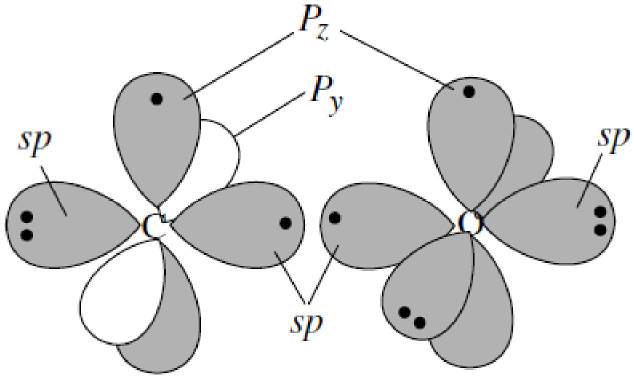
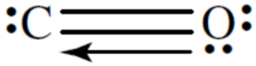
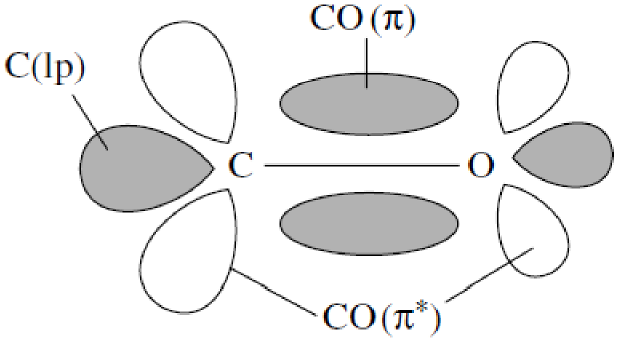
Valence Bond Description of the CO ligand

- In the CO molecule both the C and the O atoms are ***sp hybridized***.
- The singly occupied sp and p_z orbitals on each atom form a σ and a π bond, respectively.
- This leaves the C p_y orbital empty, and the O p_y orbital doubly occupied, and so the second π bond is formed only after we have formed a ***dative bond*** by transfer of the lone pair of O p_y electrons into the empty C p_y orbital.



- This transfer leads to a $C^{\delta-}$–$O^{\delta+}$ polarization of the molecule, which is almost exactly canceled out by a partial $C^{\delta+}$–$O^{\delta-}$ polarization of all three bonding orbitals because of the higher electronegativity of oxygen.
- The free CO molecule therefore has a net dipole moment very close to zero.

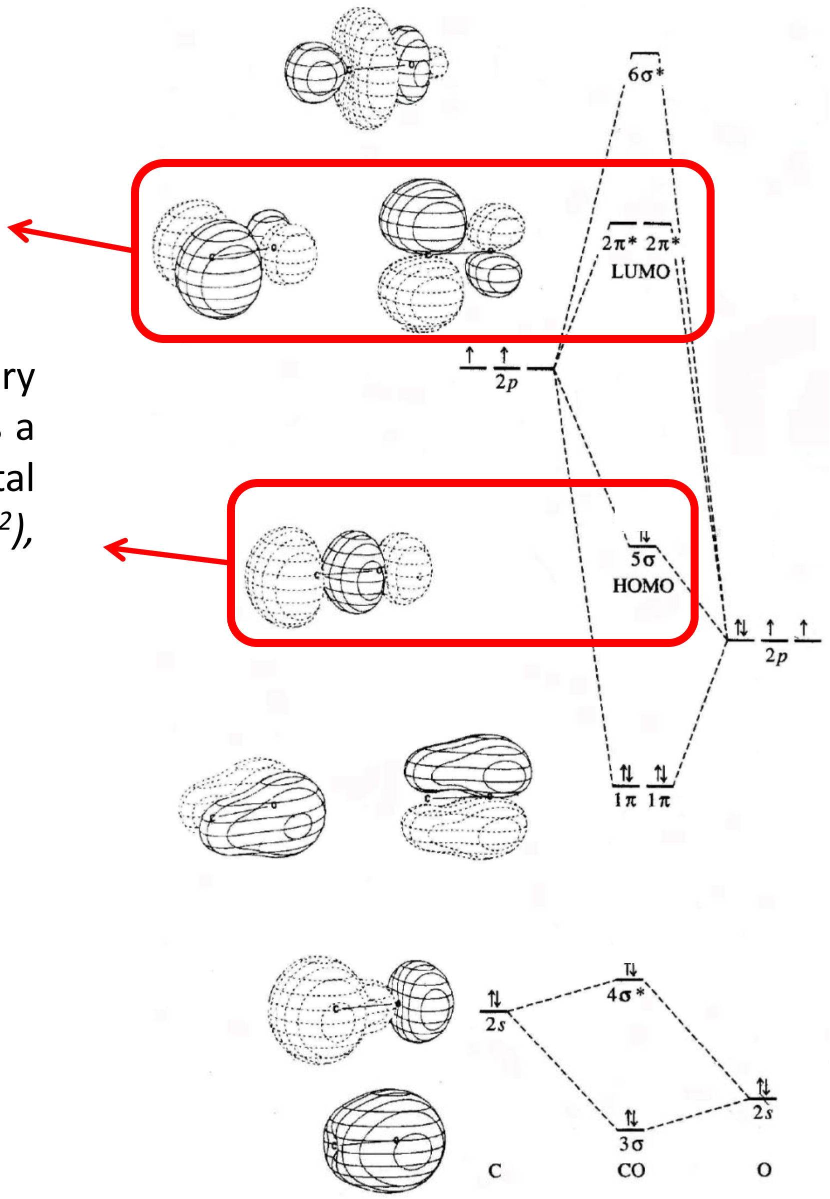


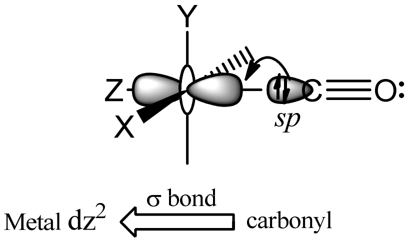


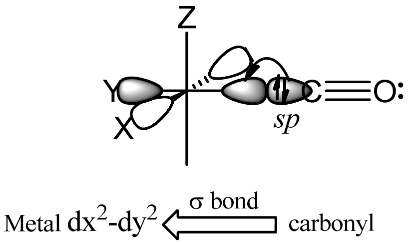
Molecular Orbital Description of the CO Ligand

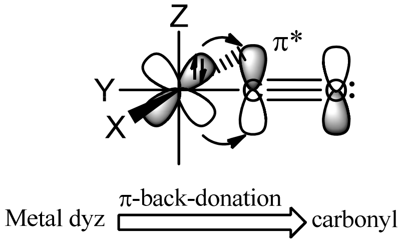
The CO LUMO orbitals are antibonding of π^* symmetry. These are empty orbitals and can accept electron density from a metal centre via π-backbonding with the metal *d(xy), d(xz)* and *d(yz),* orbitals

The CO HOMO orbital is a bonding orbital of σ symmetry with significant electron density on the carbon. This is a filled orbital and can donates electron density to a metal centre by forming a σ bond with metal *p* and $d(x^2-y^2)$, $d(z^2)$ orbitals









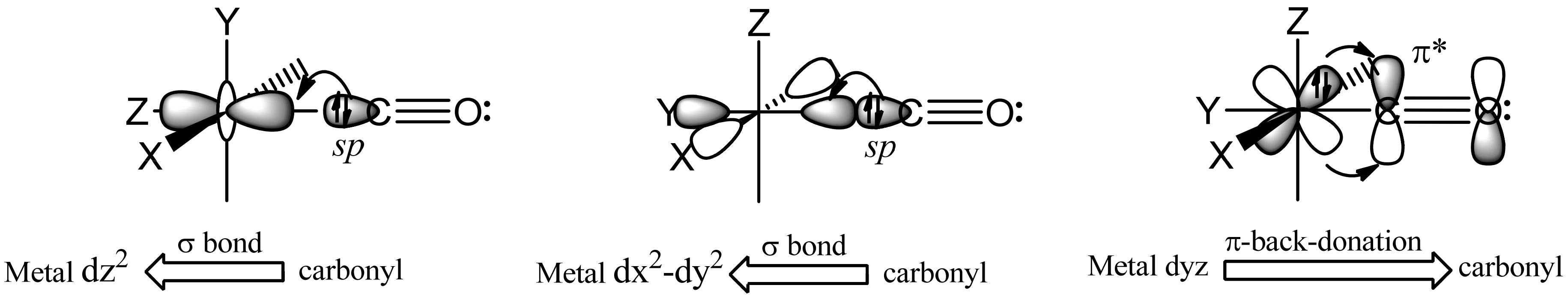
Dewar-Chatt-Duncanson model

- The ***Dewar-Chatt-Duncanson model*** explains the type of chemical bonding between an unsaturated ligand and a metal forming a π complex.
- The π-acid ligand donates electron density into a metal *d*-orbital from a π-symmetry bonding orbital between the carbon atoms.
- The metal donates electrons back from a filled *d*-orbital (usually t_{2g}) into the empty π^* antibonding orbital of the ligand (hence the description π-acid ligand).
- Both of these effects tend to reduce the ligand bond order,

  e.g., leading to an elongated $C{\equiv}O$ distance and a lowering of its vibrational frequency.
- The interaction can cause carbon atoms to "rehybridize“,

  e.g., in metal alkene complexes from sp^2 towards sp^3, which is indicated by the bending of the hydrogen atoms on the ethylene back away from the metal.
- Often the reactivity of the ligand is reversed from its free state – “***umpolung***”*.*

Dewar-Chatt-Duncanson model



- The metal *p* , *d*($x^2 - y^2$) and *d*(z^2) orbitals form σ bonds with the HOMO orbital of CO.
- As shown on previous slides this HOMO is a σ orbital based on carbon.
- The metal *d(xy)* , *d(xz)* and *d(yz)* orbitals form a π bond with the CO π* LUMO (again polarized toward C)
- The metal HOMO, the filled M dπ orbital, back donates to the CO LUMO increasing electron density at both C and O because CO π* has both C and O character.
- The result is that C becomes more positive on coordination, and O becomes more negative. This translates into a polarization of the CO on binding.

- This ***metal-induced polarization*** chemically activates the CO ligand.
- It makes the carbon more sensitive to nucleophilic attack and the oxygen more sensitive to electrophilic attack.
- The polarization will be modulated by the effect of the other ligands on the metal and by the net charge on the complex.
- In $L_nM(CO)$, the CO carbon becomes particularly δ^+ in character if the L groups are good π acids or if the complex is cationic, e.g. $Mo(CO)_6$ or $[Mn(CO)_6]^+$, because the CO-to-metal σ-donor electron transfer will be enhanced at the expense of the metal to CO back donation.
- If the L groups are good donors or the complex is anionic, e.g. $Cp_2W(CO)$ or $[W(CO)_5]^{2-}$, back donation will be encouraged, the CO carbon will lose its pronounced δ^+ charge, but the CO oxygen will become significantly δ^-.

$$\mathrm{M^- \longleftarrow C^{\partial +} \equiv O^+} \qquad \mathrm{M{=}C{=}O} \qquad \mathrm{M^+ \equiv C — O^-}$$

- The range can be represented in valence bond terms the extreme in which CO acts as a pure σ donor, through to the extreme in which both the π^*_x and π^*_y are both fully engaged in back bonding.

- Strong σ donor co-ligands or a negative charge on the metal result in CO stretches at lower frequency. **Why?**

	ν(CO) cm^{-1}
$[Ti(CO)_6]^{2-}$	**1748**
$[V(CO)_6]^{-}$	**1859**
$Cr(CO)_6$	**2000**
$[Mn(CO)_6]^{+}$	**2100**
$[Fe(CO)_6]^{2+}$	**2204**

- The greater the ability of a metal to donate electrons to the π* orbitals of CO, the lower the energy of the C-O stretching vibration.

- One of the most extreme weak metal-π-donor examples is $[Ir(CO)_6]^{3+}$ with ν(CO) bands at 2254, 2276, and 2295 cm^{-1}.
- The X-ray structure of the related complex $[IrCl(CO)_5]^{2+}$ shows the long M−C [2.02(2)A°] and short C−O [1.08(2)A°] distances expected.

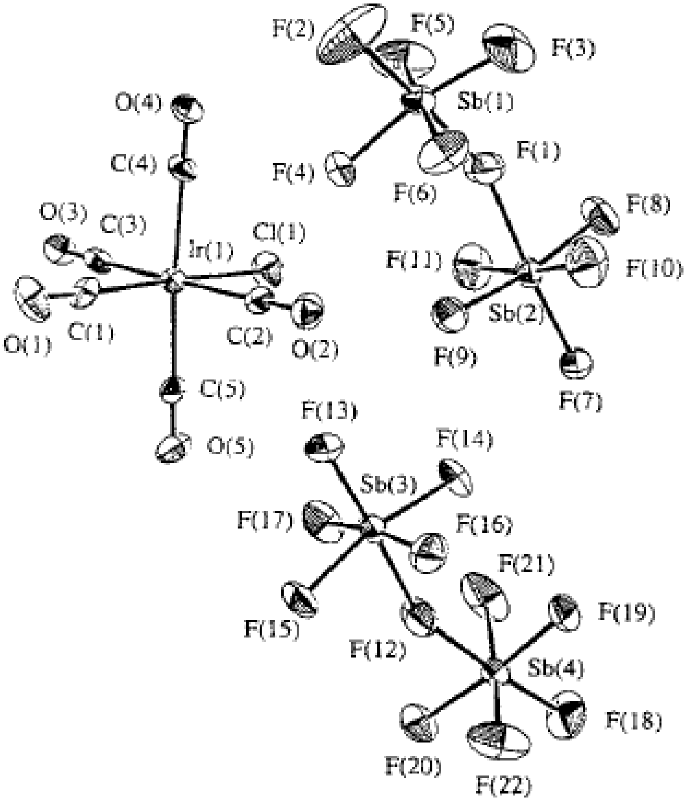
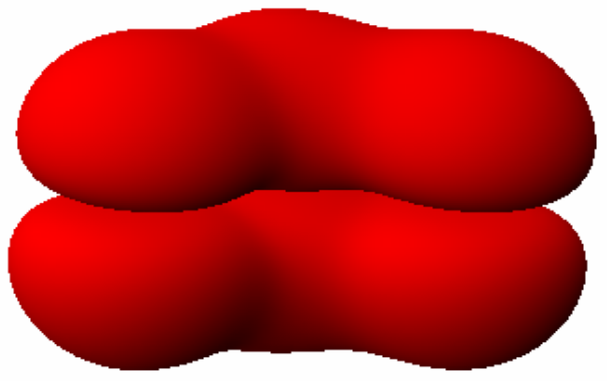


Fig. 1. Molecular structure of $[Ir(CO)_5Cl][Sb_2F_{11}]_2$ (50% probability thermal ellipsoids are shown).

MO Description of Pi-Delocalized Systems

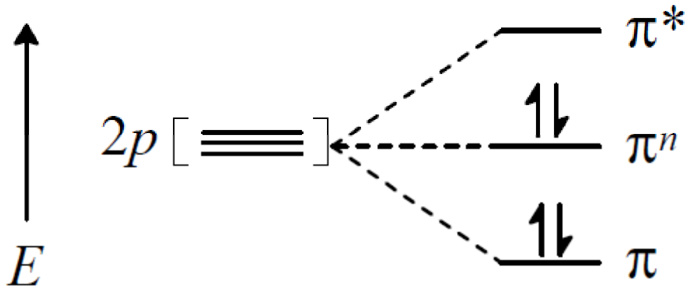
- MO theory has no difficulty explaining the π-delocalized electron density implied by resonance forms, which VB theory cannot easily represent.

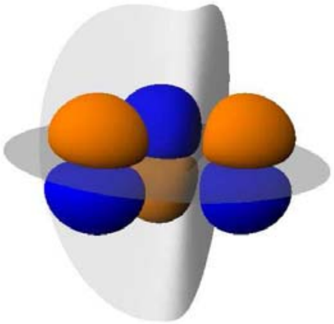


π electron density of O_3

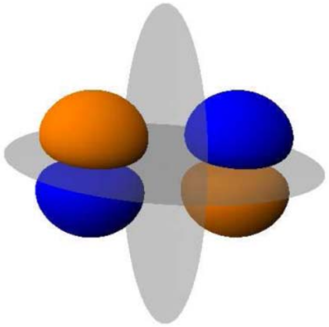
- The three 2*p orbitals perpendicular to the molecular plane* combine to form three π MOs:
  1. π – bonding MO
  2. π^n – *nonbonding MO*
  3. π* – antibonding MO
- A non-bonding MO neither builds nor destroys bonding between the oxygen atoms.

Pi MO Energy Level Scheme for O_3

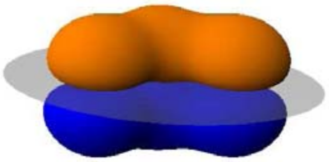




π^* – antibonding MO



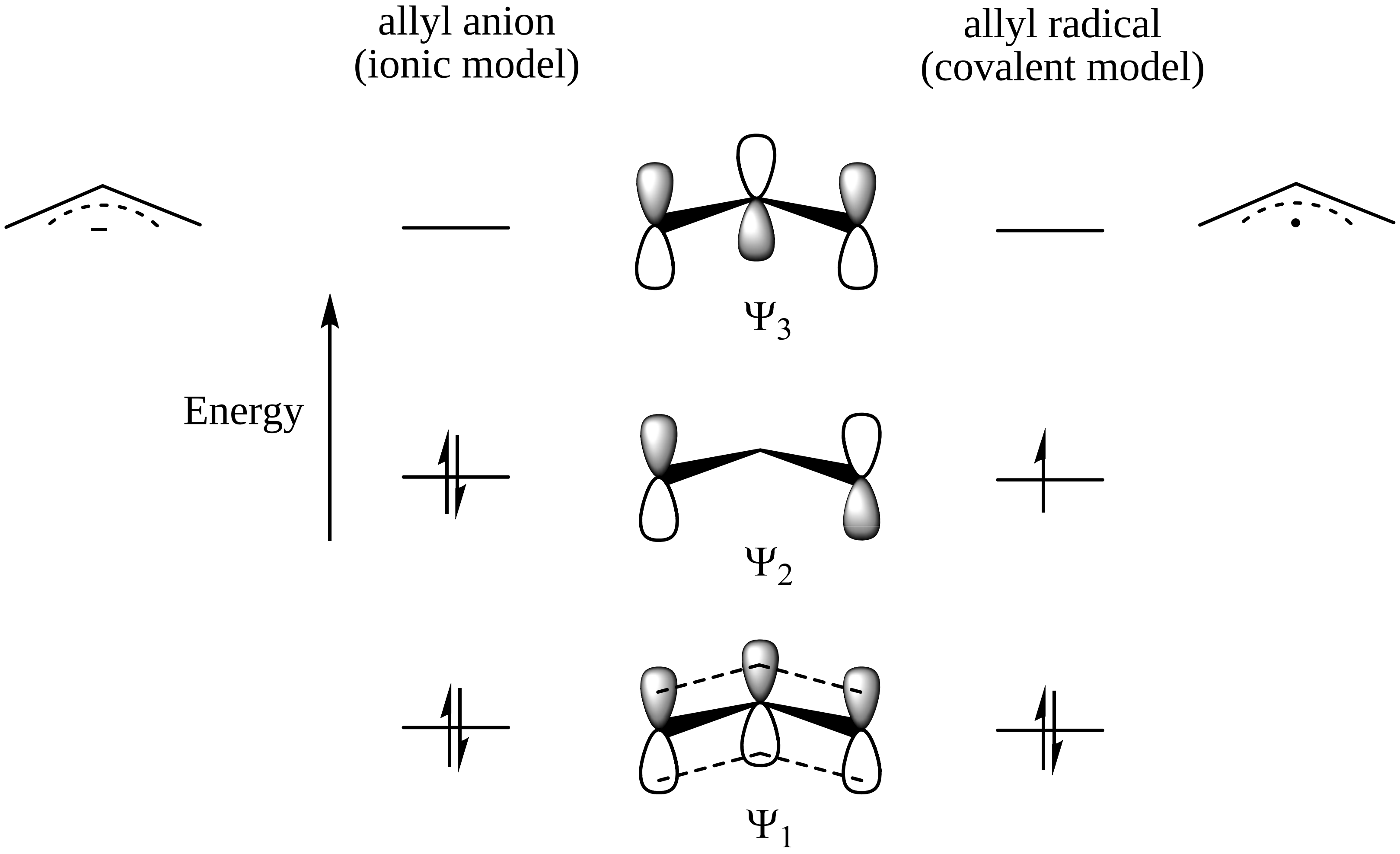
π^n – nonbonding MO



π – bonding MO

- The π system has two pairs of electrons, one pair in the π MO, and the other in the π^n non-bonding MO.
- The bonding $(\pi)^2$ configuration adds a bond order of 1 across the two O–O bonds (i.e., 0.5 to each bond).
- When this is added to the sigma bond between each oxygen pair, the O–O bond order becomes 1.5.
- The configuration $(\pi^n)^2$ neither adds nor subtracts from the overall strength of the bonds.

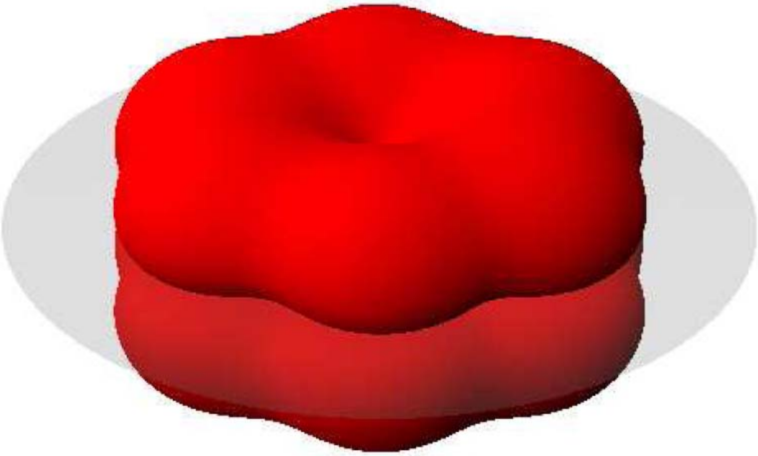
Pi MO Energy Level Scheme for the Allyl Anion $C_3H_3^-$



- As the number of nodes on the allyl ligand increase the MOs of the free ligand increase in energy, i.e. become less stable.

Pi MOs of Benzene, C_6H_6

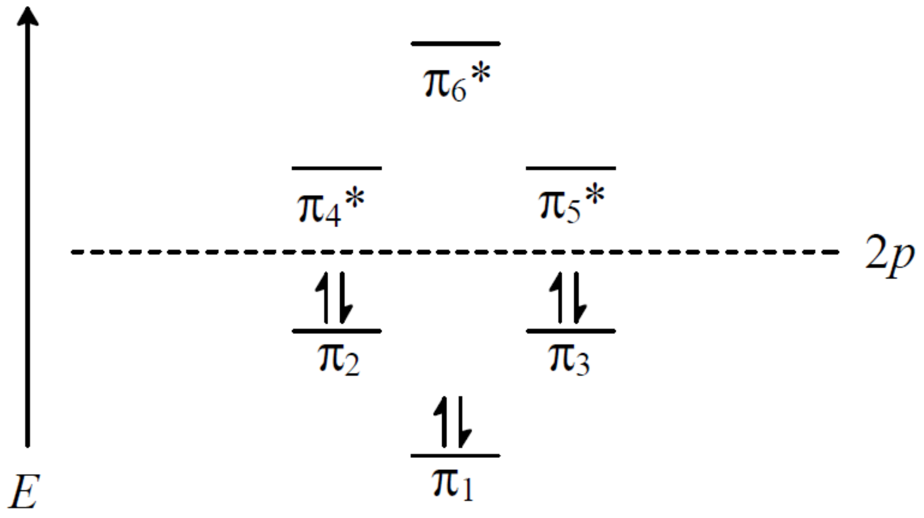
- C_6H_6, has three pairs of electrons delocalized in a π system extending around the hexagonal ring.

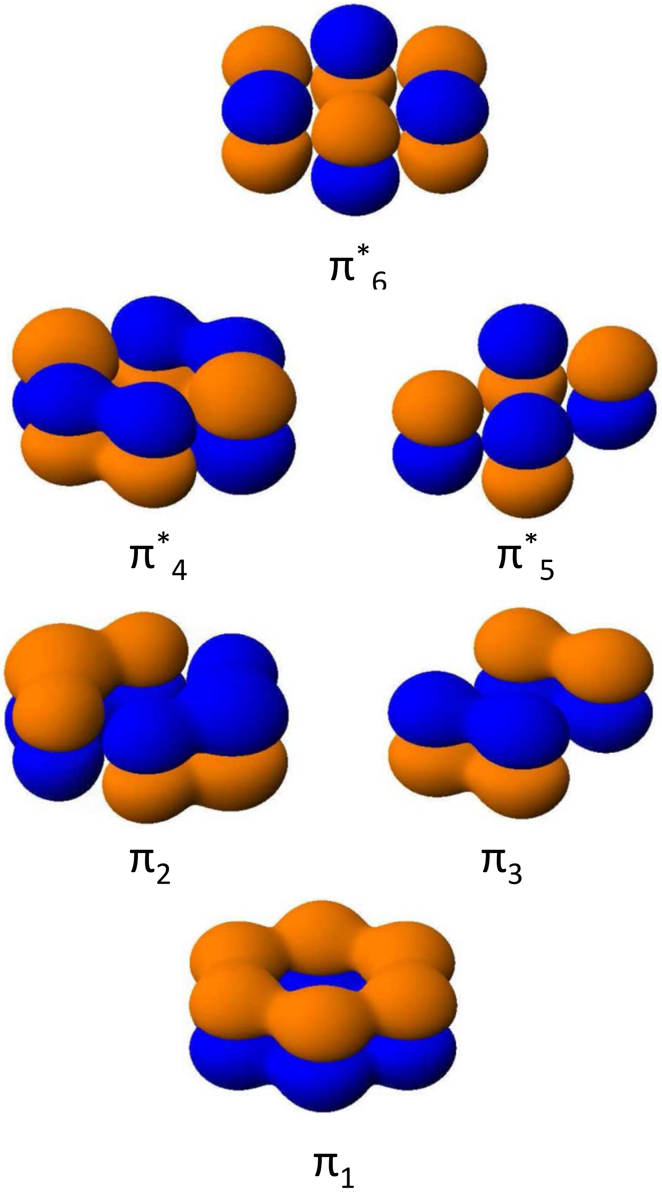


π electron density of C_6H_6

- The six 2*p orbitals perpendicular to the ring on the six carbon* atoms combine to form three bonding (π_1, π_2, π_3) and three antibonding (π_4*, π_5*, π_6*) MOs.

Pi MO Energy Level Scheme for C_6H_6





- Three pairs in bonding MOs add a total of three bond orders over six C–C linkages, or 0.5 for each.

- When this is added to the sigma bond between each carbon pair, the C–C bond order becomes 1.5.

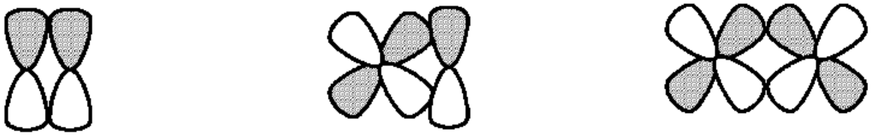
AO Shape and Symmetry

- All AOs with the same value of *l* have the same symmetry, regardless of *n*.
- As isolated orbitals, each type can be identified with a particular point group.
  - $s = R_3$
  - $p = C_{\infty v}$
  - $d = D_{2h}$ ("cloverleaf") or $D_{\infty h}$ (dz^2)
- Orbitals that have bonding combinations usually have the same kind of symmetry with respect to the internuclear axis *(rf. Slater overlap integrals)*.
- If a bonding combination can be identified for any pair of orbitals, there must also be an antibonding combination.
- Nonbonding orbitals are oriented relative to each other such that they do not have the same kind of symmetry relative to the internuclear axis.

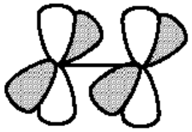
Symmetry Definition of Sigma, Pi, and Delta Interactions

- Sigma (σ) interactions are symmetrical ***relative to a C_2 axis*** collinear with the internuclear axis.

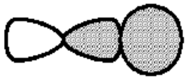
- Pi (π) interactions are anti-symmetric (Ψ changes sign) with respect to C_2 collinear with the internuclear axis and with respect to σ_v coplanar with the shared nodal plane.



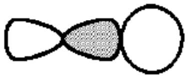
- Delta (δ) interactions are symmetric to C_2 and anti-symmetric to C_4 .



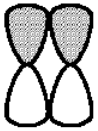
- Bonding and antibonding interactions of the same type have the same symmetry with respect to the internuclear axis.



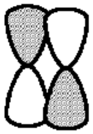
σ bonding



σ^* anti-bonding

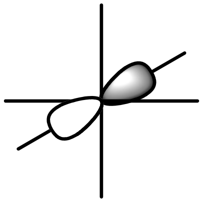


π bonding

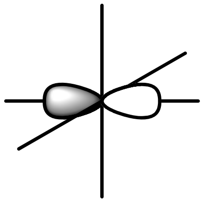


π^* anti-bonding

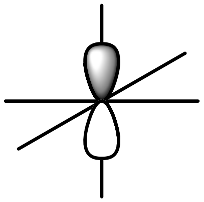
4*p*



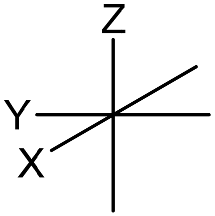
p_x



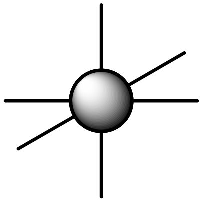
p_y



p_z

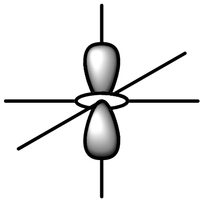


4*s*

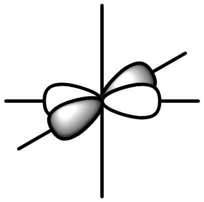


s

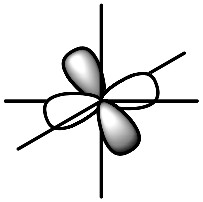
3*d*



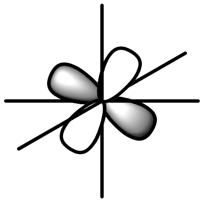
dz^2



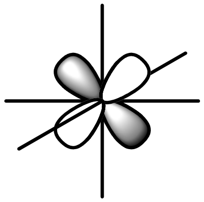
dx^2-dy^2



dxy

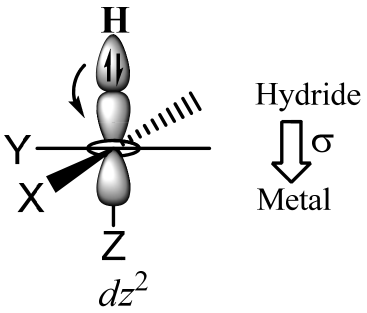


dxz

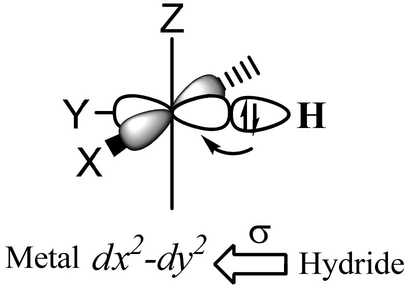


dyz

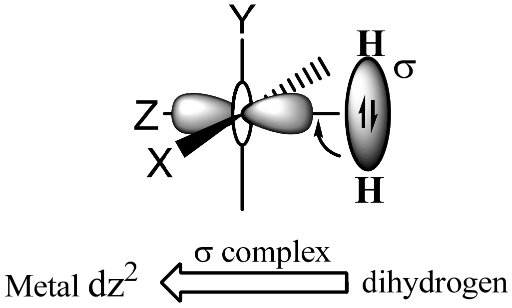
Metal Hydride

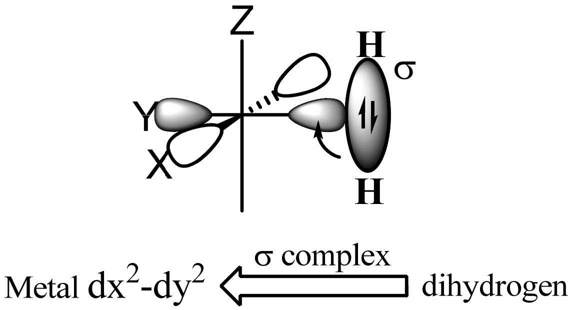


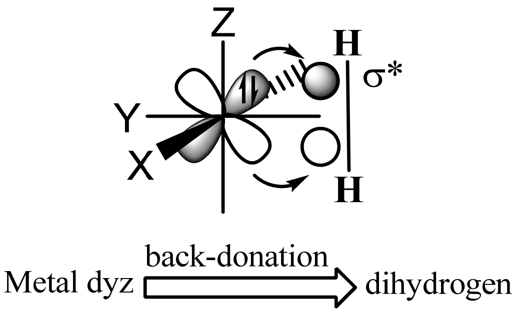
or



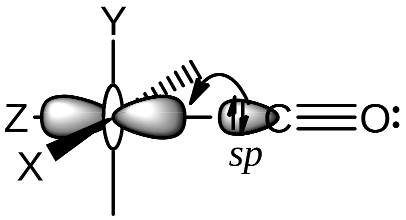
Metal Dihydrogen



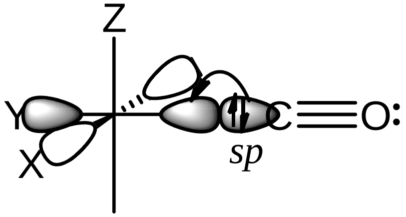




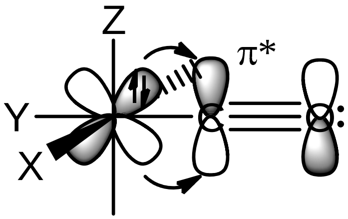
Metal Carbonyl



Metal dz^2 $\xleftarrow{\sigma \text{ bond}}$ carbonyl

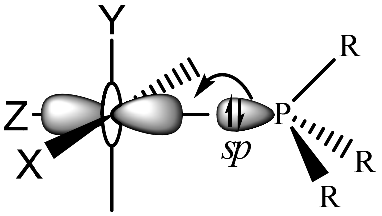


Metal dx^2-dy^2 $\xleftarrow{\sigma \text{ bond}}$ carbonyl

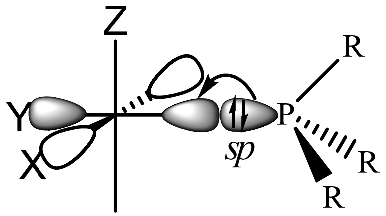


Metal dyz $\xrightarrow{\pi\text{-back-donation}}$ carbonyl

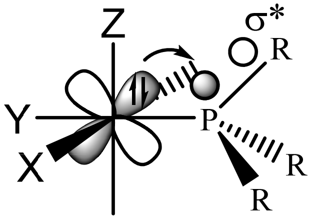
Metal Phosphine



Metal dz^2 $\xleftarrow{\sigma \text{ bond}}$ phosphine



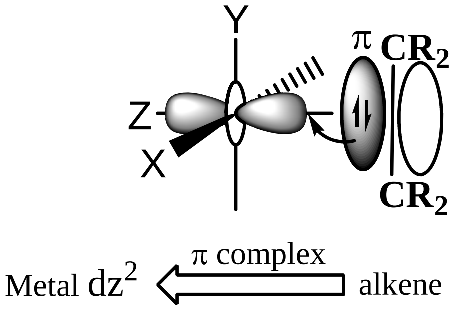
Metal dx^2-dy^2 $\xleftarrow{\sigma \text{ bond}}$ phosphine

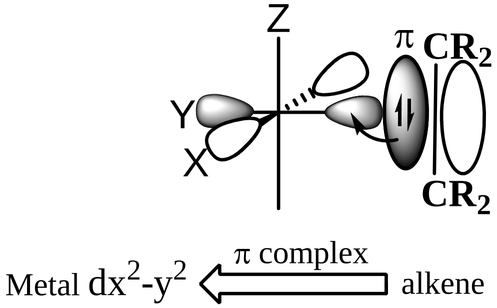


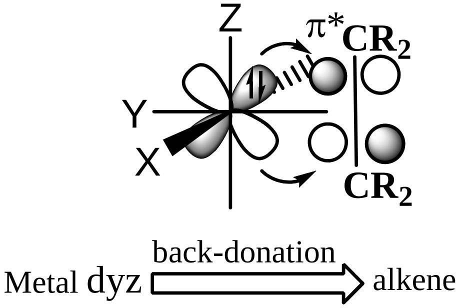
Metal dyz $\xrightarrow{\text{back-donation}}$ phosphine

Z

Metal Alkene

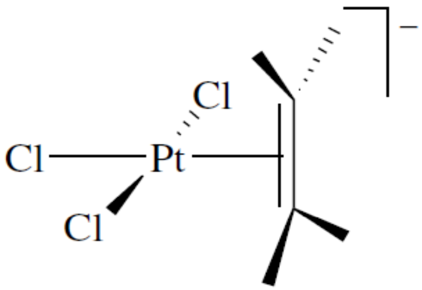


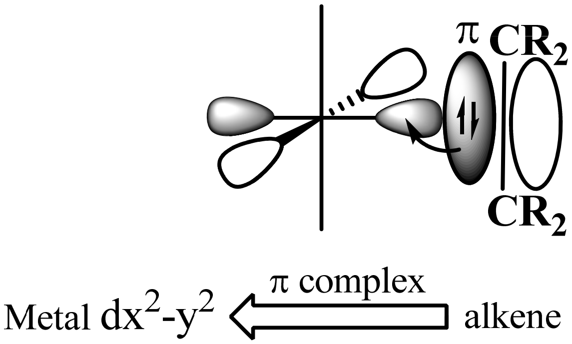


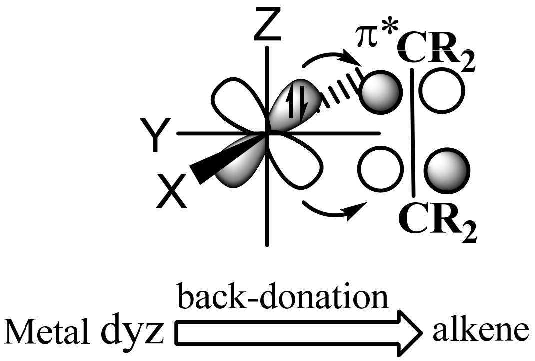


Transition metal alkene complexes

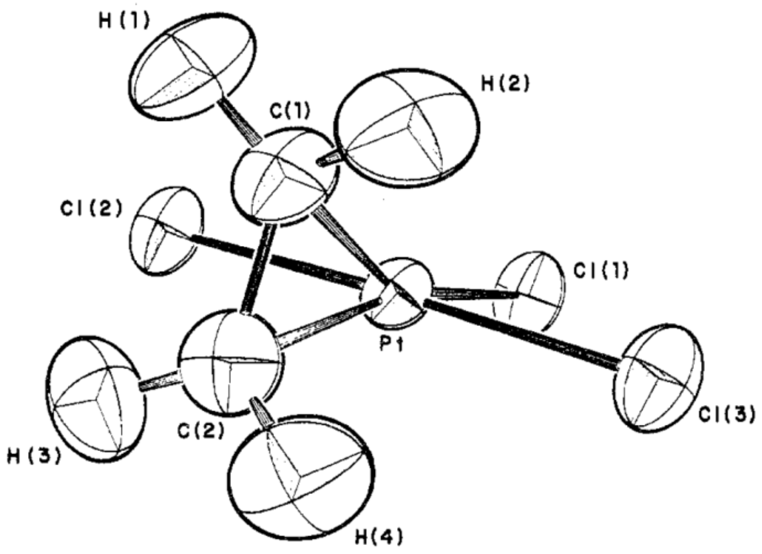
- Zeise's salt was the first organometallic compound to be isolated in pure form (1825 by William Zeise). The structure was not confirmed until 1838.
- This discovery spawned a tremendous growth in organometallic chemistry and still serves as the simplest example of transition metal-olefin complexation.
- Zeise's salt has become one of the most cited examples of the ***Dewar-Chatt-Duncanson model*** for metal-olefin complexation.







Molecular geometry of Zeise's salt (neutron diffraction)



- The **$PtCl_3$ *moiety forms a nearly planar group*** with the Pt atom.
- The Pt-Cl bond trans to the ethylene group (2.340 Å) is significantly longer than the cis Pt-Cl bonds (2.302 and 2.303 Å) – ***trans effect !!***
- The C atoms are approximately equidistant from the Pt atom (2.128 and 2.135 Å).
- The distance from the ***midpoint of the C-C bond to the Pt atom is 2.022 Å.***
- The ***C-C distance, 1.375 Å, is slightly longer than the value found in free ethylene (1.337 Å)***, indicating some $d\pi$-$p\pi^*$ back-bonding from the platinum atom to C_2H_4.
- ***Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom.***