

2.4: Structure and Bonding

Learning Objectives

In this lecture you will learn the following

- Solid state structures of nickel-arsenide, alkyl lithium and alkyl aluminium compounds

Structure and bonding

The slight differences that arise between organometallic compounds and binary hydrogen compounds are mainly due to the tendency of alkyl groups to avoid ionic bonding.

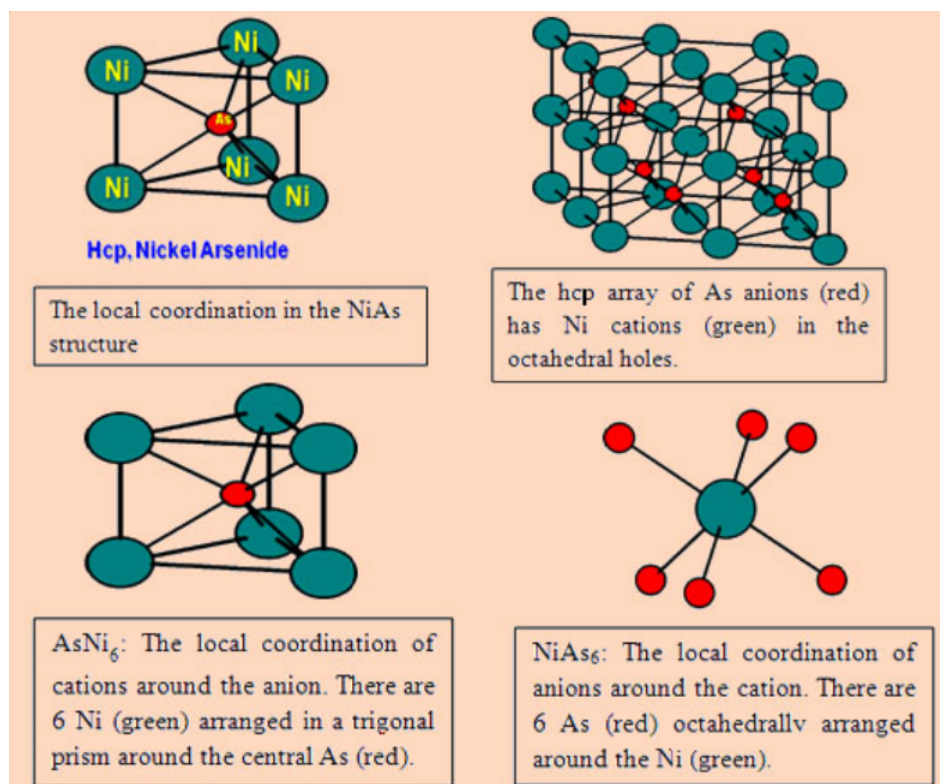
The molecular structures of AlMe_3 and MeLi differ from AlH_3 and LiH .

Even the more ionic MeK crystallizes in the nickel-arsenide structure rather than the rock-salt structure adopted by KCl .

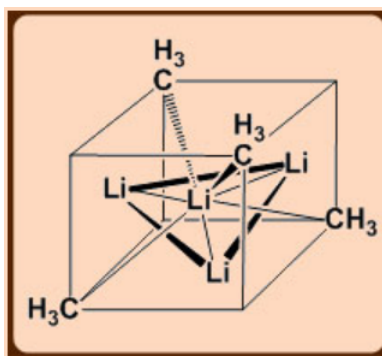
Nickel-arsenide structure is typical of soft-cation, soft-anion combinations.

Electron deficient compounds such as AlMe_3 contain 3c-2e bonds analogous to the $\text{B}-\text{H}-\text{B}$ bridges in diborane.

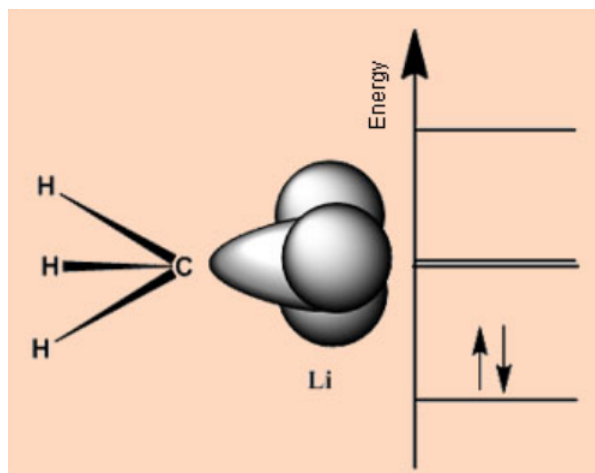
The Nickel-Arsenide, NiAs , Structure



MeLi in nonpolar solvents consists of tetrahedron of Li atoms with each face bridged by a methyl group. Similar to Al_2Me_6 , the bonding in MeLi consists of a set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals on each face of the Li_4 tetrahedron and one sp^3 hybrid orbital from CH_3 gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.



The lower energy of the C orbital compared with the Li orbitals indicates that the bonding pair of electrons will be associated primarily with the CH_3 group, thus supporting the carbanionic character of the molecule. Some analysis has indicated that about 90% ionic character for the Li-CH_3 interaction.



The interaction between an sp^3 orbital from a methyl group and the three $2s$ orbitals of the Li atoms in a triangular face of $\text{Li}_4(\text{CH}_3)_4$ to form a totally symmetric $4c, 2e$ bonding orbital. The next higher orbital is non-bonding and the uppermost is antibonding.

Me_2Be and Me_2Mg exist in a polymeric structure with two $3c, 2e$ -bonding CH_3 bridges between each metal atom.

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