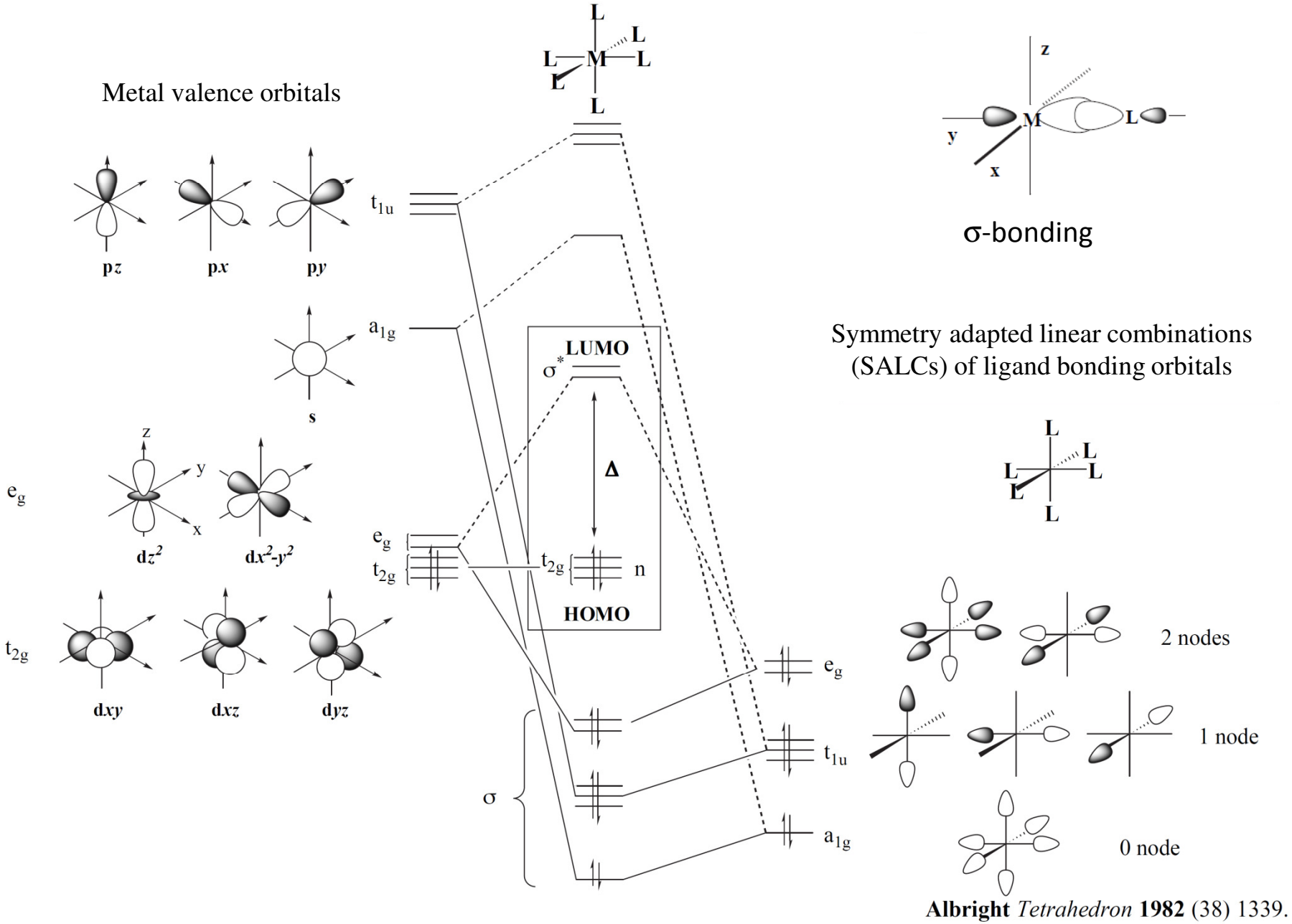
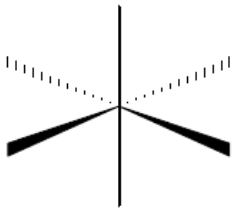
MO description of σ only bonding in an O_h transition metal complex



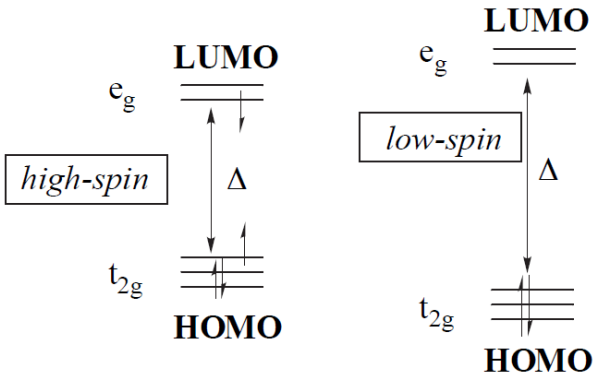
Albright *Tetrahedron* **1982** (38) 1339.

Character table for the O_h point group

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		
Γ	6	0	0	2	2	0	0	0	4	2		$x^2 + y^2 + z^2$
A_{1g}	1	1	1	1	1	1	1	1	1	1		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$



$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$



strong π donor L

strong σ donor L/
π-acceptor L

$I^- < Br^- < Cl^- < N_3^-, F^- < OH^- < O_2^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en < bpy, phen $< NO_2^- < CH_3^-, C_6H_5^- < CN^- < CO, H^-$

← π-donor, low Δ, "low field ligand"

π-acceptor/strong σ-donor, high Δ, "high field ligand" →

$Mn^{2+} < V^{2+} < Co^{2+} < Fe^{2+} < Ni^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Rh^{3+} < Ir^{3+} < Pt^{4+}$

← 1st row/low-valent, low Δ

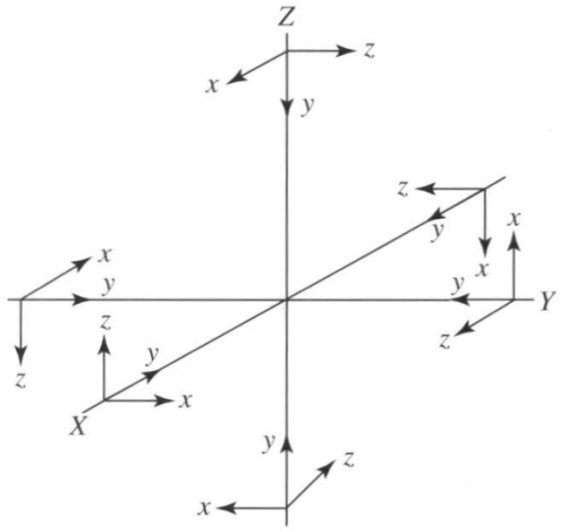
2nd,3rd row/high-valent, high Δ →

Orbital Splitting (Δ_o) and Mean Pairing Energy (Π) for Aqueous Ions[a]

	Ion	Δ_o	Π	*Ion*	Δ_o	Π
d^1				Ti^{3+}	18,800	
d^2				V^{3+}	18,400	
d^3	V^{2+}	12,300		Cr^{3+}	17,400	
d^4	Cr^{2+}	9,250	23,500	Mn^{3+}	15,800	28,000
d^5	Mn^{2+}	7,850[b]	25,500	Fe^{3+}	14,000	30,000
d^6	Fe^{2+}	9,350	17,600	Co^{3+}	16,750	21,000
d^7	Co^{2+}	8,400	22,500	Ni^{3+}		27,000
d^8	Ni^{2+}	8,600				
d^9	Cu^{2+}	7,850				
d^{10}	Zn^{2+}	0				

π bonding in an O_h system

- The ligand field p orbitals are taken as a single set of 12 orbitals in an O_h environment as each set can be converted into every other axis by a symmetry operation, i.e. they are all mutually equivalent.



$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

The axes for the ligand can be chosen in any consistent way. Here the *x* and *y* axes are orthogonal which is appropriate for p symmetry. Opposite ligands are also orthogonal to maintain O_h symmetry

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_π	12	0	0	0	−4	0	0	0	0	0	
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	(d_{xy}, d_{xz}, d_{yz})
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(p_x, p_y, p_z)
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

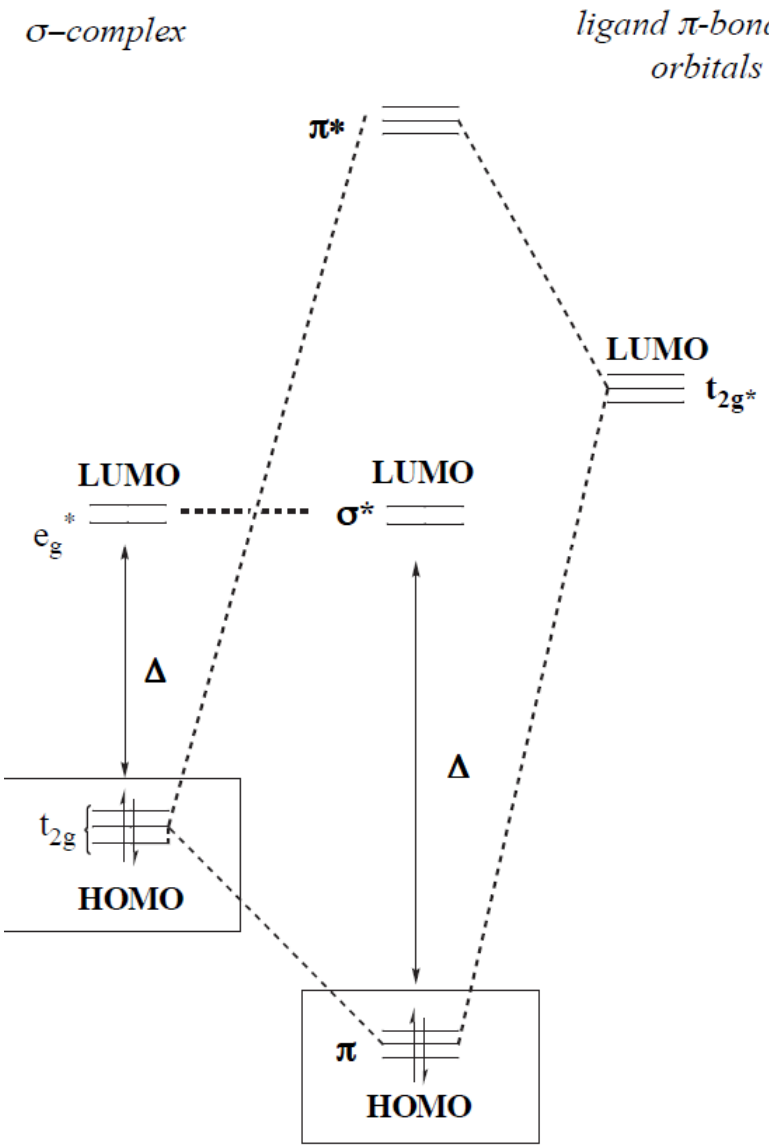
reducible representations of O_h π orbitals

- Of these four representations, the T_{1g} and T_{2u} have no match among the metal orbitals.
- However, the T_{2g} representation matches the dxy, dxz, dyz orbitals, and T_{1u} matches the px, py, pz orbitals of the metal.
- The p orbitals of the metal have more favorable σ bonding interactions with the ligands and will not overlap well with the ligand p orbitals.
- The metal t_{2g} orbitals, which are non-bonding in the σ only O_h bonding picture now participate in π bonding with the T_{2g} ligand orbital distributed over the 6 ligands producing a t_{2g} bonding and corresponding anti-bonding set.
- π bonding with transition metal complexes can occur with either filled or empty p or π^* ligand orbitals labeled π-donor and π-acceptor ligands respectively.

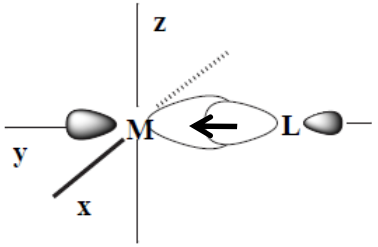
MO description for M→L π-acceptor system in an O_h complex

- In the M→L π-acceptor system empty π* ligand orbitals exist slightly higher in energy than the metal t_{2g} set with which overlap occurs.
- As a result MO's are formed with the bonding orbitals lower in energy than the initial metal t_{2g} set and the anti-bonding orbitals higher in energy than the e_g* σ anti-bonding orbitals.
- This stabilization of the t_{2g} orbitals through π-bonding increases the LFSE Δ_o and increases the bond strength of the M-L bond through an increased bond order.
- This metal to ligand π-donation also known as π-backbonding makes the metal less basic thus stabilizing electron rich, low oxidation state metals, e.g. $Cr(CO)_6$
- M→L π-backbonding represents a unique synergistic bonding situation where the greater the sigma donation to the metal, the greater the π-backbonding to the ligand.

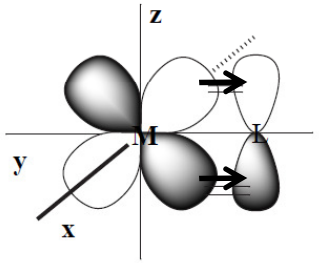
MO description for M→L π-acceptor system in an O_h complex



"synergistic effect"



L → M σ-bonding

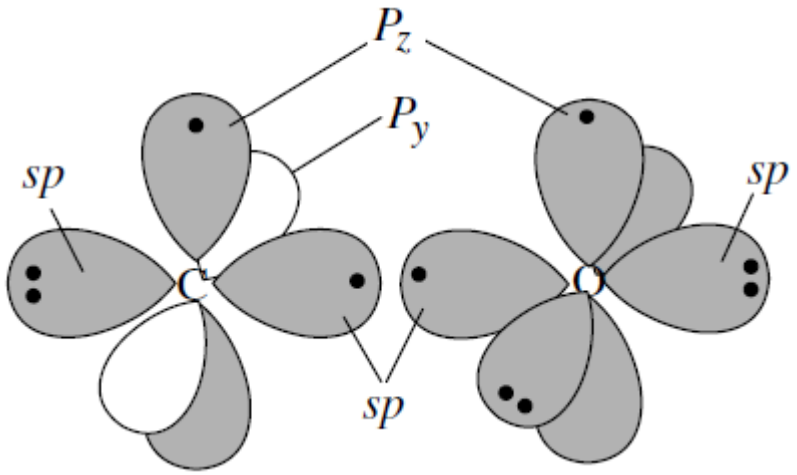


M ⟶ L π-bonding

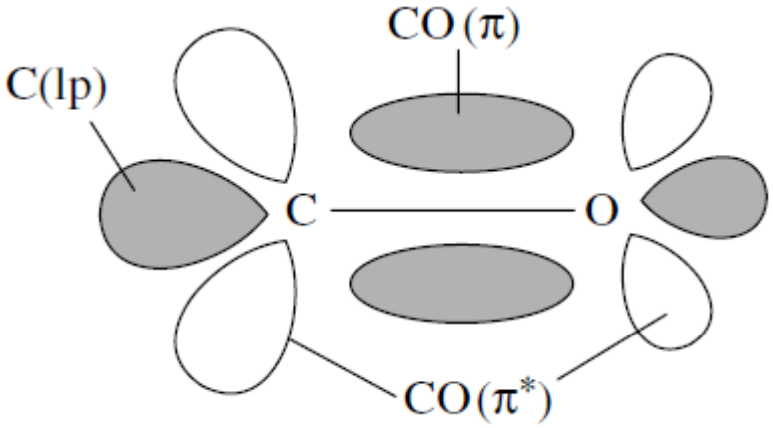
Metal to ligand π-donation (π-backbonding) lowers the energy of the HOMO making the metal <u>less basic</u>. π-backbonding stabilizes electron rich, low oxidation state metals. Very prevalent in late TM complexes.

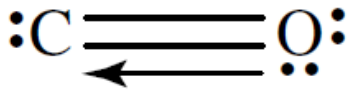
MO description of the CO ligand

- 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.



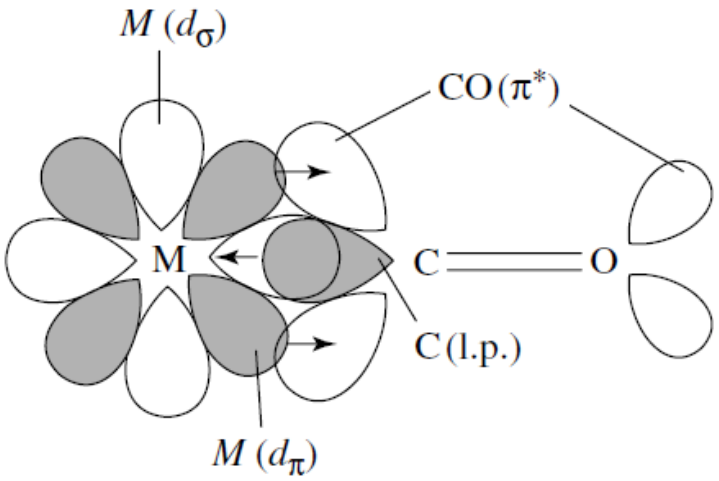


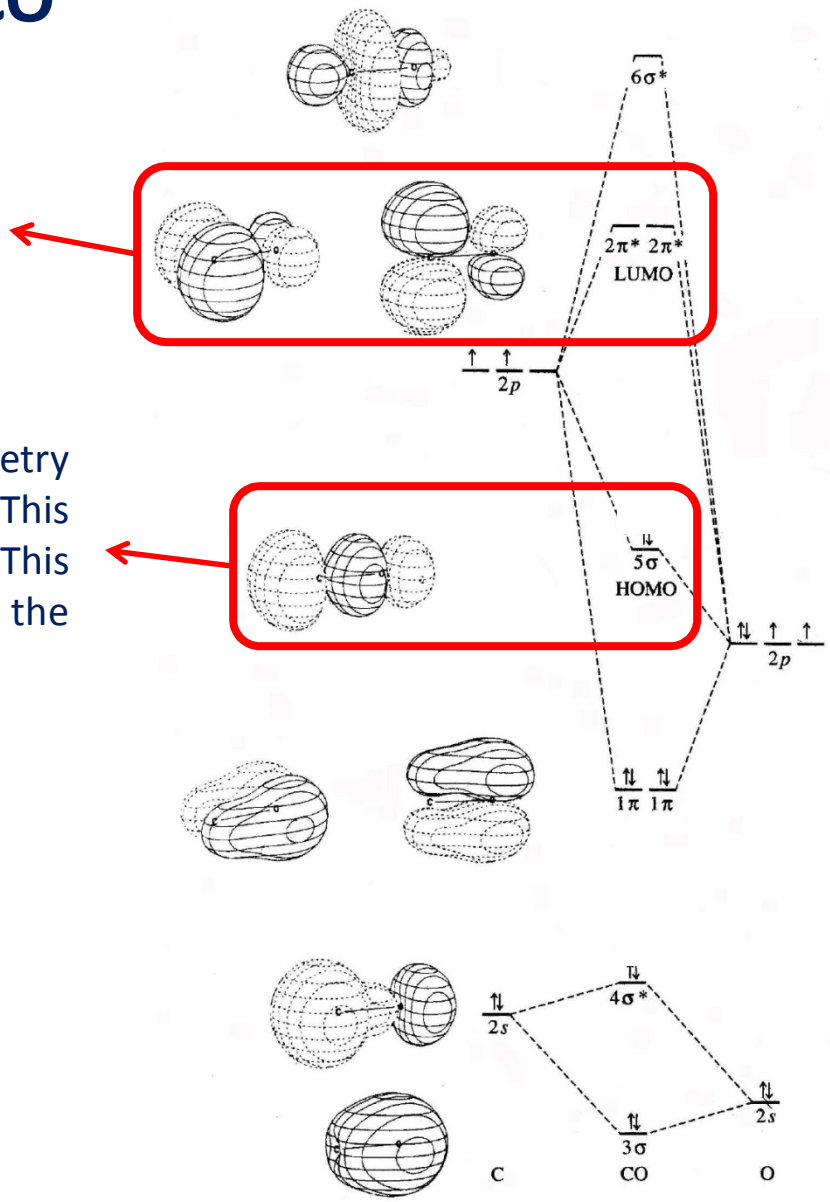
- This transfer leads to a $C^{\delta-}$–$O^{\delta+}$ polarization of the molecule, which is almost exactly canceled out by a partial $C^{\delta+}$–$O^{\delta-}$ polarization of all three bonding orbitals because of the higher electronegativity of oxygen.
- The free CO molecule therefore has a net dipole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

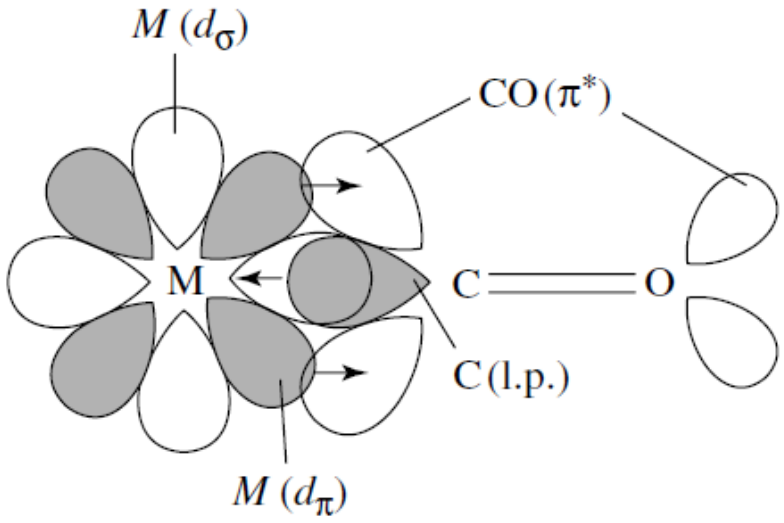
MO correlation diagram for CO

The CO LUMO orbitals are anti bonding of π^* symmetry. These are empty orbitals and accept electron density from the metal centre via π-backbonding with the metal t_{2g} orbitals.

The CO HOMO orbital is a bonding orbital of σ symmetry with significant electron density on the carbon. This orbital forms a σ bond with metal p and e_g orbitals. This is a filled orbital and donates electron density to the metal centre.

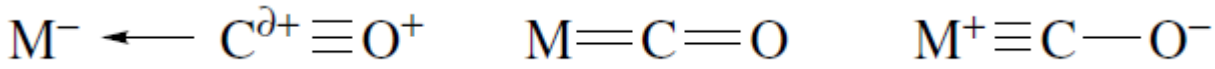






- The metal e_g orbital forms a σ bond with the HOMO orbital of CO.
- As shown on previous slides this HOMO is a σ orbital based on carbon.
- The metal t_{2g} orbitals form a π bond with the CO π^* LUMO (again polarized toward C)
- The metal HOMO, the filled M dπ orbital, back donates to the CO LUMO 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 LnM(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^-.

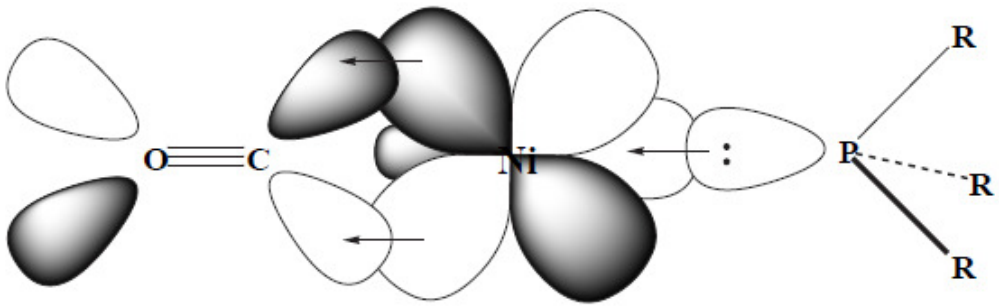


- The range can be represented in valence bond terms the extreme in which CO acts as a pure σ donor, through to the extreme in which both the π^*_x and π^*_y are both fully engaged in back bonding.

Phosphorus Ligand (L)	CO ν, cm^{-1}
$P(t\text{-}Bu)_3$	2056
PCy_3	
$P(i\text{-}Pr)_3$	2059
$P(NMe_2)_3$	2062
PMe_3	2064
$PPhMe_2$	2065
PBz_3	2066
PPh_2Me	2067
PPh_3	2069
$PPh_2(OEt)$	2072
$P(p\text{-}C_6H_4Cl)_3$	2073
$PPh(OEt)_2$	2074
$P(OEt)_3$	2077
PH_3	2083
PCl_3	2097
PF_3	2111

CO stretching frequencies measured for $Ni(CO)_3L$ where L are PR_3 ligands of different σ-donor abilities. [ν(CO) =2143 cm^{-1}]

Tolman *Chem. Rev. 1977 (77) 313*



The increase in electron density at the nickel from PR_3 σ-donation is dispersed through the M-L π system *via π-backbonding. Much of the electron* density is passed onto the CO π* and is reflected in decreased ν(CO) stretching frequencies which corresponds to weaker CO bonds.

$$\nu = \frac{1}{2\pi c}\left[\frac{f}{(M_x M_y)/(M_x+M_y)}\right]^{1/2}$$

Recall: Band position in IR is governed by :
1. force constant of the bond (*f) and*
2. individual masses of the atoms (M_x and M_y).

Stronger bonds have larger force constants than weaker bonds.

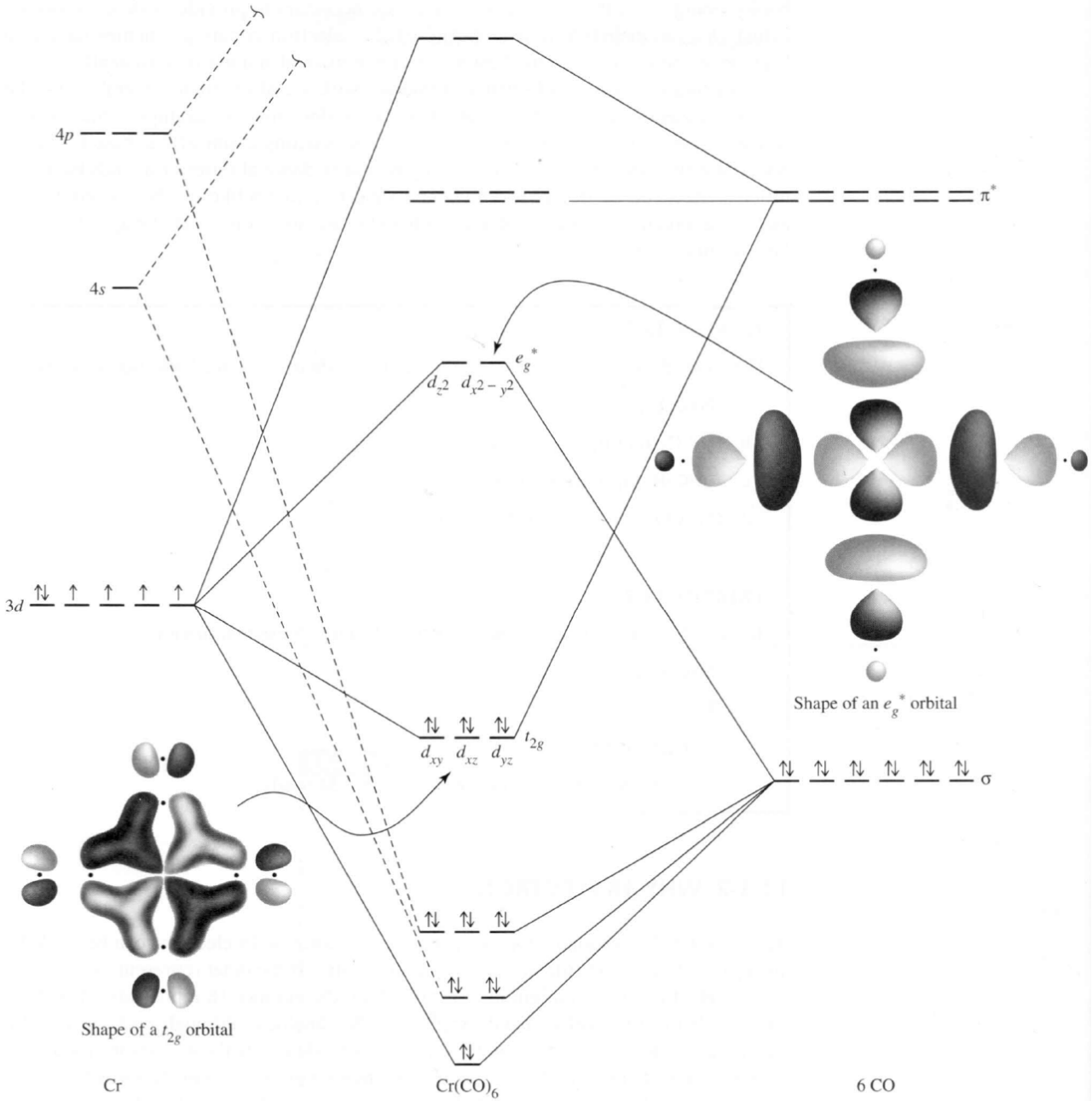
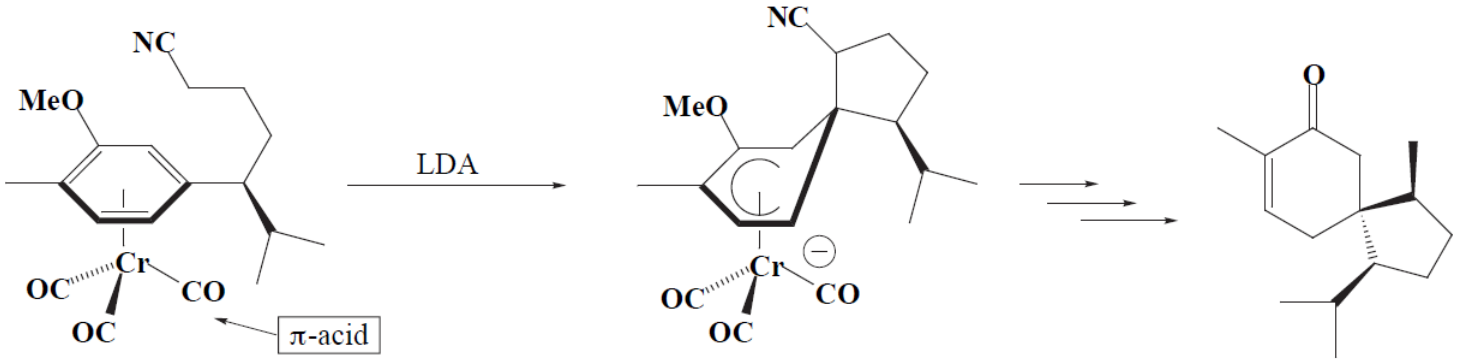


FIGURE 13-8 Molecular Orbital Energy Levels of $Cr(CO)_6$. (Adapted with permission from G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, pp. 53–54, Figs. 3-2 and 3-3.)

π-acceptor effects on reactivity

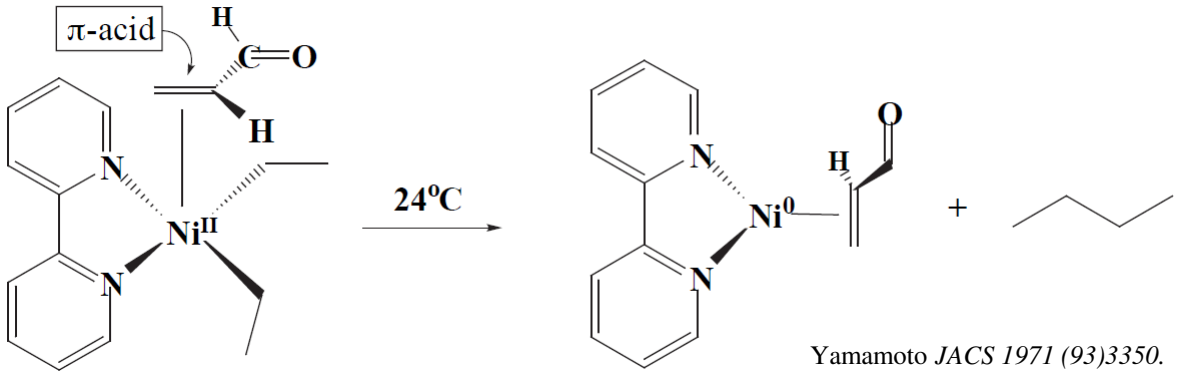


Cr(0), d^6, $18e^-$

(±)-Acorenone B

Semmelhack *JACS 1980 (102) 5926*

CO's render the electron rich Cr metal electrophilic via strong π-backbonding. Complexation of benzene with the electrophilic Cr(CO)3 fragment withdraws electon density from the aromatic ring activating it towards nucleophilic attack.



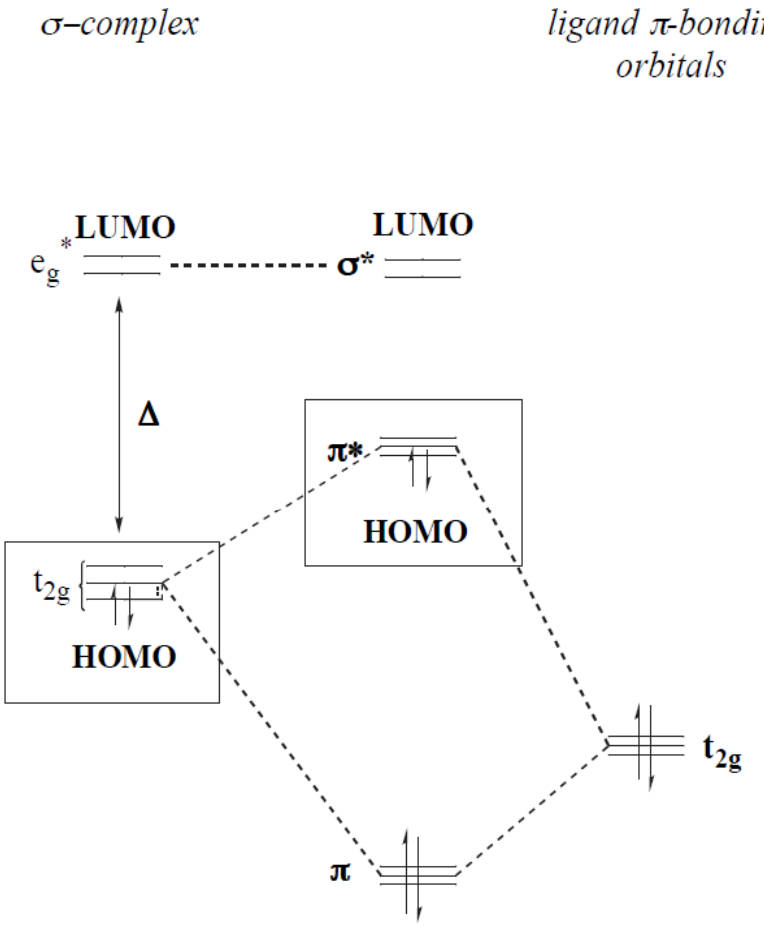
Yamamoto *JACS 1971 (93)3350.*

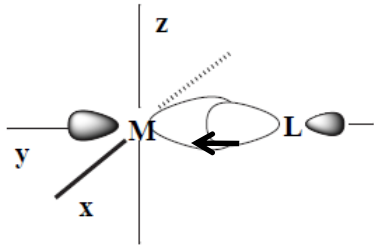
Acrolein is thought to act as a π-acid, withdrawing electron density from the Ni(II) complex via π-backbonding and promoting elimination of the diethyl fragment to reduce the metal.

MO description for L→M π-donor system in an O_h complex

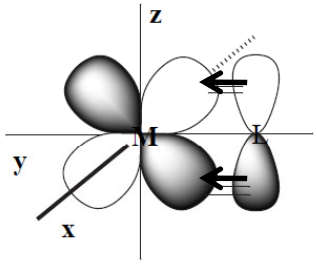
- In the L→M π-donor system filled p ligand orbitals exist slightly lower in energy than the metal t_{2g} set with which overlap occurs.
- The bonding t_{2g} MO's formed are again lower in energy than the initial metal t_{2g} set, however, the corresponding t_{2g}* anti-bonding MO's are lower in energy than the e_g* σ anti-bonding orbitals.
- Additionally, as the ligand t_{2g} p orbitals are initially filled and of lower energy than the metal t_{2g} set, the bonding t_{2g} MO's formed are filled by the ligand electrons, with the metal d electrons occuppying the corresponding t_{2g}* anti-bonding MO's .
- Thus the LFSE Δ_o is decreased. The t_{2g} bonding MO's are stabilized which is countered by occupation of the t_{2g}* anti-bonding orbitals.
- Overall this combined σ and p donation from ligand to metal results in an increased M-L bond order and a stronger bond, however, the metal now becomes more electron rich which can decrease the bond strengths of the remaining ligand set making ligand-metal π bonding a less favorable interaction.

MO description for L→M π-donor system in an O_h complex





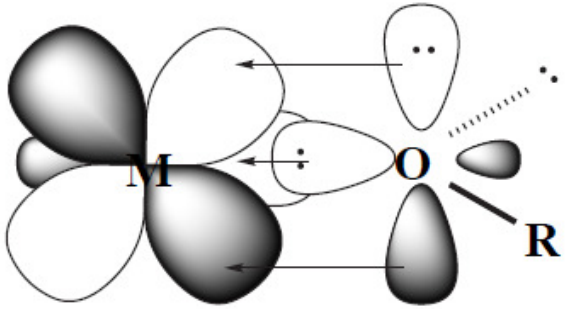
L → M σ-bonding



L → M π-bonding

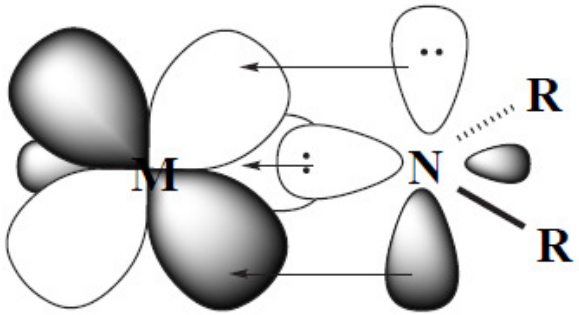
The energy of the HOMO is directly affected by M-L π-bonding. Ligand to metal π-donation increases the energy of the HOMO making the metal <u>more basic</u>. π-donor ligands stabilize electron poor, high oxidation state metals. Very prevalent for early TM complexes (low d electron count) and less so for late TM (high d electron count).

Alkoxides



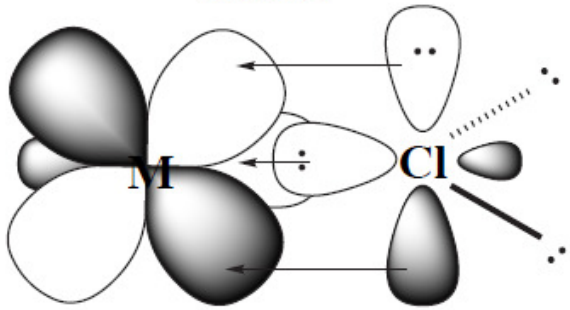
σ-bonding: L_{sp2} -> Md_{σ}
π-donation: Lp -> Md_{π}

1˚, 2˚ Amides



σ-bonding: L_{sp2} -> Md_{σ}
π-donation: Lp -> Md_{π}

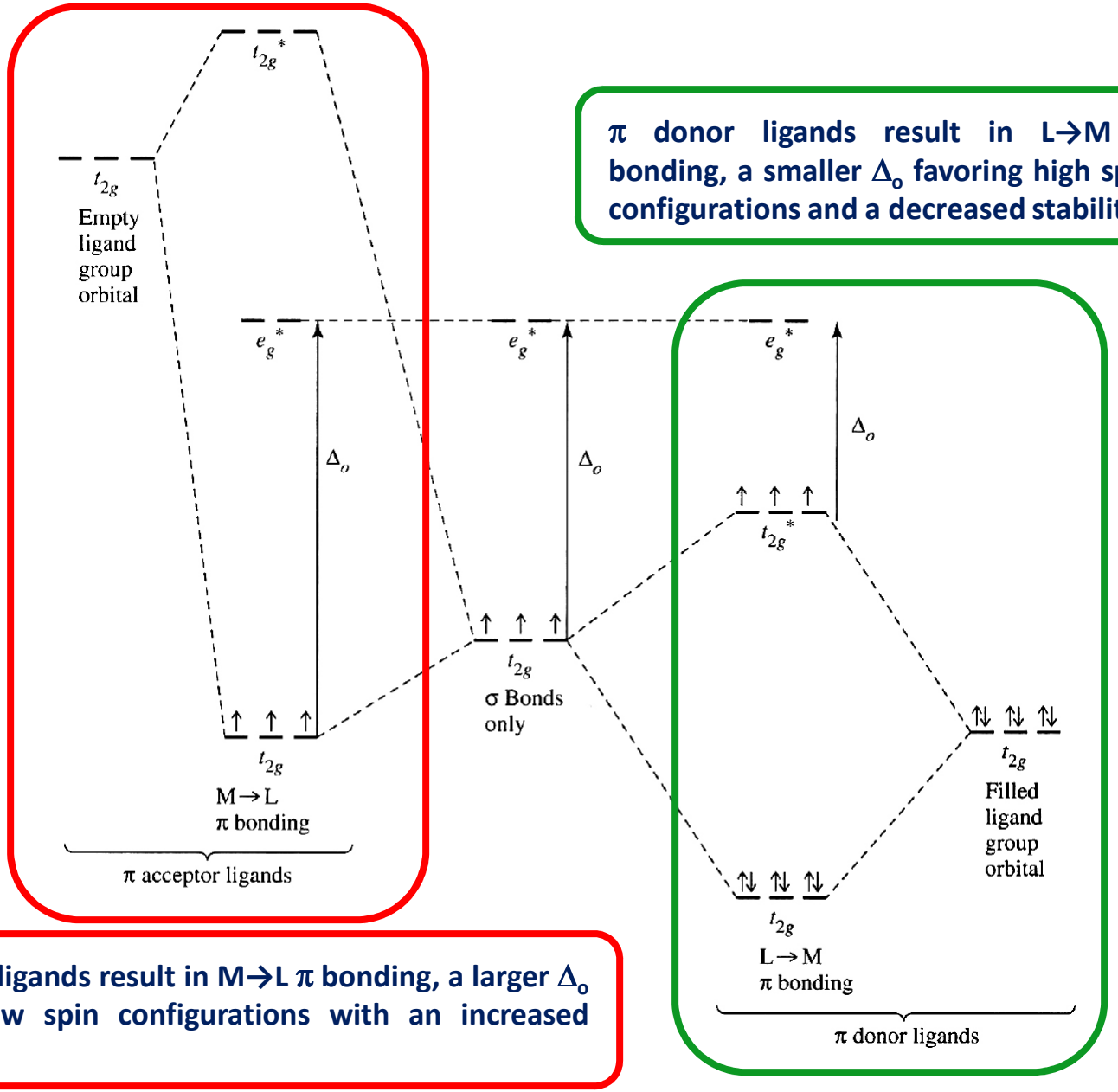
Halides



or I^-, Br^-, F^-

σ-bonding: L_{sp2} -> Md_{σ}
π-donation: Lp -> Md_{π}

Summary of π-bonding in a O_h complexes



π donor ligands result in L→M π bonding, a smaller Δ_o favoring high spin configurations and a decreased stability.

π acceptor ligands result in M→L π bonding, a larger Δ_o favoring low spin configurations with an increased stability.

MO description of σ only bonding in a square planar D_{4h} transition metal complex

- Square planar complexes are of D_{4h} symmetry, i.e. of lower symmetry than O_h.
- The reducible representations of ligand σ bonding orbitals results in the representations A_{1g}, E_u and B_{1g}
- Through symmetry considerations the metals orbitals have the representations A_{1g}, E_g , B_{1g} and B_{2g} for the d set and E_u and A_{2u} for the p set. The *s* orbital remains A_{1g}.
- Bonding and corresponding anti-bonding MO's are thus formed from matching the four metal a_{1g}, e_u , b_{1g} d orbitals and the two e_u metal p orbitals with the ligand set.
- The metal a_{1g} only has a minor contribution to ligand bonding ($x^2 + y^2$ component).
- The e_g and b_{2g} metal d orbitals and the metal a_{2u} remain non-bonding.
- Eight electrons provided by the ligands fill the lowest three levels of MO's (a_{1g}, e_u and b_{1g})
- Metal d electrons result in an equivalent filling of the b_{2g} and e_g non-bonding MO's and if necessary the a_{1g}* anti-bonding MO's.
- High spin ground states are generally not observed (even with a small Δ) as this geometry is mostly favored by complexes of d^0 and d^8 electronic configurations.

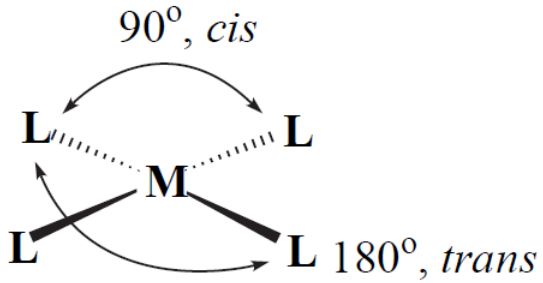
TABLE 10-9
Representations and Orbital Symmetry for Square-Planar Complexes

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1		1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1		1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1		1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1		1	−1	1	−1	1		xy
E_g	2	0	−2	0		2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1		−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1		−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1		−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1		−1	1	−1	1	−1		
E_u	2	0	−2	0		−2	0	2	0	0	(x, y)	

$$\Gamma_{p_y} = A_{1g} + B_{1g} + E_u$$

(σ) Matching orbitals on the central atom:

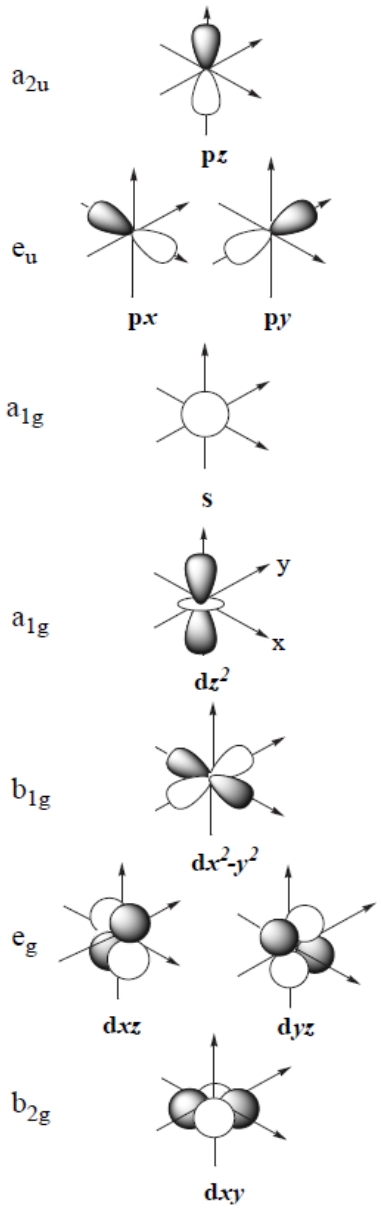
$s, d_{z^2}, d_{x^2-y^2}, (p_x, p_y)$

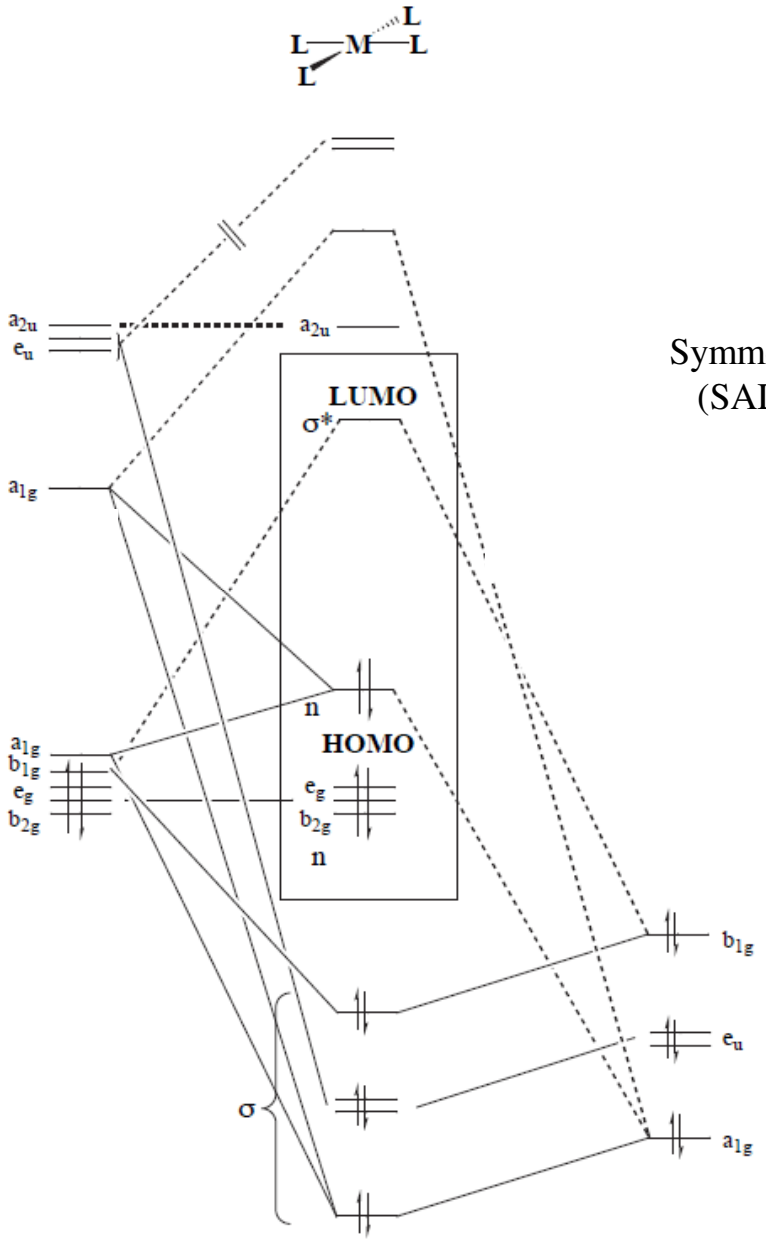


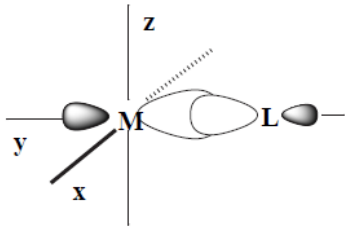
square planar

MO description of σ only bonding in a square planar D_{4h} transition metal complex

Metal valence orbitals

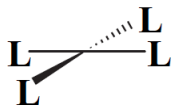


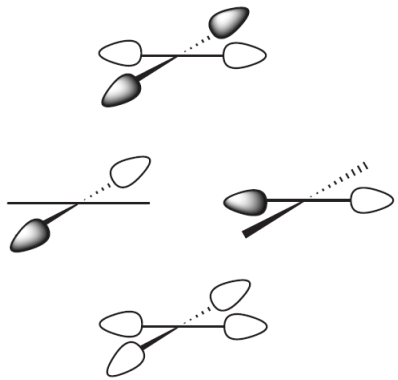




σ-bonding

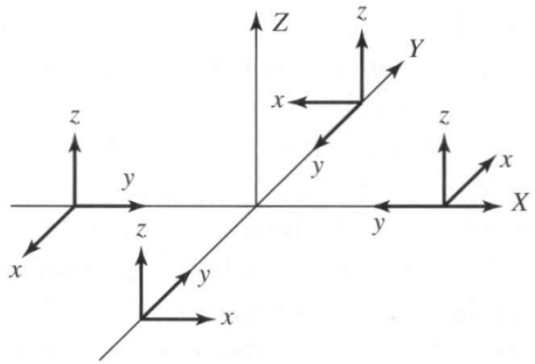
Symmetry adapted linear combinations (SALCs) of ligand bonding orbitals

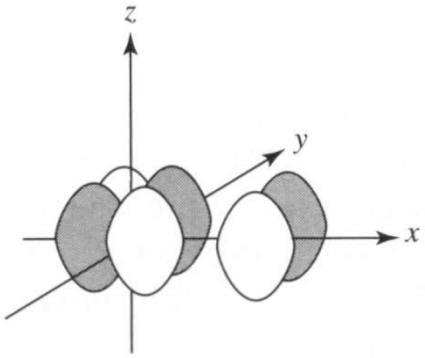




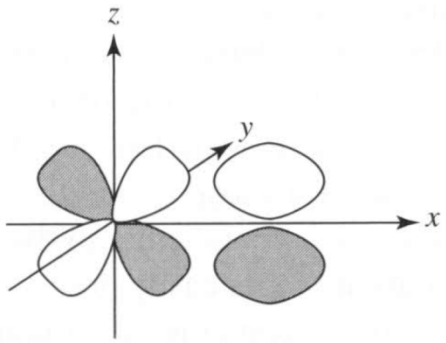
π bonding in square planar D_{4h} transition metal complexes

- There are two distinctly different sets of potential p bonding orbitals
  - The parallel set
    ($\pi_{\parallel}$ *or* p_x in the molecular plane)
  - The perpendicular set
    ($\pi_{\perp}$ *or* p_z perpendicular to the plane)

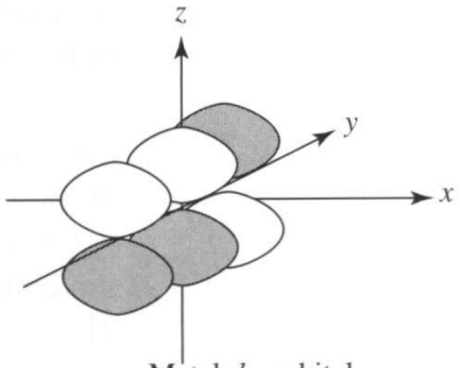




Metal d_{xy} orbital
ligand p_x orbital



Metal d_{xz} orbital
ligand p_z orbital



Metal d_{yz} orbital
ligand p_z orbital

- The b_{2g} (metal d*xy* orbital) interacts with the p_x ($\pi_{\parallel}$) ligand orbitals
- The e_g (metal d*xz* and d*yz* orbitals) interact with the p_z ($\pi_{\perp}$) ligand orbitals

TABLE 10-9
Representations and Orbital Symmetry for Square-Planar Complexes

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1		1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1		1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1		1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1		1	−1	1	−1	1		xy
E_g	2	0	−2	0		2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1		−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1		−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1		−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1		−1	1	−1	1	−1		
E_u	2	0	−2	0		−2	0	2	0	0	(x, y)	

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ_{p_x}	4	0	0	−2		0	0	4	−2	0	$p_\parallel$
Γ_{p_y}	4	0	0	2		0	0	4	2	0	p_σ
Γ_{p_z}	4	0	0	−2		0	0	−4	2	0	$p_\perp$

$\Gamma_{p_y} = A_{1g} + B_{1g} + E_u$

(σ) Matching orbitals on the central atom:

$s, d_{z^2}, d_{x^2-y^2}, (p_x, p_y)$

$\Gamma_{p_x} = A_{2g} + B_{2g} + E_u$

($\parallel$) Matching orbitals on the central atom:

$d_{xy}, (p_x, p_y)$

$\Gamma_{p_z} = A_{2u} + B_{2u} + E_g$

($\perp$) Matching orbitals on the central atom:

$p_z, (d_{xz}, d_{yz})$

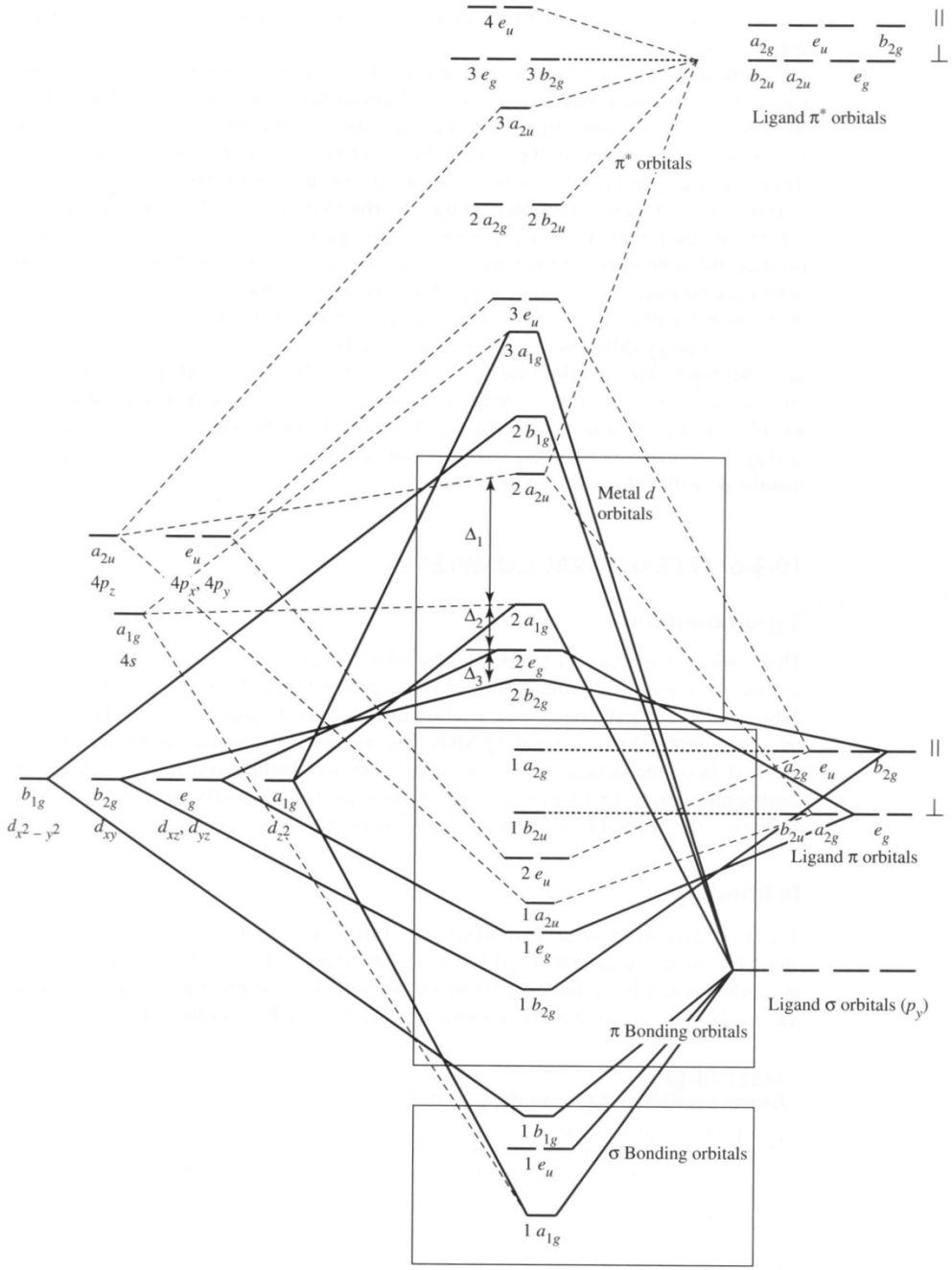


FIGURE 10-15 D_{4h} Molecular Orbitals, Including π Orbitals. Interactions with metal d orbitals are indicated by solid lines, interactions with metal s and p orbitals by dashed lines, and nonbonding orbitals by dotted lines.

- The lowest energy set contains the bonding orbitals, as in the simpler σ only diagram.
- The next higher set consists of the eight π donor orbitals of the ligand.
- Their interaction with the metal orbitals is small and has the effect of decreasing the energy difference between the orbitals of the next higher set.
- The third set of MO's is primarily metal d orbitals, modified by interaction with the ligand orbitals.
- The b_{2g} , e_g and a_{1g} orbitals are all low and have small differences in energy whereas the b_{1g} orbital has a much higher energy.
- Eight electrons from the ligands form the σ bonds and the next sixteen π electrons can either π bond or remain essentially non-bonding, and the remaining electrons from the metal occupy the third set.

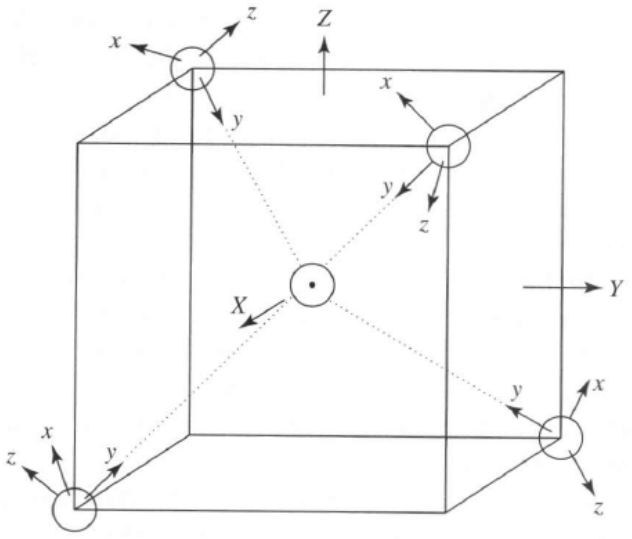
MO description of σ only bonding in a T_d transition metal complex

- The σ bonding orbitals for tetrahedral (T_d) complexes are easily determined on the basis of symmetry.
- The reducible representation of ligand bonding orbitals includes A_1 and T_2 allowing for a total of four bonding MO's.
- The energy level picture for the T_d d orbitals is inverted wrt the O_h picture, also the LFSE is now called Δ_t and is typically smaller than Δ_o .

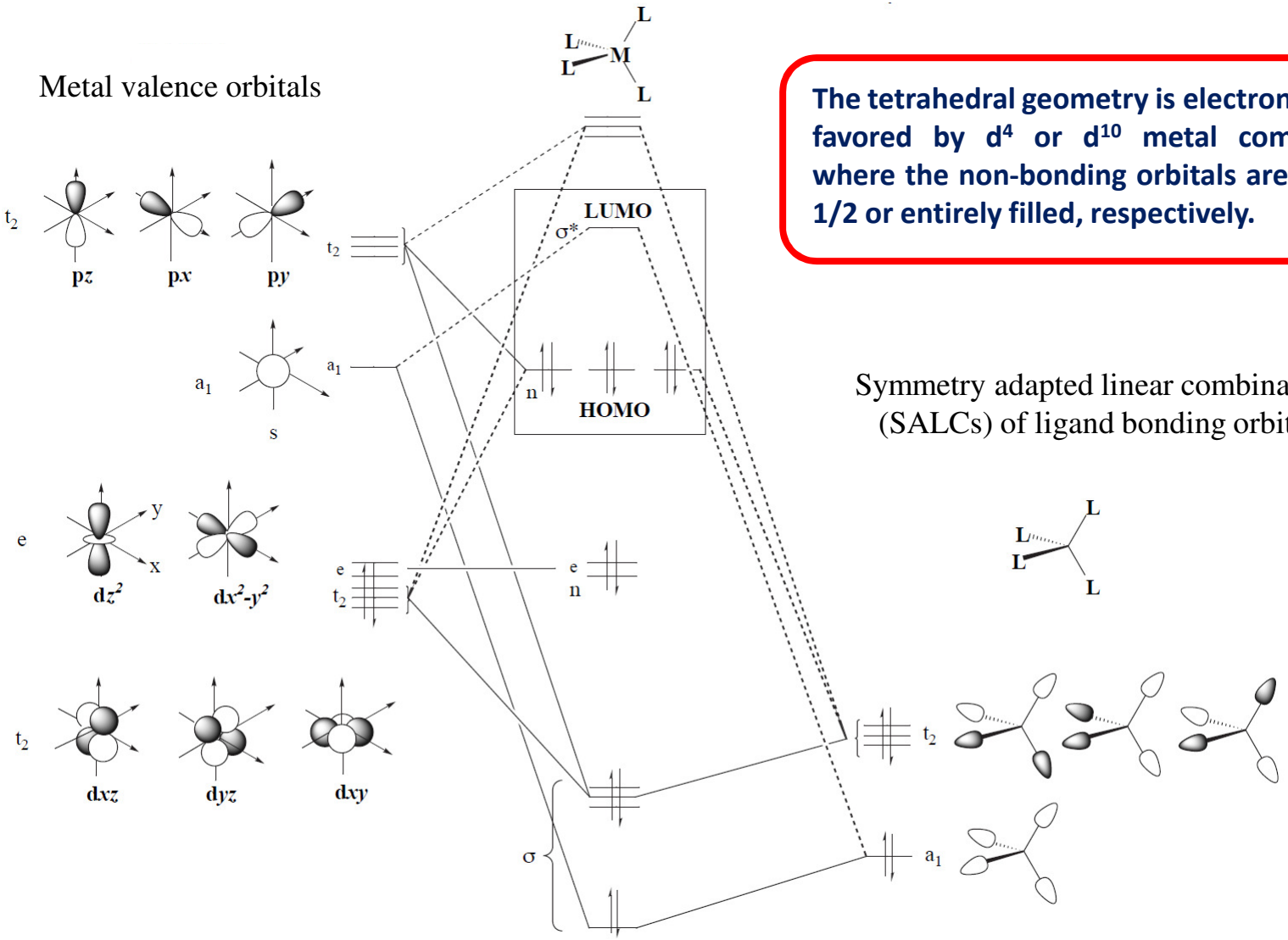
σ only

Metal $\Gamma = A_1 + E + T_2$

Ligand $\Gamma = A_1 + T_2$



MO description of σ only bonding in a T_d transition metal complex



The tetrahedral geometry is electronically favored by d^4 or d^{10} metal complexes where the non-bonding orbitals are either 1/2 or entirely filled, respectively.

π bonding in T_d transition metal complexes

- The π bonding orbitals for tetrahedral (T_d) complexes are more difficult to visualize.
- The reducible representation of π bonding ligand orbitals includes A_1 , T_1 , T_2 and *E.*
- T_1 has no matching metal orbitals, *E* matches dz^2 and dx^2-y^2, and T_2 matches dxy, dxz, and dyz metal orbitals.
- The *E* and T_2 interactions lower the energy of the bonding orbitals, and raise the corresponding anti-bonding orbitals, for a net increase in Δ_t .

TABLE 10-10
Representations of Tetrahedral Orbitals

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1			$x^2 + y^2 + z^2$
A_2	1	−1	1	−1			
E	2	−1	2	0			$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1		(R_x, R_y, R_z)	
T_2	3	0	−1	−1		(x, y, z)	(xy, yz, xz)
Γ_σ	4	1	0	0		$A_1 + T_2$	
Γ_π	8	−1	0	0		$E + T_1 + T_2$	

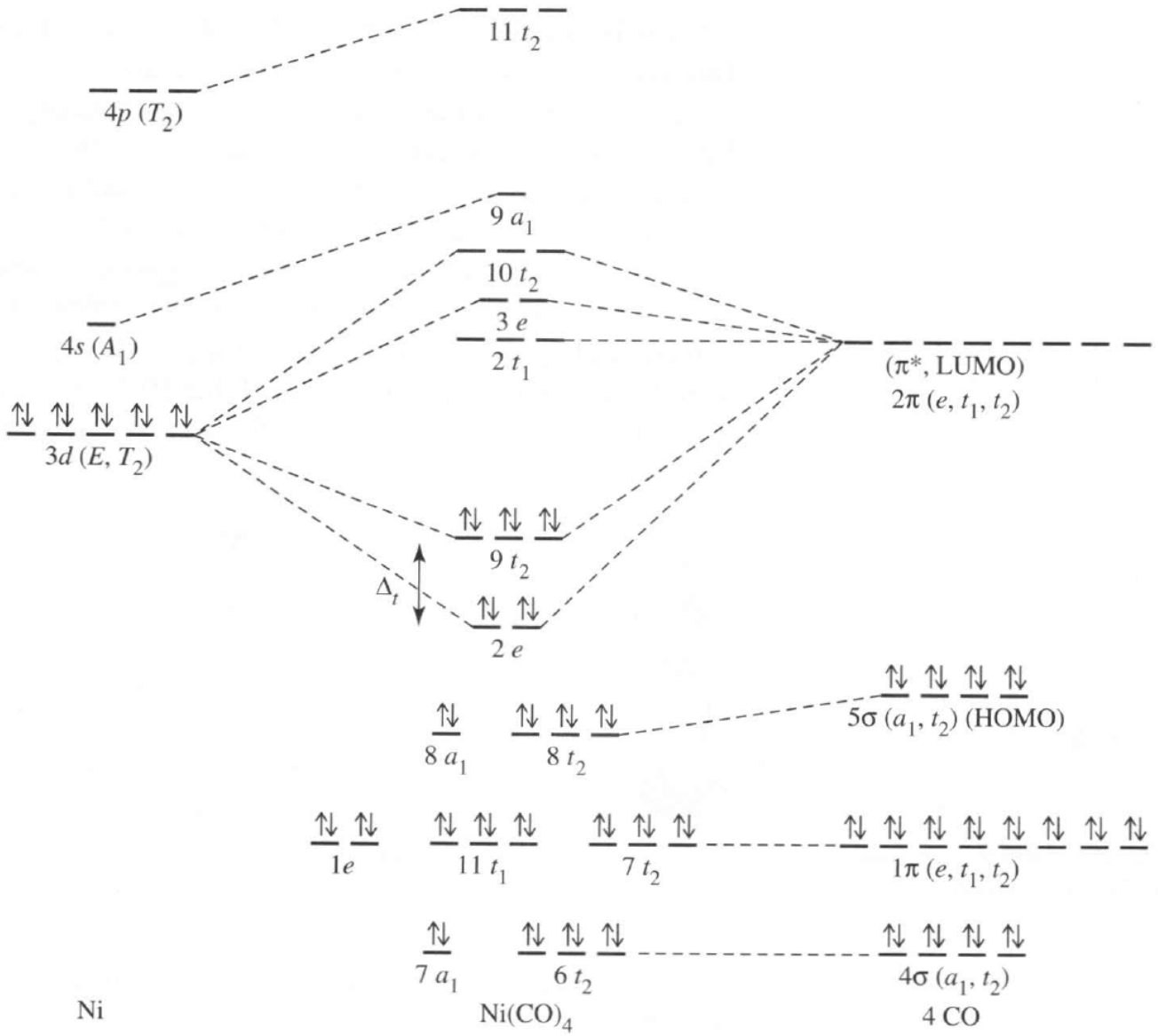


FIGURE 10-18 Molecular Orbitals for Tetrahedral $Ni(CO)_4$. C. W. Bauschlicher, Jr., and P. S. Bagus, *J. Chem. Phys.*, **1984**, *81*, 5889, argue that there is almost no σ bonding from the 4*s* and 4*p* orbitals of Ni, and that the d^{10} configuration is the best starting place for the calculations, as shown here. G. Cooper, K. H. Sze, and C. E. Brion, *J. Am. Chem. Soc.*, **1989**, *111*, 5051, include the metal 4*s* as a significant part of σ bonding, but with essentially the same net result in molecular orbitals.

- For Ni(CO)4 the interactions of the CO σ and π ligand orbitals with the metal orbitals are probably small.
- Much of the bonding is from M→L p bonding.
- In cases in which the d orbitals are not fully occupied, s bonding is likely to be more important, with resulting shifts of the a_1 and t_2 orbitals to lower energy and the 4s and 4p orbitals to higher energies.