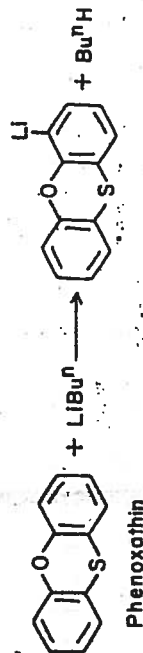


The polarization  $M^{\delta+} - C^{\delta-}$  should increase from lithium to sodium to potassium and hence, the organoalkali reagents of the latter alkali metals should be more

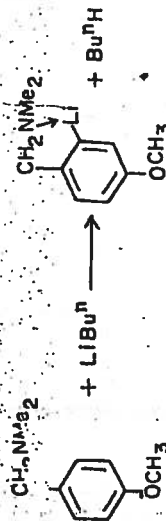
effective metallating reagents. As the alkyls of heavier alkali metals are not generally available commercially, they can be produced *in situ* by the addition of  $NaOBu^+/KOBU^+$  along with alkyl lithium reagent, e.g.,



In spite of such a varied list of metallating agents, lithium organometallics are still finding a wide application. These reactions are generally inductively controlled. For example, lithiation of phenoxathiin with  $LiBu^+$  occurs ortho to the oxygen rather than to the sulphur:



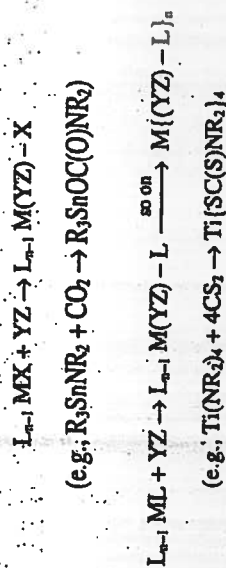
When in a disubstituted benzene ring both the substituents are ortho directing, the metallation is controlled by the group which has stronger directing properties:



The effect of coordinating solvents and ligands on enhancing the effectiveness of organolithium reagents has already been discussed above.

### 3.4.5 Metal-Hydride Additions to Alkenes

This synthetic route for organometallic derivatives involves insertion of an alkene in a metal-hydrogen bond. Generally speaking the concept of insertion reactions is of wide applicability in chemistry and can be defined as a reaction in which any atom or group of atoms (often unsaturated) is inserted between two atoms bound together:



The insertion of an alkene in a metal-hydrogen bond results in the formation of a metal-carbon bond. This is represented as follows:

## ORGANOMETALLIC COMPOUNDS OF MAIN GROUP ELEMENTS

## 3.4.8.2 Metallation of Unsaturated Hydrocarbons by Heavy Metal Salts (Especially Mercuriation and Thallation of Aromatic Compounds)

Benzene and toluene are easily mercurated in ethanol (methanol) to afford mono-substituted products:



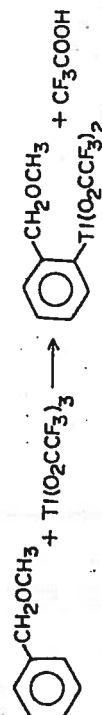
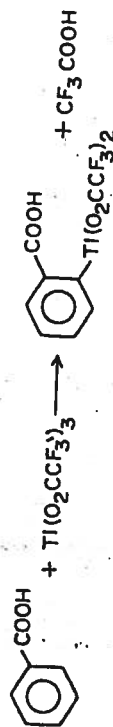
The mercuriation reactions are more facile with aromatic amines, phenols, and ethers than those with unsubstituted benzene, while halogeno- and nitro-substituted benzenes react very sluggishly. The facility of mercuriation of thiophene has been utilized to remove thiophene from benzene, since the dimercurated product is insoluble:



Similarly benzene (and thiophene) can be thallated (but at higher temperatures) in the absence of solvent:



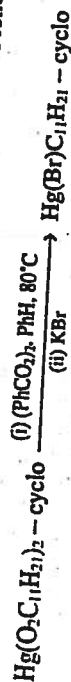
The thallation reactions essentially lead to regiospecific synthesis, e.g.:



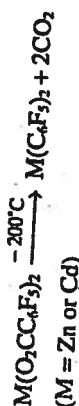
## 3.5 GROUP TRENDS (INCLUDING CHEMISTRY OF A FEW SELECTED METALS) AND SOME TYPICAL REACTIONS

Organometallic compounds in general are highly reactive towards halogens, oxygen, water, acids, amines and some multiply bonded compounds. In most of these cases, metal-carbon (M—C) bonds are readily transformed into M—X, M—O and M—N bonds on the one hand, and into C—X, C—O, C—H and C—C bonds on the other, which reflects the relative weakness of metal-carbon bonds. Generally metal alkyls and aryls,  $MR_n$ , are thermodynamically (but may not be kinetically) unstable. However, their reactivity varies to a great extent depending upon the nature of the metal; e.g., organometallics of the alkali and alkaline-earth metals are extremely reactive, whereas main group IV organometallics (e.g.  $SiMe_4$ )

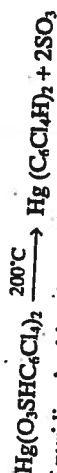
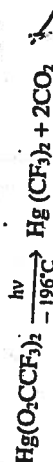
Some typical examples of radical initiated reactions are represented as follows:



A noteworthy feature of such reactions occurring via thermal decarboxylation with reasonable facility, is the requirement of the presence of electron withdrawing substituents, e.g.:

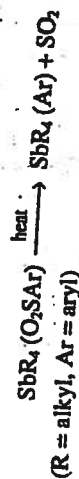
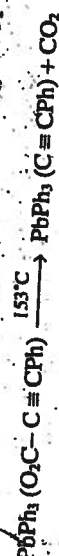
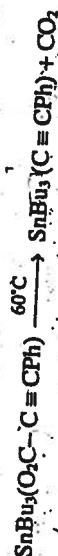
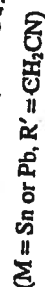


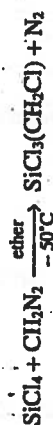
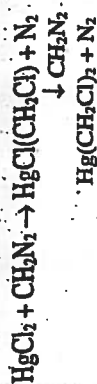
The last reaction occurs at much lower temperatures if carried out photolytically:



(The presence of pyridine in this reaction facilitates  $SO_2$  elimination at lower temperatures and also results in higher yields).

The thermal decomposition reactions in the synthesis of tin, lead, arsenic and antimony organometallics are of limited utility as compared to those for mercury and are essentially confined to the types of reactions described as follows:

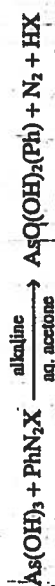




Replacement of all the metal-chlorine bonds is often difficult in the above reactions, which, therefore, generally result finally in mixed derivatives.

### 3.4.7 Reactions of Aryl Diazonium Salts with Metal Halides or Oxides in Aqueous Medium

This route is of great synthetic utility for a wide range of organometallics of heavier metals and metalloids. The accessibility of the reaction depends on two conditions: (a) the use of aqueous media possibly due to the solubility of the reactants requires the products to be hydrolytically stable and (b) the concerned central element must be prone to electrophilic attack by the diazonium ion,  $\text{ArN}_2^+$ . Probably the most successful applications are in arsenic (Bart reaction) and antimony (Schmidt reaction) chemistry:

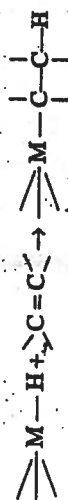
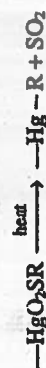
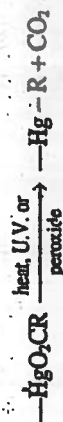


In these reactions, along with the formation of aryl derivatives, arsenic and antimony, are oxidized from trivalent to pentavalent state.

### 3.4.8 Some Other Methods for Metal-Carbon Bond Formation

#### 3.4.8.1 Elimination Reactions

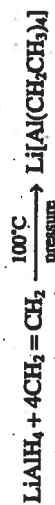
These reactions in most cases are the reverse of insertion reactions. They proceed with the elimination of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}$ , etc., from their corresponding carboxylate, sulphonate, sulphonate derivatives respectively. For example, thermal (or photolytic or radical initiated) decomposition of mercury carboxylates, sulphonates and sulphonates can lead to mercury-carbon bonded species:



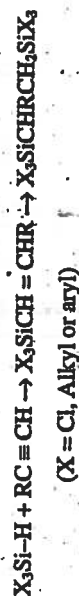
Such reactions are of interest in connection with the initiating reaction in the polymerization of alkenes by Ziegler catalysts. A few typical insertion reactions of synthetic importance in organometallic chemistry are represented by the following equations:



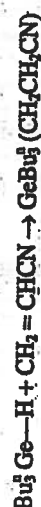
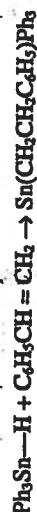
(This type of reaction is termed as 'Hydroboration' (cf. Appendix 1.3) and has been employed extensively in connection with its wide applications in organic synthesis):



The addition of Si-H bond across multiple ( $\text{C}=\text{C}$  or  $\text{C}\equiv\text{C}$ ) bonds is another reaction of great industrial potential and is known as 'hydrosilation' (cf. Section 6.4.2.2). Some typical hydrosilation reactions are represented as follows:



Insertion reactions of  $\text{C}=\text{C}$  double bonds into  $\text{Sn}-\text{H}$  and  $\text{Ge}-\text{H}$  bonds are illustrated by the following equations respectively:



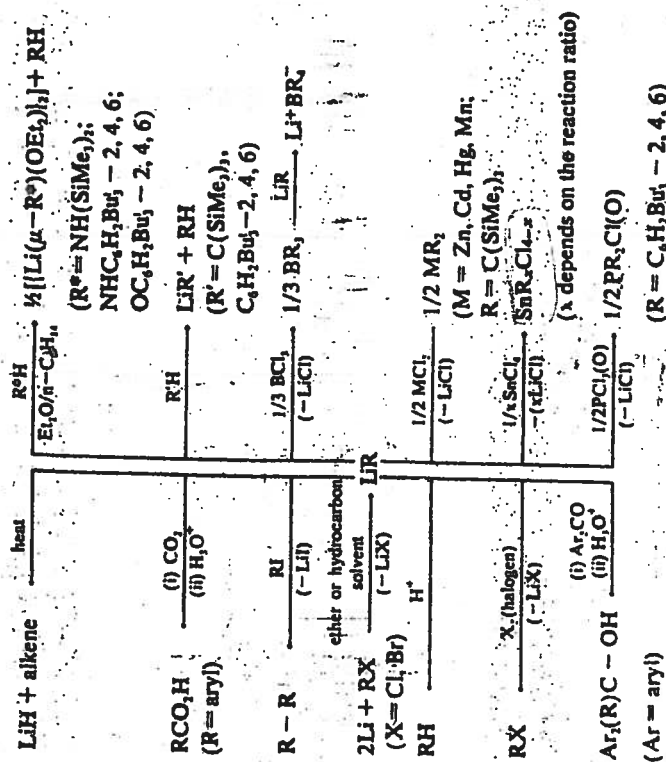
### 3.4.6 Methylene-Insertion Reactions (Methylenations)

Methylenation by diazomethane is yet another route to produce metal-carbon bonds, e.g.,





The higher ionicity of Li—C bond (~43%) compared to that of Mg—C (~34% in Grignard reagents) is responsible for greater reactivity and versatility of lithium reagents than Grignard reagents by a factor of about 100. A summary of some typical reactions of organolithium compounds, LiR, is given in Scheme 3.1.



Scheme 3.1

Indeed, a number of reactions which do not proceed under Grignard conditions may be effected with the corresponding organolithium compounds, which exhibit varied types of reactivity depending upon the nature of the solvents or/and coordinating ligands (cf. Section 3.4.4).

The chemistry of organosodium compounds and its heavier congeners parallels that of the organolithium compounds to a very large extent. The differences arise from the insolubility of these compounds, the greater metal-carbon bond polarity, an increasing cationic character in these aggregates or ion pairs, and lower values of M—C (M = Na, K, Rb, or Cs) bond dissociation energy. The last three properties together enhance the tendency of metal-hydrogen (or halogen) exchange and other nucleophilic reactions. Sometimes such higher reactivity can lead to complications such as metallation instead of addition across and alkene and Wurtz coupling instead of metal alkyl bond formation.

## 3.5.2 Group 2 Metals



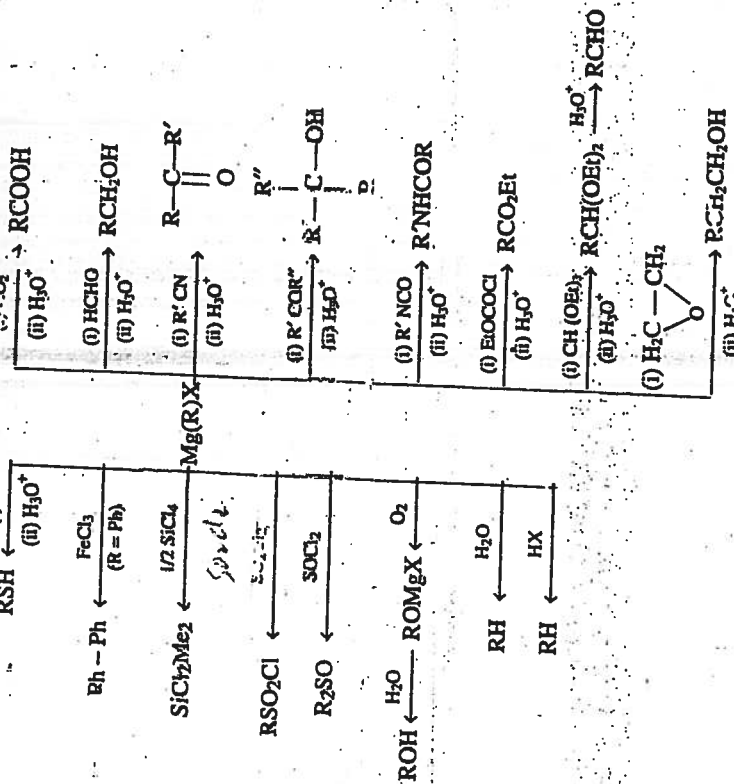
Compounds containing M—C bonds are well established for Be, Mg, Zn, Cd and Hg. By contrast, only a few organometallic compounds of Ca, Sr, or Ba have been isolated.

Organometallic compounds of alkaline-earth metals resemble the corresponding alkali metal derivatives in many of their properties. There are, of course, differences which arise from the size and varying number of valence electrons in the two groups of elements, but after making allowance for these, there is remarkable similarity in the behaviour of the two families of compounds. As with the alkali metals, insolubility and reactivity within the group increases with increasing atomic number. The elements Mg → Ra are strongly electropositive (i.e., electronegativities vary in the range 1.6–0.9) and form ionic metal-carbon bonds; this tendency increases for the heavier elements of the group.

As a result of  $1s^2 2s^2$  electronic configuration, high ionization energies, and small size of the beryllium atom coupled with high polarizing power of its dipositive cation, organoberyllium compounds are predominantly covalent in nature in a coordination state of two, three or four. Four would be the maximum coordination number accessible for beryllium, as the atomic orbitals of the next principal quantum number (3) are energetically too high to participate in bond formation. Beryllium dialkyls with two vacant *p* orbitals on the beryllium atom are coordinatively unsaturated. They are, therefore, strong Lewis acids, leading either to self-association or adduct formation with donor ligands.

Magnesium organometallic compounds also exhibit appreciable covalent behaviour, but as expected these are more reactive (as a consequence of greater polarity of Mg—C bond) than the corresponding beryllium compounds. The heavier congeners (Ca, Sr and Ba) form essentially ionic organometallic compounds, but these are generally too reactive to be useful as synthetic reagents. On the other hand, organomagnesium compounds (e.g., Grignard reagents) with moderate reactivity find wide applications in organic and organometallic transformations, which are represented schematically in Scheme 3.2.

The dialkyls of Zn, Cd, and Hg are all highly toxic, volatile liquids and are extremely air- and moisture-sensitive, except for mercury alkyls (HgR<sub>2</sub>), which are stable towards air and water. Their non-reactivity with oxygen (of the air) and water arises from the comparative weakness of Hg—O bond compared to the strength of the Hg—C bond. In fact, the latter is weak, being generally of the order of only 121 kJ mol<sup>-1</sup> (compared to 176 and 138 kJ mol<sup>-1</sup> respectively for Zn—C and Cd—C bonds). This weakness of the Hg—C bonds is reflected in their thermal and photochemical instability, requiring mercury organometallics to be stored (in some cases) at lower temperature in the dark. Indeed, the weakness of Hg—C bonds renders them to be useful as synthetic reagents, as the mercury in these, can be replaced with facility by other metals, the bonding energy of which with carbon is comparatively larger (cf. Section 3.3.1).



W

their d orbitals, compounds permits them to exhibit coordination numbers higher than four (cf. Section 3.6).

### 3.5.3 Group 13 Elements (B, Al, Ga, In and Tl)

The chemistry of the organometallics of the Main Group III elements (B  $\rightarrow$  Tl), particularly that of boron and aluminium has been the subject of intensive research during the past 3–4 decades.

In view of their  $ns^2 np^1$  electron configuration in the valence shell, all these elements are predominantly trivalent and favour the formation of three normal  $\sigma$  (two electron two centre) bonds in typical  $MR_3$  compounds. However, the availability of only three electron orbitals contributes to covalent bonding involving  $ns$ ,  $np$ ,  $3d$ ,  $4s$ ,  $4p$ ,  $4d$  and  $4f$  in organometallics of the type  $(MR)_3$  renders their compounds 'electron deficient'. These, therefore, show a marked tendency to increase their covalency from three to four and thus, attain the effective atomic number of the next noble gas.

Table 3.5 Some Typical Coordination Geometries of Group II Organometallics

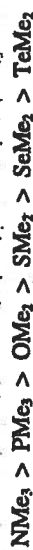
Type of hybridization	Coordination number	Geometry	Examples
$sp$	2	Linear	$BeBu_2$ , $ZnMe_2$ , $HgMe_2$
$sp^2$	3	Trigonal planar	$[PF_3Be(\mu-PF_3)_2]$ , $BeMe_2 \cdot NMe_3$ , $BePh_2 \cdot [MeZn(\mu-NPh_2)_2]$
$sp^3$	4	Tetrahedral	$BeMe_2 \cdot 2NMe_3$ , $BeMe_2 \cdot TMEDA$ , $BeMe_2 \cdot [EtMg(\mu-B)(OEt)_2]_2$ , $ZnMe_2 \cdot DME$
$sp^3 d$	5	Trigonal bipyramidal	$Mg(Br)_2 \cdot 3THF$
$sp^3 d^2$	6	Octahedral	$[MgCl_2(Ph)(THF)_3]_2$

Their strong electron pair acceptor behaviour (Lewis acidity) and high affinity for oxygen and nitrogen (hard-bases) and even for carbanions lead to formation of a large number of compounds (including adducts) in different geometries, as illustrated in Table 3.6:

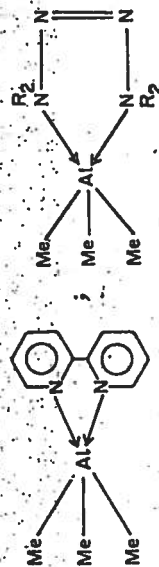
Table 3.6 Some Typical Coordination Geometries of Main Group III Organometallics

Type of hybridization	Coordination number	Geometry	Examples
$sp^2$	3	Trigonal planar	$BMes$ , $Al(CH_3SiMe_3)_3$ , $[Ga(CH(SiMe_3)_2)_3]$ , $[In(CH(SiMe_3)_2)_3]$
$sp^3$	4	Tetrahedral (neutral derivatives)	$BMes_3$ , $OEt$ , $AlMe_3 \cdot OEt$ , $Me_2Al(\mu-Me)_2AlMe_2$ , $Ga(CH_3SiMe_3)_3 \cdot NMe_3$ , $In(CH_3SiMe_3)_3 \cdot THF$ , $TlMe_3 \cdot PMe_3$
$sp^3$	4	Tetrahedral (anionic derivatives)	$[BPh_4]^-$ , $[AlMe_4]^-$ , $[GaMe_4]^-$ , $[TlMe_4]^-$
$sp^3$	4	Tetrahedral (anionic derivatives)	$[BPh_4]^{+}$ , $[AlEt_4]^{+}$ , $[GaMe_4]^{+}$
$sp$	2	Linear	$[TlMe_2]^+ X^-$ ( $X = Cl, I$ )
$sp^2 d$	5	Trigonal bipyramidal	$AlMe_2(bipy)$

The general reactivity pattern and Lewis acid strength of main group III trialkyls vary in the sequence;  $BR_3 < GaR_3 < InR_3 > TlR_3$  and this variation can be easily understood, in terms of the electronegativity of the elements (except in the pair  $BR_3 < AlR_3$ , in which steric factors play a predominant role). As expected triorganoaluminums achieve four-coordination in the presence of donor species such as an amine, ether, phosphine, sulphide, selenide, telluride, and a carbanion ( $R^-$ ), with the donor ability towards aluminium decreasing in the order:



The formation of  $[MR_3L]^+$  cations. Isoelectronic with main group II, can be expected for main group III elements. Such cations are particularly stable in the case of Tl ( $R_2Tl^+$  is isoelectronic with  $HgR_2$ ). The  $R_2B^+$  cations, can be stabilized by bidentate ligands (such as bipy), generating a tetrahedral species,  $[R_2B(bipy)]^+$ . Similarly ortho-phenanthroline can stabilize  $R_2Al^+$  cations, otherwise incapable of free existence. The tendency to form  $R_2M^+$  cations and their stability increase from  $B \rightarrow Tl$ . Although aluminium in purely inorganic compounds can utilize 3d-orbital in achieving higher coordination numbers (e.g.  $AlH_3$ , bipy,  $[AlF_4]^+$ ,  $Al(acac)_3$ ), yet organometallic compounds of aluminium in coordination numbers higher than four are extremely rare (two such examples of pentacoordinated aluminium are known, in compounds of the following types):

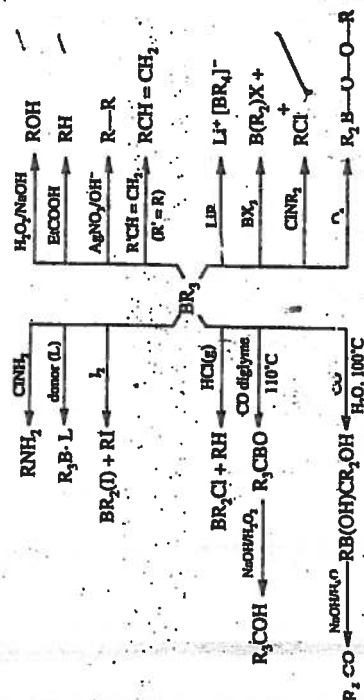


The element-carbon bond distance increases from boron to thallium and consequently element-carbon bond energies in these trialkyls fall with increasing atomic numbers (cf. Section 3.3.1). The same sequence,  $B > Al > Ga > In > Tl$  is followed in the thermal stability of the trialkyls.

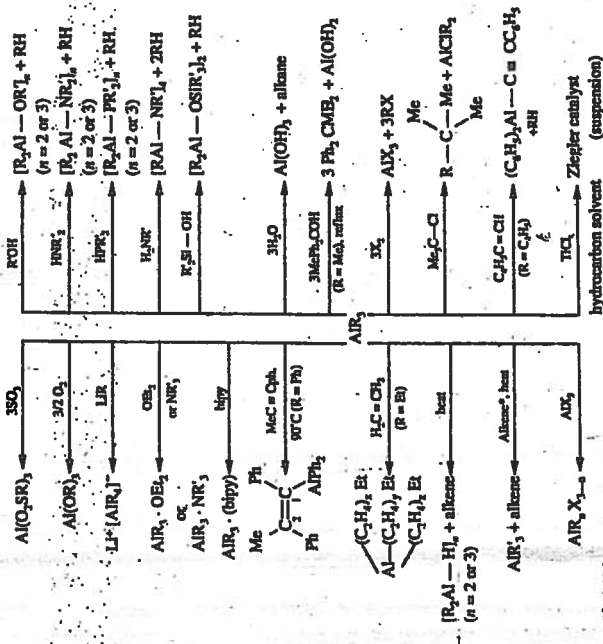
The electron deficient character of these trialkyls could be expected to lead to their dimerization, but the reasons for this behaviour-being observed only in the case of some aluminium trialkyls have been discussed earlier (cf. Section 2.5.3).

The electron deficient characteristics of these alkyls (particularly those of boron and aluminium) and their sensitivity to oxygen (most are pyrophoric in air) and oxidizing agents as well as to compounds with active hydrogen (such as water, alcohols, amines, and hydrogen halides) have been exploited extensively in 'hydroboration' and other synthetic reactions, as illustrated in schemes 3.3 and 3.4.

Organoaluminium compounds find unique applications in organic as well as organometallic synthesis and coordination catalysts for alkene polymerization and other reactions. The properties of organoaluminium compounds that make them a



Scheme 3.3 Some Reactions of Triorganoboranes



Scheme 3.4 Some Typical Reactions of Organoaluminium



versatile reagent are the dynamic nature of Al—C bond; their alkylating ability and tendency to reduce certain transition metal salts; their ready reactions with oxygen and carbonyl containing compounds; their tendency to form bridged complexes containing other metals; and various reactions they undergo with alkenes. Some of these reactions are illustrated in Scheme 3.4.

### 3.5.4 Group 14 Elements (Si, Ge, Sn and Pb)

These elements have  $ns^2np^2$  electronic configuration in their valence shell and, therefore, two oxidation states, i.e., +4 and +2 (due to 'inert s-pair effect') are possible. The extraordinary stability (to heat, oxygen, and moisture) of organometallic derivatives of these elements in tetravalent state is reflected in the vast amount of growing literature about them. By contrast, their bivalent organometallic derivatives are much less stable, and these are also beginning to attract attention particularly with sterically demanding ligands (cf. Section 3.1) and  $\pi$ -bonding ligands (cf. Section 3.8).

As in the other groups of the periodic table, the metal-carbon bonds (which have pronounced covalent character) become weaker from silicon to lead (cf. Section 3.3.1). In contrast to elements of other groups, members of main group IV show a special characteristic of element-element bond formation. This 'catenation' tendency, so marked with carbon and resulting in such a large number and variety of organic compounds, becomes much less apparent on passing from silicon to lead; some typical examples are linear  $\text{Si}_2\text{Me}_6$ , cyclic  $\text{Ge}_3\text{Ph}_3$ , and  $\text{Sn}_9\text{Me}_{18}$ , and branched  $(\text{PbPh}_3)_3\text{Pb}$ .

In view of an extensive chemistry associated with C=C double bonds, the possibility of the existence of similar derivative of other main group IV elements has been arousing interest, but success has been achieved in isolating only a few  $\text{Si}=\text{Si}$ ,  $\text{Si}=\text{C}$  (cf. Section 3.8),  $\text{Ge}=\text{Ge}$ , and  $\text{Sn}=\text{Sn}$  (cf. Section 3.1) derivatives in recent past.

Stable organometallic compounds of main group IV elements with oxidation number +3 are accessible only with the sterically demanding ligands  $\text{SiMe}_3$  as  $\text{CH}(\text{SiMe}_3)_3$ , e.g.,  $[\text{M}(\text{CH}(\text{SiMe}_3)_2)_3] (\text{M}=\text{Si, Ge, Sn})$ .

The trialkyl and -aryl compounds of main group IV elements differ from the corresponding derivatives of the elements in neighbouring groups because of their relatively low reactivity. This is often a result more of kinetic than of thermodynamic factors (cf. Section 3.3.2). The main group IV alkyls and aryls behave as saturated compounds, and these elements show little tendency to increase their coordination numbers above four unless they are bonded to more electronegative atoms or groups. In the latter cases, the participation of the  $d$  orbitals expand the covalency of the central atom resulting in the formation of derivatives in coordination states, five ( $sp^3d$  hybridization), six ( $sp^3d^2$  hybridization), and seven ( $sp^3d^3$  hybridization) as is illustrated in Table 3.7. Coordination numbers greater than six are extremely rare; the two organometallic compounds,  $\text{SnMe}_6(\text{C}_6\text{H}_5)_2$  and  $[\text{Pb}(\text{COCOC}_6\text{H}_5)_3]\text{Ph}$  provide examples of increased coordination numbers seven and eight respectively.

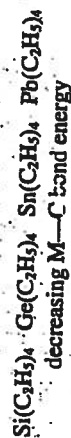
Table 3.7 Some Typical Coordination Geometries of Main Group IV Organometallics

Type of hybridization	Coordination number	Geometry	Examples
$sp^3$	4	Tetrahedral	$\text{SiMe}_4$ ; $\text{GeMe}_4$ ; $\text{SnMe}_4$ ; $\text{PbMe}_4$
$sp^3d$	5	Trigonal bipyramidal	$\text{SiEt}_5^+$ (Me) <sup>+</sup>

$sp^3d^2$	6	Octahedral	$\text{SnClMe}_5(\text{C}_6\text{H}_5\text{N})$ ; $[\text{PbClPh}_3]$
$sp^3d^3$	7	Pyramidal	$[\text{SiF}_4\text{Ph}_3]^{2-}$ ; $\text{Sn}(\text{acac})_3 \text{Me}_2$ ; $[\text{PbCl}_2\text{Me}_2]_n$ , $\text{PbCl}_2\text{Ph}_2(\text{bipy})$
	3	Pyramidal	$[\text{M}(\text{CH}(\text{SiMe}_3)_2)_3]$ (M = Si, Ge or Sn)
	3	Environment around the central atom intermediate between pyramidal and planar	$\text{Si}(\text{C}_6\text{H}_5)_2\text{Me}_2$ , $\text{M}_2\text{R}_4$ (M = Ge, Sn, or Pb); (R = CH (Si Me) <sub>3</sub> )

Within main group IV, the reactivity of the M—C bond in tetra-alkyls or aryls ( $\text{MR}_4$ ) increases progressively from silicon to lead as (i) the bond energy decreases in the same sequence (cf. Section 3.3.1):

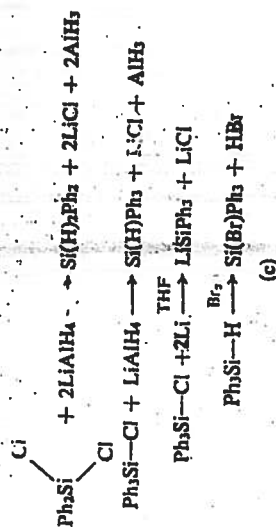


decreasing thermal stability

and (ii) as expansion of the coordination number of the metal (M) becomes easier with increasing atomic size and decreasing difference between  $np$  and  $nd$  orbitals.







**Scheme 3.5** Some Typical Reactions of (a) Chloropropene, *isoprene*, (b) Chloromethyltrimethylsilane, and (c) Chloro- and phenylsilanes

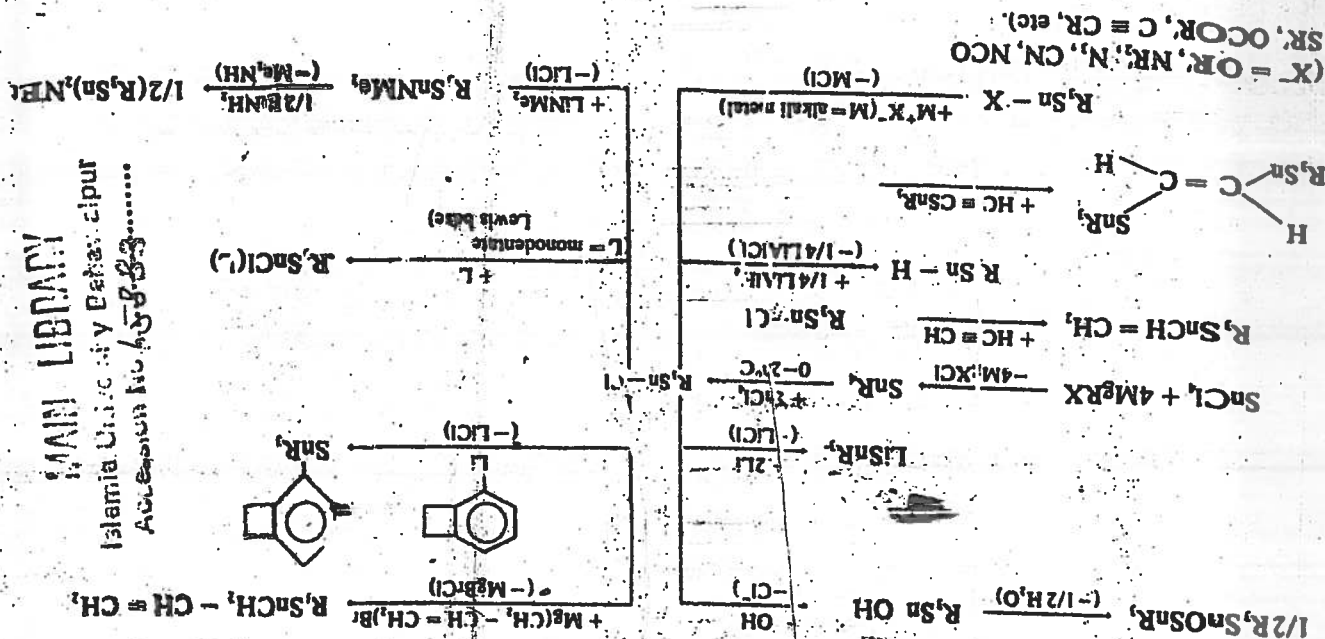
### 3.5.5 Group 15 Elements (As, Sb, and Bi)

All the elements with  $ns^2np^3$  valence electronic configuration form basically covalent organometallic compounds in both the +3 and +5-oxidation states. The general types of group V organometallics and their stereochemical possibilities are depicted in Table 3.8:

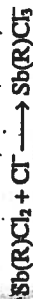
Table 3.8 Some Typical Coordination Geometries of Main Group V Organometallics

Formal valence	Types of hybridization	Coordination number	Geometry	Examples
1	$sp^2$	2	Linear	$As[Cr(CO)_5]_2Ph$
3	$sp^2$	3	Trigonal pyramidal	$MR_3$ ( $M = As, Sb, \text{or } Bi$ ; $R = Me, Ph, \text{or } p-ClC_6H_4$ )
				$AsR_2X(X = Me \text{ or } Ph)$
				$As_2(Me)_4$ $[AsMe_4]^-$
5	$sp^3$	4	Tetrahedral	$AsMe_3, AsPh_3, AsBr_2(CH_3)_3$
	$sp^3 d$	5	Trigonal bipyramidal	$Sb(p-MeC_6H_4)_3$ $SbCl_3(CH_3)_3$ $BiPh_3, BiCl_3Ph_3$
	$sp^3 d$	5	Square pyramidal	$SbPh_5$
	$sp^3 d^2$	6	Octahedral	$[SbPh_6]^-$ , $[SbF_6Me]_2$

As a consequence of the well known 'inert s-pair effect', the stability of organometallics in trivalent state generally increases from arsenic to bismuth. Although the reverse trend in stability should be expected for pentavalent derivatives, yet  $\text{SbMe}_5$  is more stable than  $\text{AsMe}_5$  as well as  $\text{BiMe}_5$ . In addition to these two oxidation states, organometallics of these elements are also known in other oxidation states such as +1, +2, and +4, which have been stabilized in the form of a complex or radical, e.g.,  $[(\text{OC})_2\text{Cr}_2\text{AsPh}_4]_2$ ,  $[\text{As}(\text{CH}(\text{SiMe}_3)_2)_2]$ ,  $\text{AsPh}_4$ , respectively. In a particular oxidation state, the polarity of metal-carbon bond increases on descending ( $\text{As} \rightarrow \text{Bi}$ ) the group.



Scheme 3.6a Some Typical Reactions of Chlorinorganotin.


$$9\text{Sb}(\text{CF}_3)_3 + \text{C}_5\text{H}_5\text{N} \longrightarrow \text{Sb}(\text{CF}_3)_3 (\text{C}_5\text{H}_5\text{N})$$


A large number of organometallics,  $MX_3$ , are known. The thermal and photolytic stability of these compounds which decreases in the sequence,  $M = As > Sb > Bi$ , can be rationalized in terms of steady decrease in the mean  $M-C$  bond dissociation energy (cf. Section 3.3.1) in the same direction. The organobismuth derivatives are the least stable and the most reactive.

The metal-metal bond formation (i.e. catenation) ability does exist in this group also, but as expected, the metal-metal bond strength decreases with increasing atomic number:

M =	As	Sb	Bi
DM-M	280	267	200 kJ mol <sup>-1</sup>

This is reflected in the fact that compared to a number of organoarsenic compounds with As—As bonds, e.g.,  $\text{As}_2\text{Me}_4$ ,  $\text{AsPh}_3$ , or  $(\text{AsPh})_3$ , well-defined examples of antimony and bismuth derivatives are only  $\text{Me}_3\text{Sb}$ — $\text{SbMe}_3$  (and possibly  $\text{Ph}_3\text{Sb}$ — $\text{SnPh}_3$ ) and  $\text{Me}_3\text{Bi}$ — $\text{BiMe}_3$  (the least stable respectively).

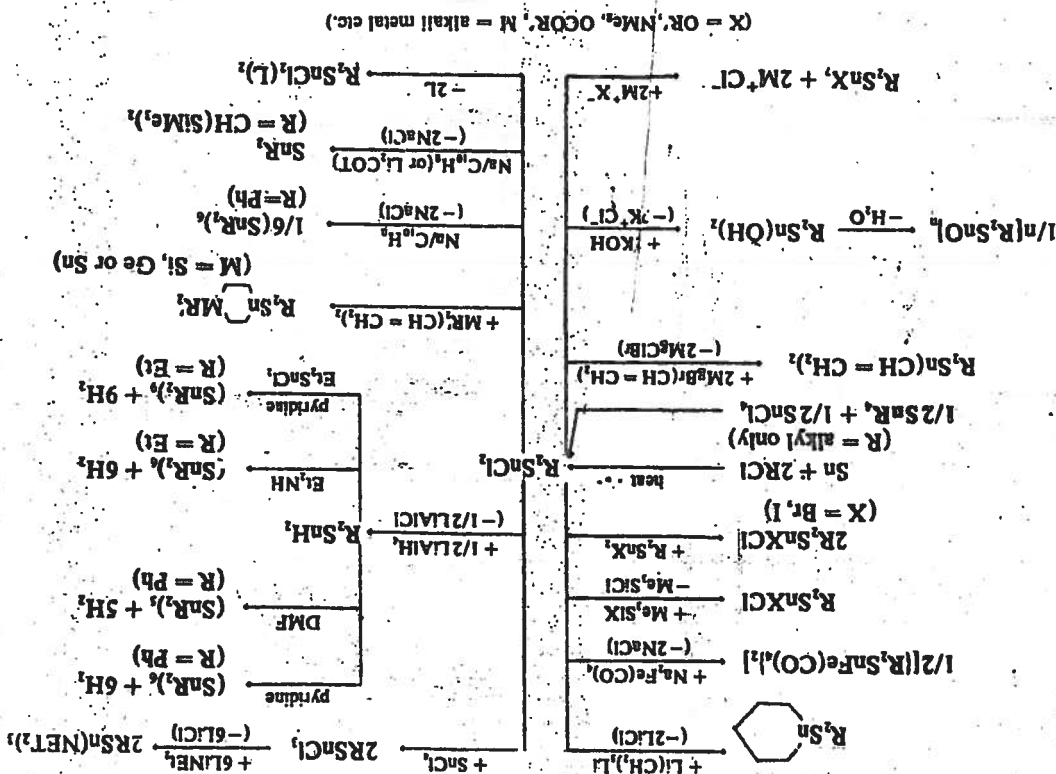
The multiply-bonded well characterized acyclic compounds are known only for arsenic, e.g., PhAs = C(X)Bu<sup>1</sup> (when X = OSiMe<sub>3</sub> or N(R)SiMe<sub>3</sub>) or 2, 4, 6-trimethyl-2,4,6-trisilyl-1,3,5-triazine-2,4,6-trisulfonates.<sup>2</sup> By contrast, cyclic multiply bonded compounds for main group V elements are large in number. The stability of cyclic multiply bonded compounds, e.g., the heterobenzenes  decreases with increasing atomic number (i.e. in the sequence M = As > Sb > Bi). In the case of acyclic derivatives only arsenic derivatives have so far been characterized: The penta-alkyls and -aryls, ARD, are of great interest because of their structural (*cf.* Section 3.6.5) features.

Compounds of the type  $MR_3$ , do not obviously exhibit electron donating properties, but these may act as Lewis acids in forming  $MR_3^-$  anions. Generally the ease of preparation and overall stability of these anions reaches maximum with the general inorganic chemistry of these elements.

### 3.5.6 Group 16 Elements (Se and Te)

Like that of sulphur, the organo-selenium and -tellurium chemistry is a fastly expanding field with quite distinct features. Similar to the electronic configuration of sulphur  $\{[\text{Ne}]3s^2 3p^4\}$ , those of selenium and tellurium are  $\{[\text{Ar}]3d^{10} 4s^2 4p^4\}$  and  $\{[\text{Kr}]4d^{10} 5s^2 5p^4\}$  respectively. However, the comparative similarity in energy levels of vacant  $4d$  and  $5d$  orbitals to the  $4p$  and  $5p$  orbitals respectively in selenium and tellurium facilitate the involvement of these  $d$  orbitals in hybridization with

Scheme 3.6b Some Representative Reactions of Diorganotin Compounds (especially of Dichlorides).



the corresponding *s*- and *p* orbitals. This results in an increasing tendency of attainment of higher (5 or 6) covalencies (coordination states) from sulphur to tellurium in their covalent organo-derivatives. In Table 3.9 are listed the coordination geometries of a few typical organo-derivatives of these elements.

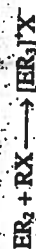
Table 3.9 Typical Coordination Environments of Organo-selenium and -tellurium Compounds

Compound ER <sub>3</sub>	Hybridization	Shape Bent
[EMe <sub>3</sub> ] <sup>+</sup> [BPh <sub>4</sub> ] <sup>-</sup> [EMe <sub>3</sub> ] <sup>+</sup> T <sup>-</sup>	<i>sp</i> <sup>3</sup> <i>sp</i> <sup>2</sup> <i>d</i> <sup>2</sup>	Pyramidal cation Pseudo-trigonal bipyramidal configuration due to close association of the cation with iodide
Me <sub>3</sub> ECI <sub>2</sub> [EMe <sub>3</sub> ] <sup>+</sup> [TeMe <sub>3</sub> ] <sup>-</sup>	<i>sp</i> <sup>3</sup> <i>d</i> <i>sp</i> <sup>2</sup> <i>d</i> <sup>3</sup>	Pseudo-trigonal bipyramidal cation and anion, both six-coordinate pseudooctahedral (cf. Sec- tion 3.6.6)
PhTeCl <sub>3</sub>	<i>sp</i> <sup>3</sup> <i>d</i>	Two independent tellurium atoms in square based pyramidal geometry which are bridged by chlorine atoms to give a chain struc- ture (cf. Section 3.6.6).

In the first two pairs of species (i.e., SeR<sub>2</sub>, TeR<sub>2</sub>; [SeMe<sub>3</sub>]<sup>+</sup> and [TeMe<sub>3</sub>]<sup>+</sup>), the central elements, selenium and tellurium attain an octet (noble gas) configuration. In addition to the above, elements of this group (apparently even polonium which is most metallic) exhibit a decreasing tendency to attain noble gas (*ns*<sup>2</sup>*np*<sup>6</sup>) configuration by accepting two electrons from metals and forming dinegative ions, E<sup>2-</sup>.

As in the case of main group elements N, P, As, Sb and Bi, the Lewis base character of compounds ER<sub>3</sub> of main group VI elements decreases with the rise of atomic number from oxygen to tellurium, with the exception of selenium compounds which in some isolated cases appear to be slightly stronger nucleophiles than their sulphur analogues.

The presence of lone pair of electrons on ER<sub>3</sub> (E = Se or Te) permits the formation of trivalent derivatives such as [SeR<sub>3</sub>]<sup>+</sup>X<sup>-</sup> and [TeR<sub>3</sub>]<sup>+</sup>X<sup>-</sup>:



This type of reaction is more facile with selenium and tellurium derivatives compared to that with sulphides because of the greater nucleophilicity (due to the presence of lone pair electrons on 4*p* and 5*p* orbitals) of the easily polarizable selenium and tellurium atoms respectively. Predictably alkyl (aryl) selenides are alkylated to give selenonium salts with greater difficulty than the alkylation of dialkylselenides, e.g., interaction of Se(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> with CH<sub>3</sub>I gave dimethylphenyl selenonium salts in only a poor yield.

The order of nucleophilicity appears to follow the sequence: CH<sub>3</sub>SeR > CH<sub>3</sub>SR > C<sub>6</sub>H<sub>5</sub>SeR > C<sub>6</sub>H<sub>5</sub>SR > CH<sub>3</sub>TeR > C<sub>6</sub>H<sub>5</sub>TeR.

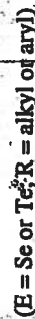
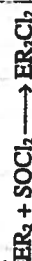
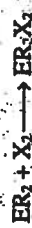
The reactions of diorganotellurides are generally more facile than those of selenium analogues and follow the same pattern:



These combinations proceed quite vigorously with lower aliphatic tellurides and methyl iodide; in the case of aromatic and higher aliphatic tellurides, the mixture requires heating to facilitate the reaction.

Although the stability of E—C bond in the group decreases with increasing atomic number, yet Se—C and Te—C bonds are surprisingly stable to bases and heat in the absence of oxidizing agents. The reactive site in diorgano-selenides and -tellurides could be the chalcogen element (Se or Te) itself; the element-carbon bond; or the organic group attached to the element, resulting in the following reactions types.

(a) Reactions involving increase in the oxidation state of the chalcogen element such as oxidative addition of organic and inorganic halides, halogens or halogenation accompanied by oxidation:



Halogenolysis works well for both aliphatic and aromatic diselenides or -tellurides.

(b) *Cleavage of E—C bond*: The lower strength of tellurium-carbon bond is depicted by the following reactions in which dialkyl-selenide undergoes merely oxidation (with retention of selenium-carbon bond) whereas in the tellurium analogues, the tellurium-carbon bond undergoes cleavage:



or  
alkaline H<sub>2</sub>O<sub>2</sub>

With sulphur, however, both selenium and tellurium derivatives undergo cleavage reactions:



(c) *Formation of addition complexes*

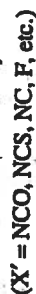


Other metal halides which have been found to form complexes are  $\text{CdI}_2$ ,  $\text{CuCl}$ ,  $\text{AgI}$ ,  $\text{AuCl}_3$ ,  $\text{PdCl}_2$ ,  $\text{PtCl}_2$ , etc. By contrast, organotellurium halides exhibit Lewis acid character:



In addition to these, a few types of reactions are more pronounced with organotellurium halides:

#### (d) Nucleophilic substitution



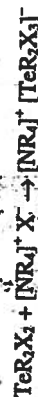
#### (e) Reduction elimination



or



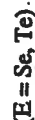
#### (f) Anionic complex formation:



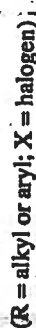
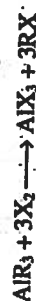
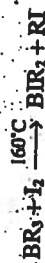
In addition to nitrogen reagents, those of P, As, and Sb could also be used. Various permutations and combinations have yielded a large number of water soluble biologically active derivatives.

### 3.5.7 Reactions With Oxygen and Halogens

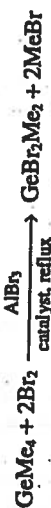
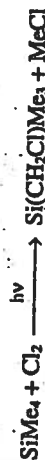
Most organometallic compounds of the first three main group elements react exothermally with oxygen. Although many of these (especially the lower alkyls of alkali and alkaline-earth metals, Be, Mg, Zn, Cd, B, Al, Ga, In and Tl) are spontaneously inflammable in air, yet under carefully controlled milder conditions, alkyls of some of these metals may be oxidized to the alkoxide stage only. Tetra-alkyls of main group IV elements, on the other hand, generally show stability towards molecular oxygen. By contrast, triorgano-derivatives,  $\text{MR}_3$  of main group V elements ( $\text{M} = \text{P, As, Sb and Bi}$ ) and diorgano-derivatives,  $\text{ER}_2$  of main group VI elements ( $\text{E} = \text{Se, or Te}$ ) are oxidized in limited supply of oxygen to  $\text{MR}_2(\text{O})$ ,  $\text{ER}_2(\text{O})$  respectively with the retention of element-carbon bonds:



Halogens generally cleave (the ease and completion of cleavage reactions are largely dependent on the electropositive character of the concerned element, i.e., more electropositive the metal, more reaction will go to completion) the metal-carbon bonds:



The action of chlorine on tetra-alkyls of main group IV elements provides an interesting illustration of gradation in chemical reactivity with increasing atomic weight:



(The reaction with tetramethyltin is carried out under controlled conditions to get monochlorotrimethyltin, otherwise formation of bis-product is more favourable).



When the above reaction is carried out at low temperature ( $-60^\circ\text{C}$ ) a mixture both of  $\text{PbMe}_3\text{X}$  and  $\text{PbMe}_2\text{X}_2$  is obtained:

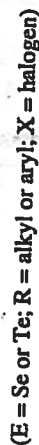
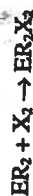
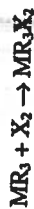


An interesting feature to note is that when both alkyl and phenyl groups are present in the same molecule, the latter is preferentially cleaved, e.g.:

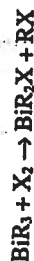




By contrast, the trialkyls and the triaryls of P, As and the triaryls of Bi as well as diorgano derivatives of Se and Te undergo oxidative addition with halogens. A few illustrative examples are given below:



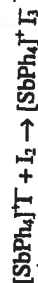
For trialkylbismuth, however, cleavage of a bismuth-alkyl bond by halogens occurs in preference to oxidative-addition:



Phenyl groups are readily cleaved from pentaphenyls of arsenic, antimony, and bismuth on reactions with halogens, giving rise to tetraphenyl-arsonium, stibonium, and -bismuthonium trihalides respectively:



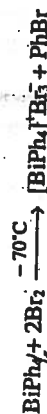
Reaction of bromine or iodine with pentaphenylantimony takes place in two stages, e.g.:



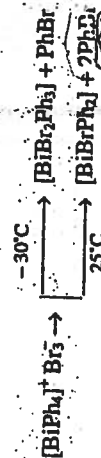
By contrast, interaction of pentaphenylbismuth with bromine at room temperature gives  $BiPh_5$ :



However, at  $-70^\circ\text{C}$  bismuthonium tribromide is formed:



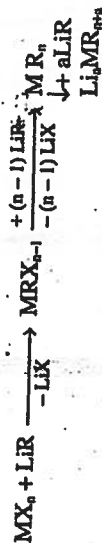
Tetraphenylbismuthonium tribromide decomposes in two different ways on raising the temperature:



### 3.5.8 Alkylation (or Arylation) Reactions

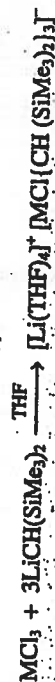
As discussed earlier (Section 3.4.3), the reactions of some alkylating or arylating reagents, which are typical organometallic compounds, e.g.,  $LiR$ ,  $Mg(R)X$ ,  $ZnR_2$ ,  $AlR_3$ ,  $SnR_4$ ,  $PbR_4$ , etc., with the halide (or sometimes alkoxide/amide) of another

metal can under suitable conditions lead to the synthesis of new organometallic derivatives:

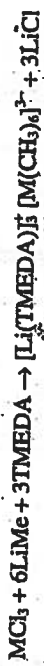


The synthesis of organometallic derivatives by the above types of reactions can be termed as alkylation (or arylation). The reactions of these alkylating agents with main group metal halides, etc., have already been discussed in the earlier Section 3.4.3.2, and we shall, therefore, concentrate in the following pages on the reactions of these alkylating agents with transition metal halides or other derivatives.

In contrast to the reactions of a bulky reagent like  $LiCH(SiMe_3)_2$  leading to the formation of only disubstituted products,  $[MCl] [CH(SiMe_3)_2]_2$  in cases of B and Al and trisubstituted products  $[M(CH(SiMe_3)_2)_3]$  in case of Ga, In and Bi (cf. Section 3.4.3.2), the reaction proceeds further with the formation of 'ate' products in the case of larger atoms like those of lanthanoids:



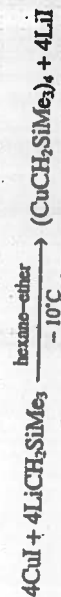
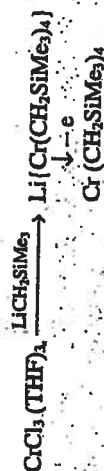
It is noteworthy to mention that trichlorides of lanthanoid metals react with a less sterically demanding ligand, like  $LiMe$  in the presence of chelating diamines like TMEDA to afford 'ate' complexes with octahedral environment around the metal atom:



Alkylation of tetrachlorides of titanium, zirconium and hafnium with suitable lithium alkyls (e.g., neopentyls; cf. Section 4.2.2.1) generates isolable (at ambient temperatures) homoleptic derivatives:



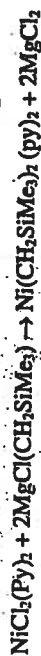
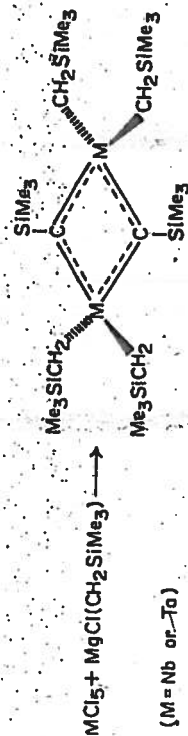
Some other alkylation reactions by lithium alkyls can be represented by the following reactions:



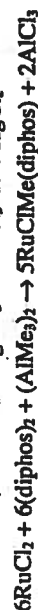
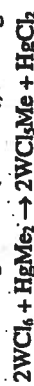
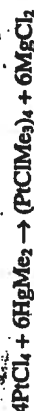
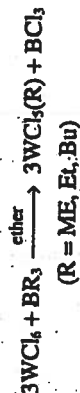
Complementary to organolithium reagents are organomagnesium compounds, with which also a few typical reactions are represented by the following equations:



(M = Ti, Zr, Hf or Nb)



Although organolithium or organomagnesium reagents are much more versatile and widely used alkylating or arylating agents, the use of other alkylating (aryllating) agents (such as  $\text{ZnR}_2$ ,  $\text{HgR}_2$ ,  $\text{BR}_3$ ,  $\text{AlR}_3$ ,  $\text{PbR}_4$ ,  $\text{SnR}_4$ ) has been found advantageous where comparatively a milder non-basic reagent is required due to the following reasons: (a) the need of partial alkylation or arylation, and (b) to avoid reduction of the transition metal ions. A few examples of such reactions are represented below:



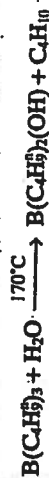
### 5.9 Reactions with Protic Reagents

Alkyls (aryl)s of the first three main group elements are highly reactive towards water and in most cases lead to violent reactions. These reactions can be represented by the following general equation:



(M = elements of group IA, IIA, and IIIB where n = 1, 2, or 3 respectively).

The vigour of such reactions is influenced by the electronegativity of the metal, associative tendency of the metal alkyls, and steric bulk of the alkyl groups. For example, lower the electropositivity of the element, lesser would be the reactivity of its metal alkyls with protic reagents like water. Thus, for the alkyls of less electropositive elements such as boron, cleavage of element-carbon bond by water requires higher temperatures ( $-170^\circ\text{C}$ ) and even then, only one boron-carbon bond appears to be cleaved:

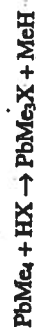


The reactivity of alkyls of main groups IV and V elements towards other protic agents, such as alcohols, diminished remarkably (which may be due to kinetic factors) and these do not appear to react with water under normal conditions.

The reactivity of metal alkyls towards other protic agent, such as alcohols, amines, cyclopentadiene and other reagents having acidic hydrogen atoms is generally milder and some of these can be illustrated by the following equations:



With stronger protic agents like hydrogen halides, the alkyls of first three group metals are generally converted into corresponding metal halides; but alkyls of even fourth main group metals tend to react in a limited manner with hydrogen halides, e.g.,



The organo-derivatives of main group V elements show an interesting variation in their reactivity towards hydrogen halides. For example, the reaction of  $\text{AsPh}_3$  in liquid hydrogen chloride has been represented by the following equation on the basis of conductance measurements:



Antimony trialkyls, however, are such strong reducing agents that these are oxidised even by hydrogen halides to pentavalent antimony derivatives:



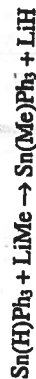
By contrast, interaction of triphenylbismuth with hydrogen chloride yields bismuth chloride:



This can be rationalized in terms of (i) the greater stability of bismuth in its trivalent state, and (ii) the weakest nature of Bi—C bond amongst main group V elements.

## 3.5.10 Reactions with Hydridic Hydrogen

A few organometallic reagents such as organolithium or organomagnesium compound can substitute an organic group for hydrogen in hydrides of some metalloids, e.g.:



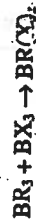
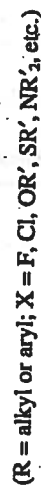
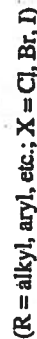
By contrast, the reaction of  $Ge(H)Ph_3$  with methyl lithium can be represented as:



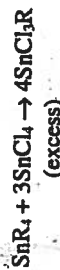
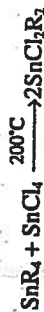
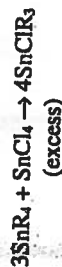
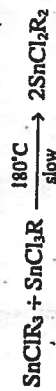
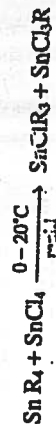
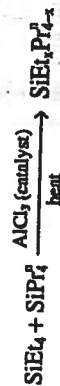
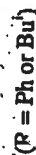
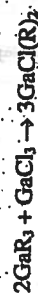
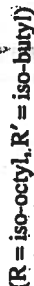
This reaction has been cited as an evidence of germanium showing greater electronegativity compared to that of tin as well as silicon (cf. Section 3.5.4).

## 3.5.11 Redistribution Reactions

The redistribution reaction (exchange of groups between two derivatives of the same elements) is a general feature of the main group organometallics and the course of the reaction can generally be monitored by n.m.r. techniques. A few examples of reactions which have been investigated in detail are represented by the following equations:



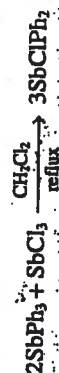
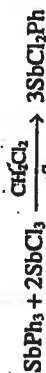
(excess)



Redistribution reactions have also been proved useful synthetic route for making mixed alkyl (aryl) halide derivatives of arsenic and antimony:

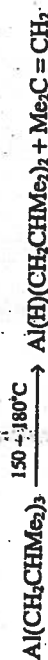
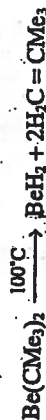
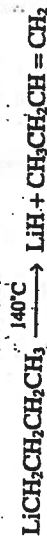


(R = larger alkyl groups, trimethylarsine does not behave in this way; X = Cl, Br, I)



## 3.5.12 Pyrolysis

The thermally unstable alkyls of some metals like lead (or bismuth) on heating lead to the generation of radicals, which play a key-role in the antiknock properties of PbEt<sub>4</sub>. Pyrolysis of more reactive alkyls generally leads to production of a metal hydride and the elimination of an alkene (a type of reaction which is more prevalent in transition metal organometallics; cf. Section 4.1), e.g.,



Reactions of the above type generally lead to the formation of very complex mixtures of products, due to the fact that alkenes so produced undergo rearrangement and polymerization reactions.

By contrast, dimethyls of Be, Mg and Hg, decompose on heating in quite different manner:

