

MD-Modell/-Theorie

$$\nabla B: (n-1)d \quad n \leftarrow n-p$$



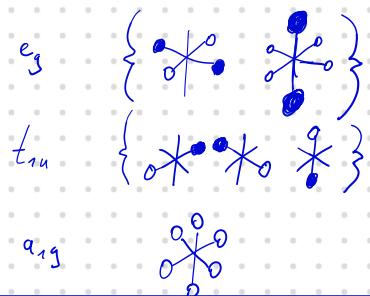
CF -- eg
 -- -- t

Molecular orbital energy level diagram:

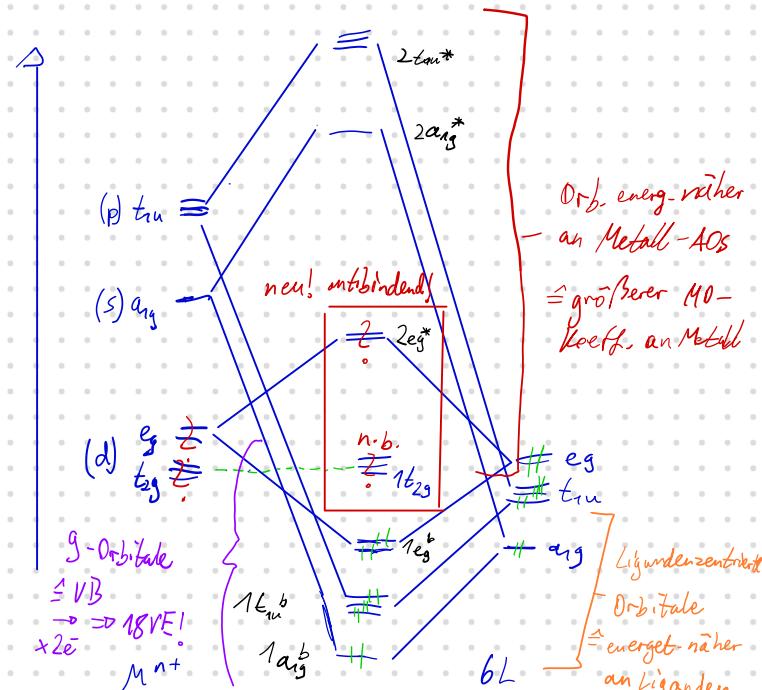
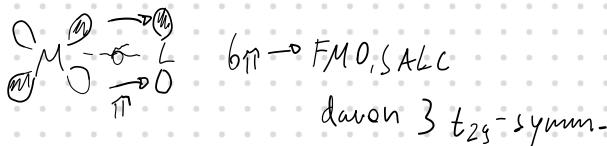
- Vertical axis:** MO.. (Molecular Orbital) at the top, and M^{n+} (Metal cation) at the bottom.
- Orbitals:**
 - n p:** A horizontal row of three boxes.
 - ns:** A single box.
 - (n-1)d:** A horizontal row of five boxes.
 - Empty boxes:** Three boxes above the ns orbital, and two sets of three boxes below the M^{n+} label.
- Curved arrows:** Indicate electron movement from the $n p$, ns, and $(n-1)d$ orbitals into the empty boxes.

Sei: $M_{L_6} - 6L$ je 1 σ -Orbital

- SALC-Fragment MOs: (symmetrieadaptierte Linear kombinationen)



$\text{M}-\text{Wh Lig} \longleftrightarrow \text{M}$



- bindende Orbitale müssen besetzt sein
 $6 \times 2 e^- = 12 e^-$

- nicht bindende Mo₅ können besetzt sein?

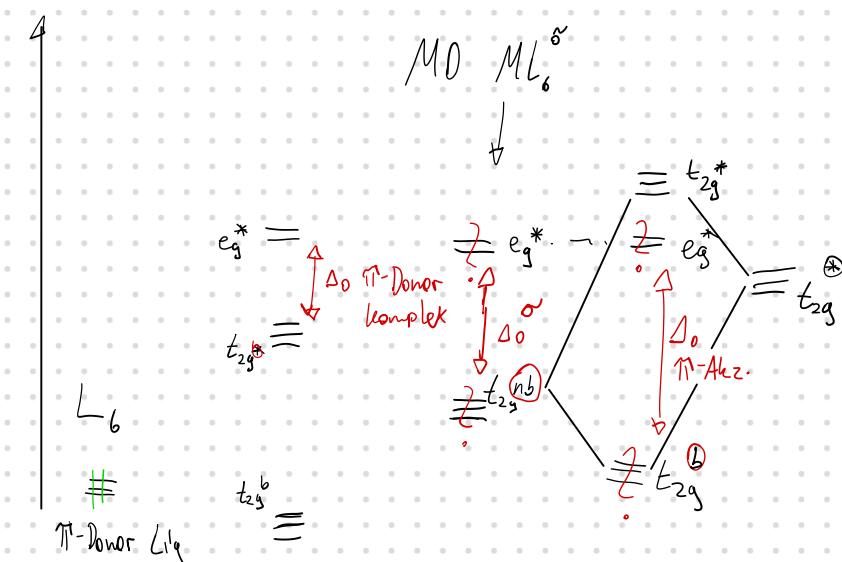
$$h_{\text{ter}} t_{\text{nb}} = 12 + 3 + 2 = 18 \text{ VE}$$

bei Organometall-Komplexen - t_{2g} (b)

bei klass. Komplexen t_{2g}^{nb} oder t_{2g}^* \Rightarrow 12-22 VE

- stark antibindende MOs leer

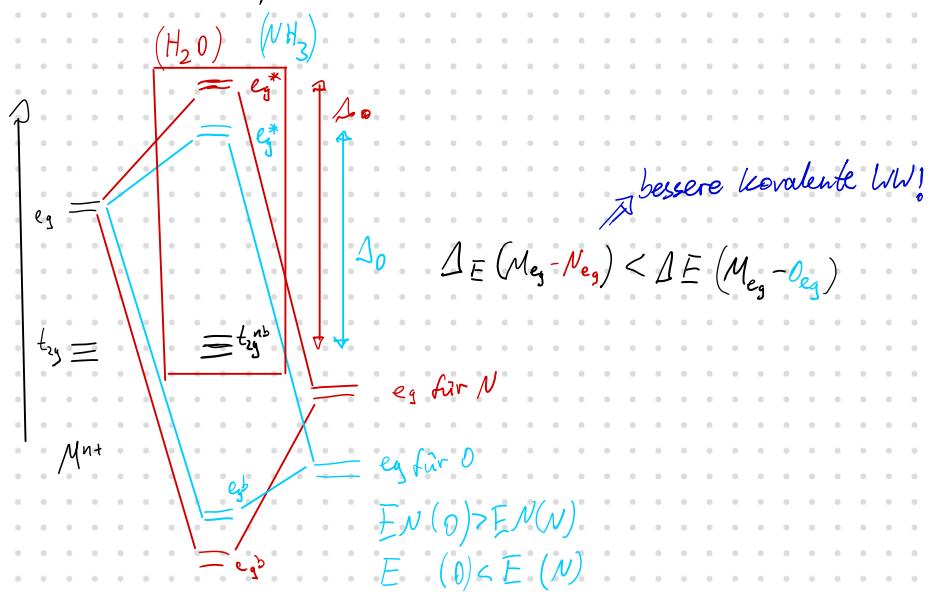
$$2a_{1g}^*, 2t_{1u}^*$$



- energet. Unterschiede $\Delta_\text{o}(\pi\text{-Donor}) < \Delta_\text{o}(\sigma\text{-Komplex}) < \Delta_\text{o}(\pi\text{-Akzeptor})$

spektrochem. Reihe

Vgl. für O, N-Donoren - reine δ
 $O < N$



π -WW

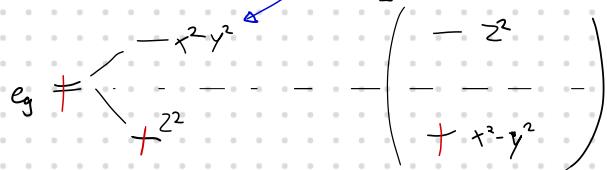
π -Donoren

Δ_o π -Donoren - klein \leftrightarrow (Vgl. Δ_o^δ) \leftrightarrow $\Delta_o^{\pi\text{-Akz}} - \text{groß}$
 ↓
 schwache Lig
 $\text{Hal} < S < O < N < P \lesssim C < NO^+$

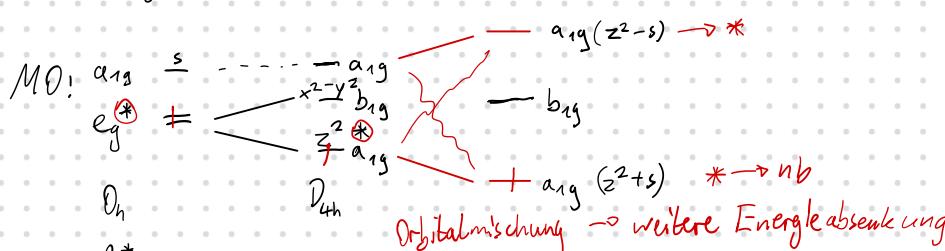
π -Akz.
 oder sehr starke δ -Donoren
 $Bsp.: HO, CH_3, SCN$
 nur geringe EN , $\Delta EN (M-L)$
 \Rightarrow hoch liegende δ -Orbitale
 \hookrightarrow sehr gute kov.-LW!
 \Rightarrow große $t_{2g}^{nb} - e_g^*$ -Aufspaltung

Jahn-Teller:

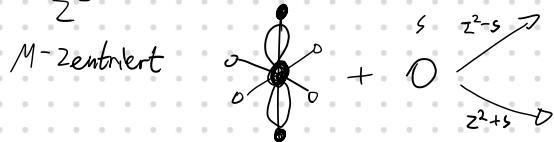
d^4 -hs, d^7 -hs, d^9 - Streckung! (Spannung)



$O_h \rightarrow D_{4h}$
 Tetragonale BiPy



M -zentriert

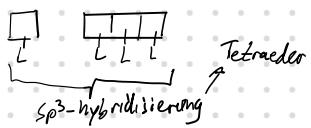


\rightarrow stärkere antibind. LW zu z -Ligand \Rightarrow Entfernung (Streckung vorteilhaft)
 \rightarrow antibind. LW z^2-x, y -Liganden $\Rightarrow M-L_{eq}$ wird kleiner

$-x^2-y^2 - b_{1g}$ kein Mixen mit M -Orbitalen

d¹⁰-Konfiguration:

$$VB : \boxed{1L \mid 1L \mid 1L \mid 1L \mid 1R}$$



$\text{CF}! \neq \text{eg}$

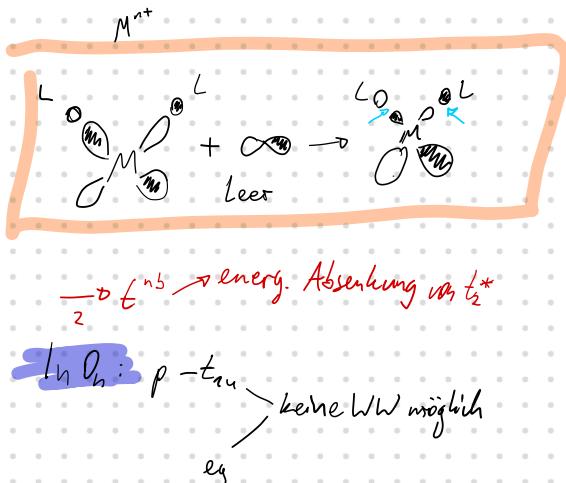
$$\text{CFSE} \neq 0$$

~~≠~~ eq

~~t_{2y}~~
D_k

MO:

$\overline{T_d}$



Stabilität bei Komplexen

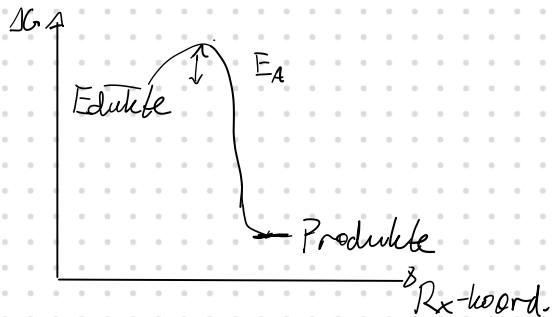
- thermodynamisch

SG, JH, AS

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln K$$

$$\Delta G = -z \bar{F} \Delta E$$



-kinetic} ch

$$E_4(E^*, E^\neq)$$

$$t_{1/2} = A \cdot e^{-\frac{E_A}{RT}}$$

-E_a-groß-kinet. stabil \equiv inert, metastabil

$E_A - h \text{ kinh} - h \text{ kinet}$. instabil \equiv labil