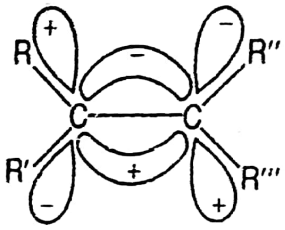
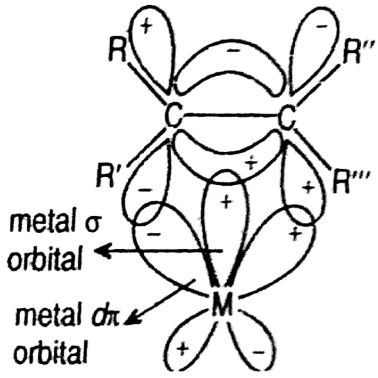
BONDING IN Pi METAL ORGANOMETALLIC COMPLEXES

1. Bonding in π-Metal Olefin or Alkenyl Complexes

A traditional representation of a metal-olefin bond is as shown :





In the olefin ligand, in addition to a σ bond formed due to the overlapping of sp^2 hybrid orbitals of the two carbon atoms, the p_z orbitals of the two carbon atoms overlap to form a π bonding and a π* antibonding molecular orbital. The π bonding molecular orbital is occupied whereas π* antibonding molecular orbital is vacant.

The occupied π bonding molecular orbital of alkene then overlaps with empty σ orbital of the metal while one of the filled $d\pi$ orbitals of the metal interacts with the empty π* antibonding molecular orbital of alkene resulting in a bond with π symmetry about the Z-axis. Thus, the metal-alkene bond consists of two components, *viz.*, σ donation from ligand to metal and simultaneous π donation from metal to ligand. The metal–carbon bond is, thus, similar to the metal–carbon bond in metal carbonyls. Both alkene and CO are very weak σ donors but the presence of low energy empty π* molecular orbitals on these ligands makes the $d\pi$–π* bonding possible. The transfer of electrons from ligand to metal during the formation of σ bond is enhanced by simultaneous removal of charge from the metal through $d\pi$–π* back donation. This effect, known as **synergic effect**, would strengthen the M -C bond. It is very difficult to assess the relative extent of σ and π bonding in such cases. However, there is evidence to suggest that, in general, π

bonding makes greater contribution to M—C bond in these alkenyl complexes.

The structure of the alkenyl complex $K^+[PtCl_3(C_2H_4)]^-$ has been established to be approximately square planar as shown. The olefin-metal bond lies perpendicular to the plane containing Pt and the three Cl atoms. In this compound, the dsp^2 hybridised σ orbital of Pt overlaps with π bonding molecular orbital of ethene. Simultaneously, the filled $d\pi$ orbital of Pt overlaps with π^* orbital of C_2H_4. The two carbon atoms of C_2H_4 are equidistant from Pt. The ethene group lies perpendicular to the Pt—Cl bond which is trans to the C_2H_4 ligand.