

Electron-Deficient Organometals. Organometallic compounds of the smallest and most electropositive main-group metals (Li, Be, Mg, Al, and, to some extent, B and Zn) have a structural chemistry and reactivity strongly influenced by their having too few electrons and too many valence orbitals to obey the octet rule as monomers. They form aggregates in the solid state in which the "sigma" electrons are delocalized in multicentered bonds. The tendency toward aggregation increases with metal electropositivity; it decreases as the steric requirements of the alkyl group increase. $\text{LiMe}(s)$ (Figure 13.15) is a tetramer whose unit cell contains a body-centered packing of Li_4 tetrahedra. A methyl caps each triangular face. Each C in the $[\text{LiMe}]_4$ unit interacts with an adjacent Li_4 , providing bond-

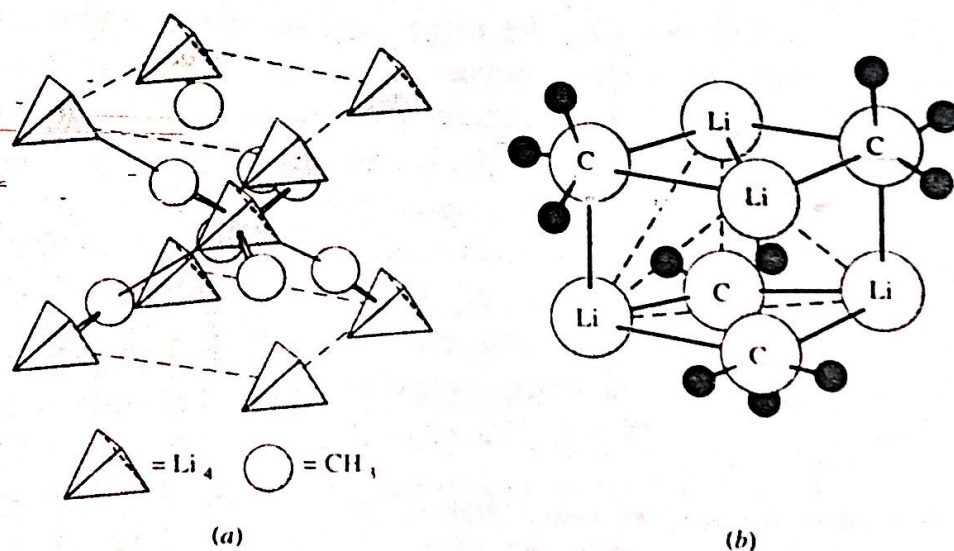


Figure 13.15 (a) Unit cell of $\text{LiMe}(s)$. (After E. Weiss and E. A. C. Lucken, *J. Organomet. Chem.* 1964, 2, 197. (b) Schematic drawing of $(\text{LiMe})_4$ unit.

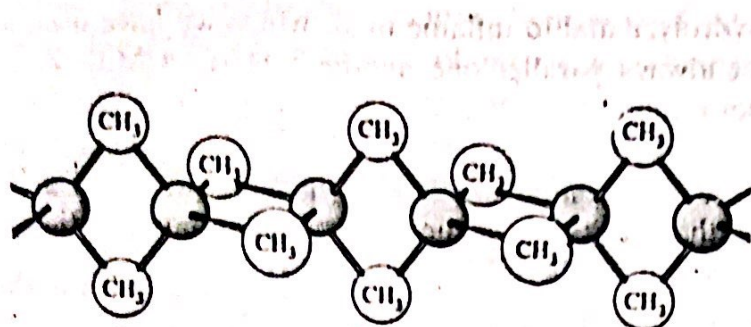


Figure 13.16 Chain structure of MMe_2 ($M = Be, Mg$).
(The chlorides also have this structure.)

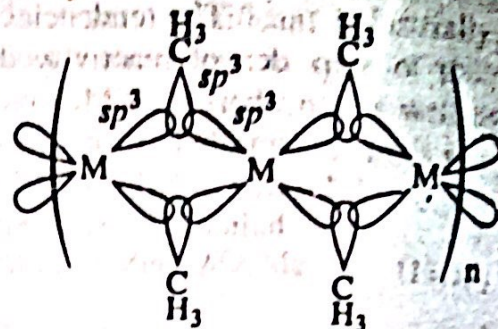


Figure 13.17 Three-center bonding with bridging methyls.

ing throughout the solid lattice which accounts for the low solubility of $LiMe$ in poorly solvating media. $NaMe(s)$ has a similar structure. Alkyls of other alkali metals are best considered as ionic compounds. [KMe has the $NiAs$ structure (Figure 5.6) with methyl carbanions.] They are intractable white solids that decompose on heating and are insoluble in virtually all solvents. Extremely bulky R groups can lead to monomers; for example, $Li(2,4,6-Ph_3C_6H_2) \cdot OEt_2$ is a monomer with three-coordinate Li .

$BeMe_2(s)$ and $MgMe_2(s)$ (Figure 13.16) are long-chain polymers having metals tetrahedrally coordinated by $\mu-Me$. The bridging entails three-center bonding in which each metal contributes two empty sp^3 orbitals while each Me contributes one sp^3 hybrid filled with two electrons (Figure 13.17). In contrast, more electronegative Zn , Cd , and Hg form alkyls R_2M which are linear volatile monomers. However, Ph_2Zn crystallizes as a $PhZn(\mu-Ph)_2ZnPh$ dimer.

$(AlMe_3)_2$ (Figure 13.18) is a dimer having terminal and bridging methyl groups both in the solid and vapor phase. "Simple" organoaluminum compounds such as $(Ph_3Al)_2$ are dimers or, in some cases, such as $(PhCH_2)_3Al$, chain oligomers. A dimer-monomer equilibrium exists for straight-chain Al alkyls in solution in inert solvents. The equilibrium lies progressively farther toward the monomer with increasing chain length and steric bulk. $(2,4,6-Me_3C_6H_2)_3Al$ is a monomer in solution. Ready formation of bridging alkyls provides a facile mechanism for alkyl exchange. Hence, mixtures of Al alkyls equilibrate with a statistical distribution of different alkyl groups around each Al . Bridging alkyls are involved in the ability of organometals to behave as good alkylating agents. The lower dialkyl aluminum halides R_2AlX form structures with μ -halides (Figure 13.19); the halide bridges involve only two-center bonds.

In contrast to Al , the trialkyls of less electropositive B , Ga , In , and Tl are all monomeric trigonal-planar molecules. B forms a wide range of compounds with $\mu-H$ which are treated in Chapter 17.

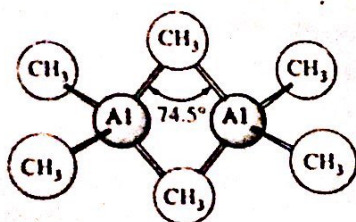


Figure 13.18 Structure of $(AlMe_3)_2$.

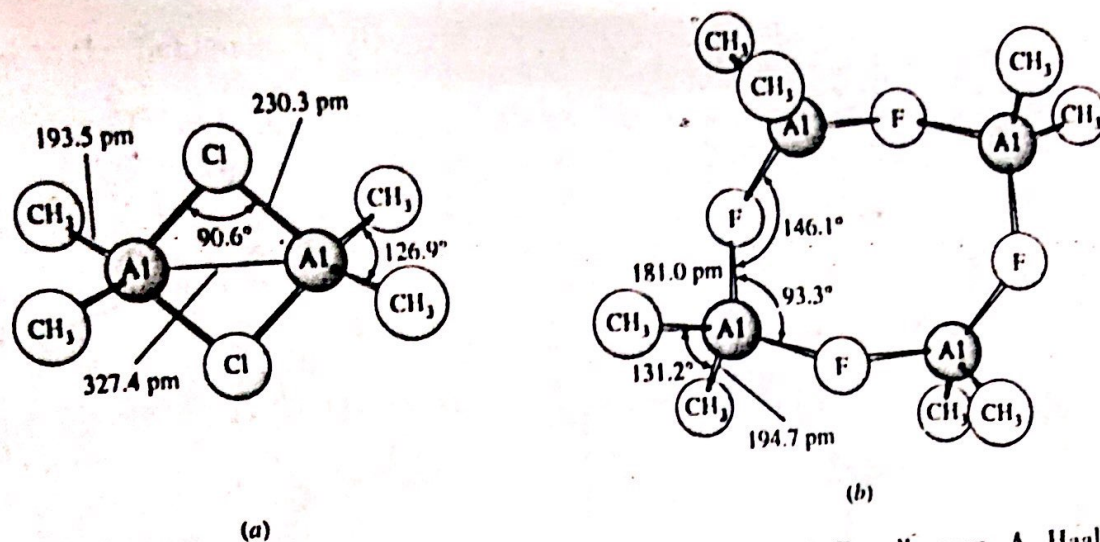


Figure 13.19 Molecular structure of (a) $(\text{Me}_2\text{AlCl})_4$. (From K. Brendhaugen, A. Haaland, and D. P. Novak, *Acta Chem. Scand.* 1974, 28A, 45.) (b) Molecular structure of $(\text{Me}_2\text{AlF})_4$. (From G. Gundersen, N. T. Haugen and A. Haaland, *J. Organomet. Chem.* 1973, 54, 77.)

Availability of empty metal orbitals leads to Lewis acid behavior by Groups 1, 2, 12, and 13 compounds. Complexes such as $\text{Me}_3\text{B} \leftarrow \text{NMe}_3$, $\text{Et}_3\text{Al} \leftarrow \text{OEt}_2$, $\text{Li}[\text{ZnEt}_4]$, and $\text{Ph}_2\text{Mg} \leftarrow \text{OEt}_2$ are formed. Complexation of Li^+ in LiR by *tmeda* which enhances the reactivity has been noted above. In contrast, trialkylboranes and trialkylalanes form strong complexes with ethers which reduce the reactivity by blocking the one remaining coordination site.

Solid-state structures of organo halides, alkoxides, and amides of the most electropositive elements are often polymeric as a result of Lewis acid-base behavior. Figure 13.20a shows the solid-state structure of EtZnI which consists of sheetlike layers in which each

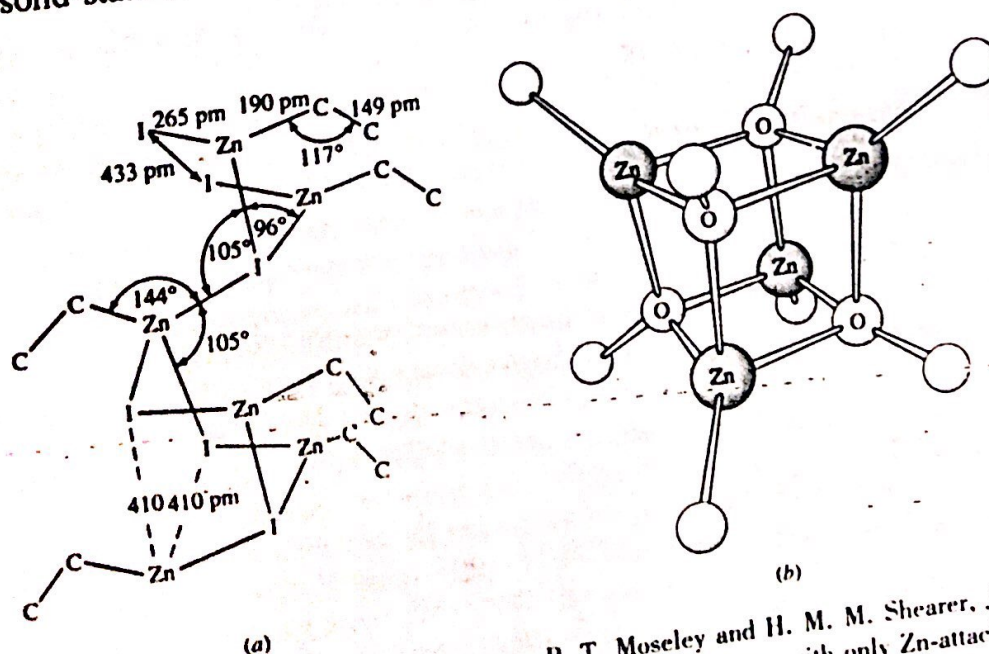


Figure 13.20 Structure of (a) EtZnI . (From P. T. Moseley and H. M. M. Shearer, *J. Chem. Soc. Chem. Commun.* 1966, 876.) (b) Structure of $(\text{EtZn}(\text{OMe}))_4$, with only Zn-attached C's shown. (From H. M. M. Shearer and C. B. Spencer, *J. Chem. Soc., Chem. Commun.* 1966, 194.)

Alkyls

30. Draw the structure of methyl lithium. In which category of organometallic compounds will you place it? What are the coordination numbers of Li and C in the tetramer?
31. Both $AlEt_3$ and $AlCl_3$ dimerize but the nature of alkyl bridging and halide bridging in the dimers are different. Justify.
32. Draw the structure of dimeric trialkyl aluminium and explain why all Al – C bond lengths are not identical.