

Alkyl Organometallics

Both transition and non-transition metals form alkyl complexes. However, the alkyl compounds of non-transition metals are more in number and more stable as compared to their counterparts of transition metals. Moreover, the non-transition metal-alkyls are not only commercially important compounds but are also intermediates in the synthesis of other organometallics. Their utility stems from the fact that the metal-carbon bond is quite weak as compared to metal-oxygen or metal-halogen bonds. This, in turn, allows transfer of alkyl group to other chemical entities.

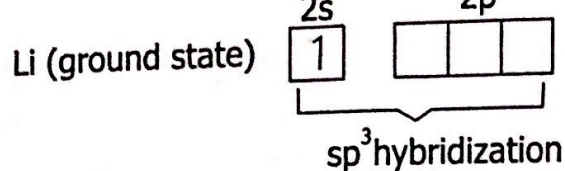
Considering methyl group as a representative alkyl function and considering lithium, beryllium and aluminium as the representative metals of Group 1, 2 and 13, respectively, we describe here the chemistry of methyllithium(I), dimethylberyllium(II) and trimethylaluminium(III).

Methyllithium(I)

Methyllithium(I) is a colorless liquid soluble in hydrocarbon and non-polar solvents. It shows the properties of a typical covalent compound. It has better thermal stability as compared to other methyl derivatives of alkali metals. It ignites spontaneously in air, water and even in water vapors.

Structure

Methyllithium(I), in its natural liquid state as well as in the solid state, possesses a body-centered cubic (BCC) structure (see Chapter 3, p. 122). The building blocks of the structure are tetrameric $[\text{CH}_3\text{Li}]_4$ unit cells. In each unit cell, the lithium atoms are sp^3 hybridized.



The four lithium atoms in each $[\text{CH}_3\text{Li}]_4$ unit cell are held at the edges of a tetrahedron. Four electrons (one contributed by each lithium atom) are delocalized throughout the tetrahedral skeleton. This skeleton, like the skeleton of any other tetrahedron, has four triangular faces. A methyl group is positioned above the center of each triangular face.

Figure 25.14 shows the position of one methyl carbon over one of the tetrahedral faces. The methyl carbon has one electron in a sp³ hybrid orbital which it contributes for bonding. The three lithium atoms on the edges of the triangular face of tetrahedron contribute one electron (from the four delocalized electrons in the tetrahedron) for bonding.

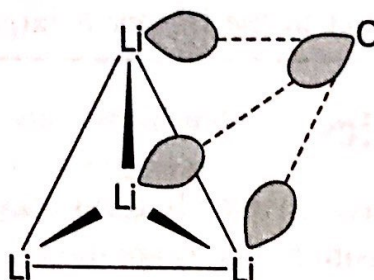


Fig. 25.14 Bonding between one methyl group and three lithium atoms in a $[\text{CH}_3\text{Li}]_4$ cluster

The two electrons span over four atoms, one carbon and three lithium atoms, of a triangular face of the tetrahedron. Accordingly, a two-electron–four-center bond is formed. A similar multicenter bond is formed on the remaining three faces of the tetrahedron as well.

As a result of the two-electron–four-center bonding, the lithium–carbon and lithium–lithium bonds are held together in a cluster. The unit cell emerging from the $[\text{CH}_3\text{Li}]_4$ cluster is shown in Fig. 25.15.

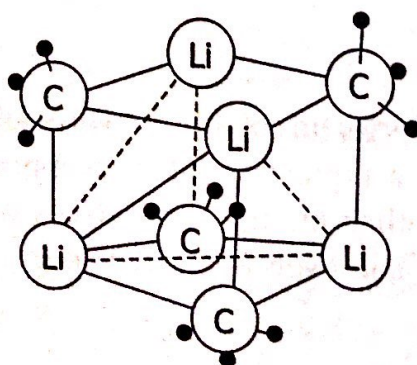


Fig. 25.15 Bonding in a $[\text{CH}_3\text{Li}]_4$ unit cell

In each unit cell, the methyl carbon has a coordination number of 6; it is bound to three hydrogen atoms and three lithium atoms of any one face of the tetrahedron.

Nine unit cells are packed into a BCC arrangement. Eight of them occupy the edges of the cube and the ninth one occupies the center of the cube. This arrangement is shown in Fig. 25.16.

The unit cells are interconnected along the cube diagonals through the bridging methyl groups. Now, the methyl carbon has a coordination number of 7; it is bound to three hydrogen atoms, three lithium atoms of one unit cell and one lithium atom of the diagonally opposite unit cell.

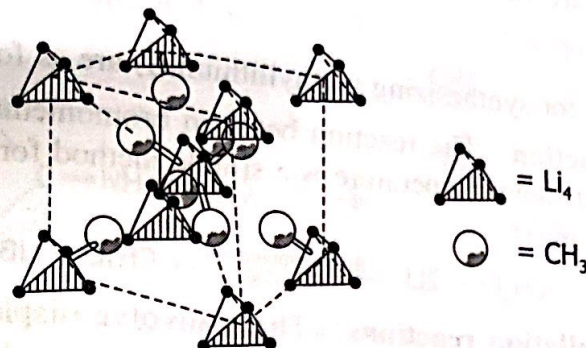


Fig. 25.16 Body-centered cubic structure of methyllithium(I)

Bonding

Figure 25.15 shows that one methyl group and three lithium atoms of a $[\text{CH}_3\text{Li}]_4$ unit cell are held together by a two-electron–four-center bond. There are four such multicentered bonds in each unit cell. While the methyl group contributes one electron for bonding, the other comes from the delocalized cloud spanning over the lithium tetrahedron.

The two-electron–four-center bonding may be explained on the basis of molecular orbital theory. An sp^3 hybrid orbital of methyl carbon combines with the sp^3 hybrid orbitals of three lithium atoms (of any one face of the tetrahedron) to give one bonding molecular orbital (a) two non-bonding molecular orbitals (b and c) and one anti-bonding molecular orbital (d). The energy pattern of these orbitals is shown in Fig. 25.17.

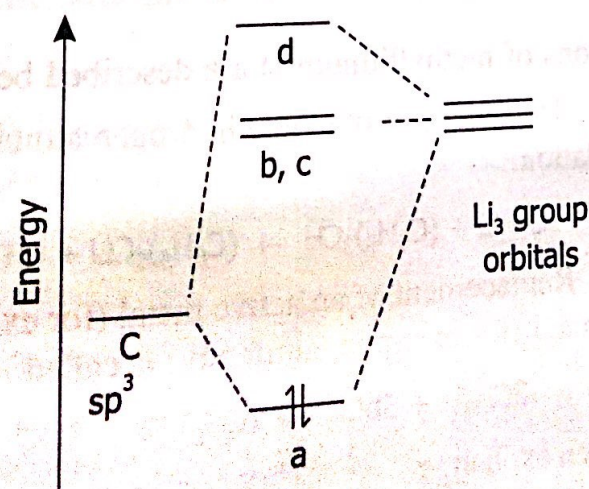


Fig. 25.17 Molecular orbital diagram for one of the four two-electron–four-center bonds in $[\text{CH}_3\text{Li}]_4$ unit cell

The two electrons that hold the four atoms together occupy the bonding molecular orbital, σ . Although too few electrons are available for bonding yet the unit cells are stable. The stability is attributed to two factors. First, the bonding molecular orbital has very low energy as compared to the non-bonding and anti-bonding molecular orbitals. Second, only the lowest energy bonding molecular orbital is occupied; the relatively high-energy, non-bonding and anti-bonding molecular orbitals are vacant.

Trimethylaluminium(III)

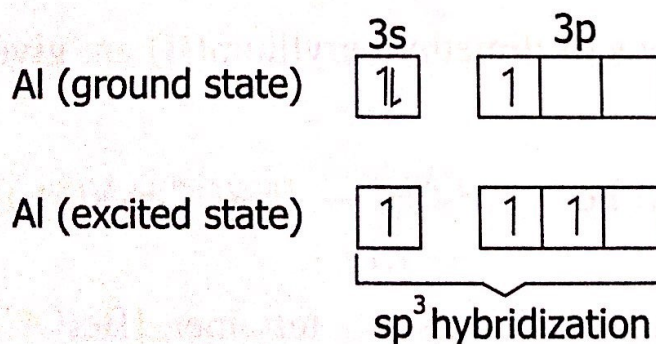
Trimethylaluminium(III) is a colorless, mobile liquid. It is an exceptionally reactive compound. It is pyrophoric in nature, i.e., it catches fire in air. It reacts explosively with water. For these reasons, it is preserved under the protective atmosphere of argon.

Structure

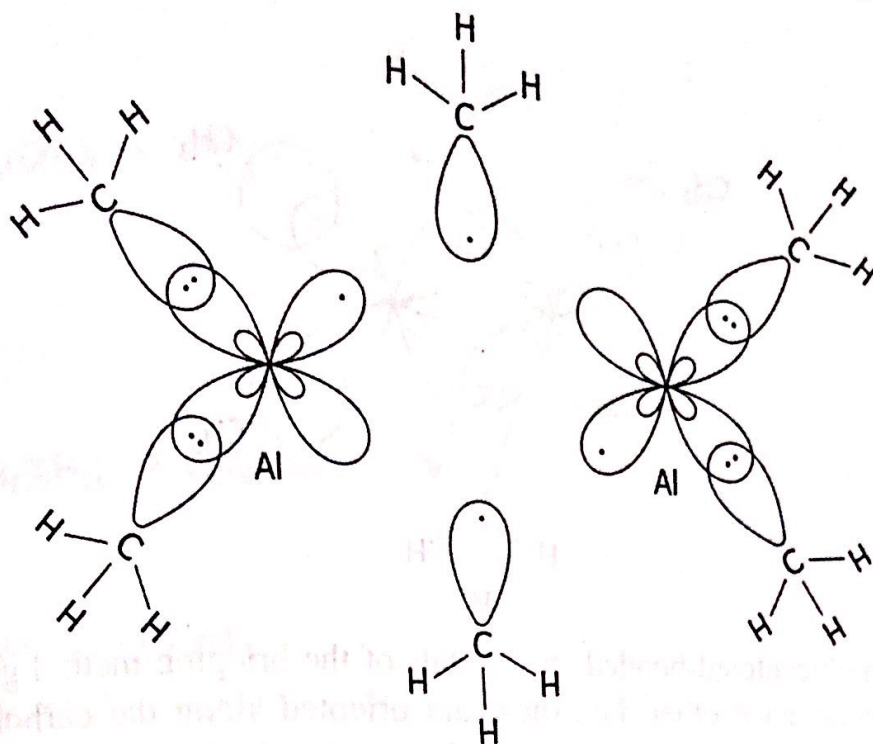
Trimethylaluminium(III) has a dimeric structure, the composition being $[\text{Al}_2(\text{CH}_3)_6]$. Each aluminium atom is tetrahedrally coordinated to four methyl groups, two terminal and two bridging. The aluminium–carbon(terminal) bond lengths are shorter than the aluminium–carbon(bridging) bond lengths. The structure is depicted in Fig 25.2b.

Bonding

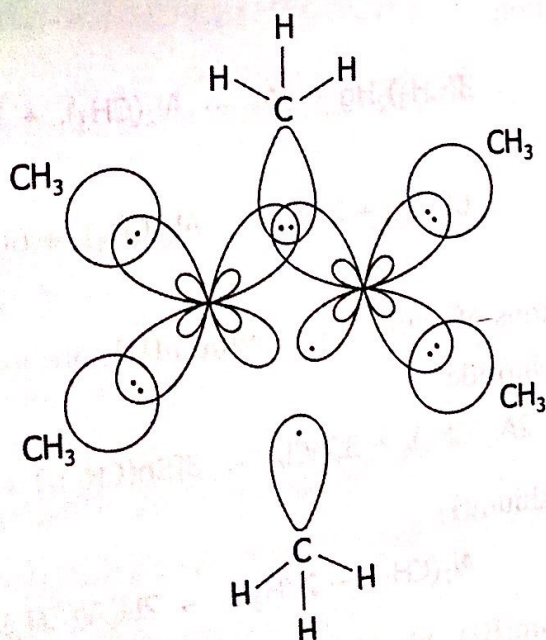
Aluminium, in trimethylaluminium(III) molecule, is sp^3 hybridized.



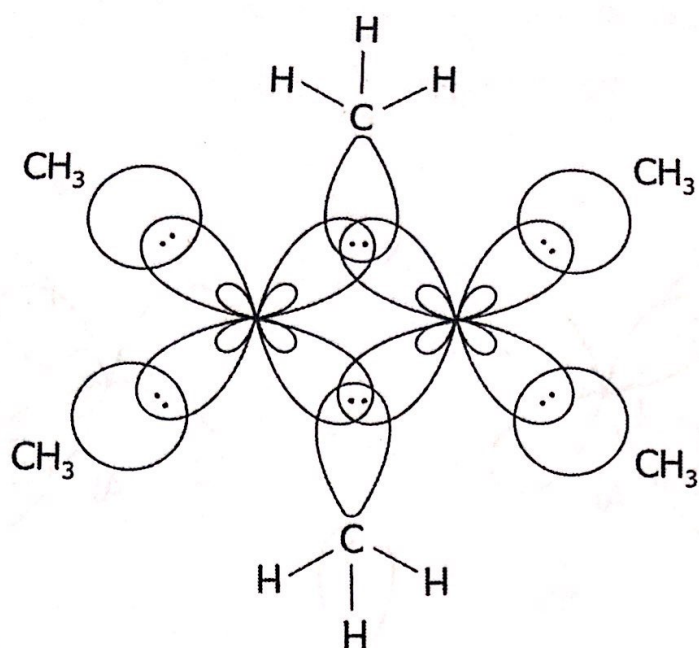
Three of the sp^3 hybrid orbitals contain one electron each, while the fourth one is vacant. Two sp^3 hybrid orbitals are used by each aluminium to form two normal, two-electron–two-center bonds with terminal methyl groups. The $[\text{Al}(\text{CH}_3)_2]$ fragment is now left with two sp^3 hybrid orbitals—one vacant and the other having one electron.



Each of the two bridging methyl groups has one unbound, singly occupied sp^3 hybrid orbital on its carbon atom (the remaining three being bound to hydrogen atoms). This methyl orbital overlaps with a vacant sp^3 hybrid orbital of one aluminium as well as with the singly occupied sp^3 hybrid orbital of the other aluminium. Thus, a two-electron-three-center bond, spanning over aluminium-carbon-aluminium, results.



The second bridging methyl group then enters into a similar overlap, resulting in another two-electron-three-center bond.



The two multicentered-bonded sp^3 orbitals of the bridging methyl groups are directed towards each other, i.e., these are oriented along the carbon-carbon axis. This means that the two-electron-three-center bond forming sp^3 hybrid orbital of one methyl group is directed along the line joining the carbon of other methyl group. Effective overlap of these orbitals with sp^3 hybrid orbitals of aluminium is possible only if the bond angle is not very large. Accordingly, the aluminium-carbon-aluminium bond angle in trimethylaluminium(III) is only 70° .