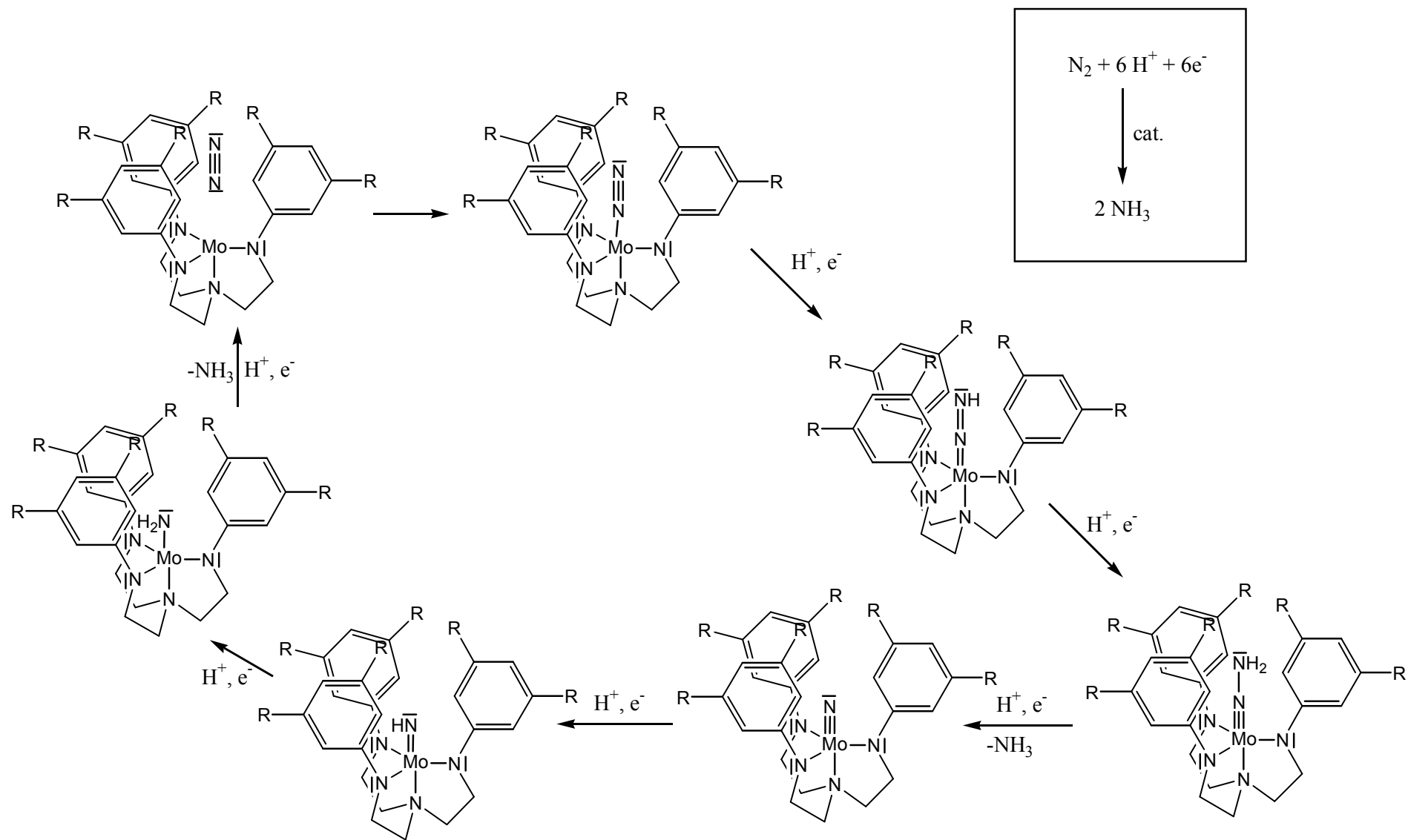
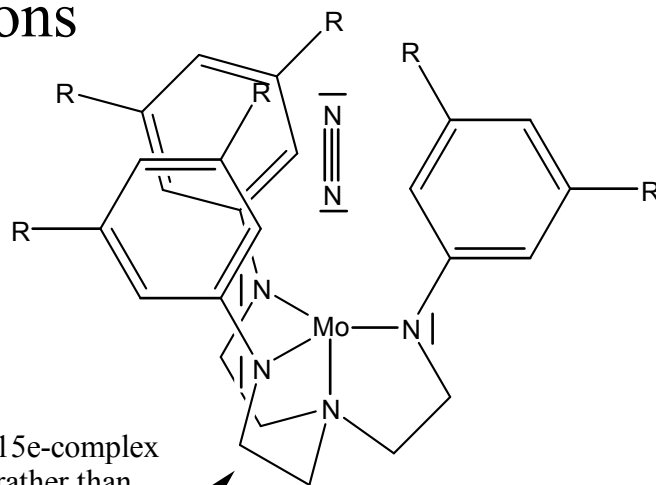


Steric restrictions

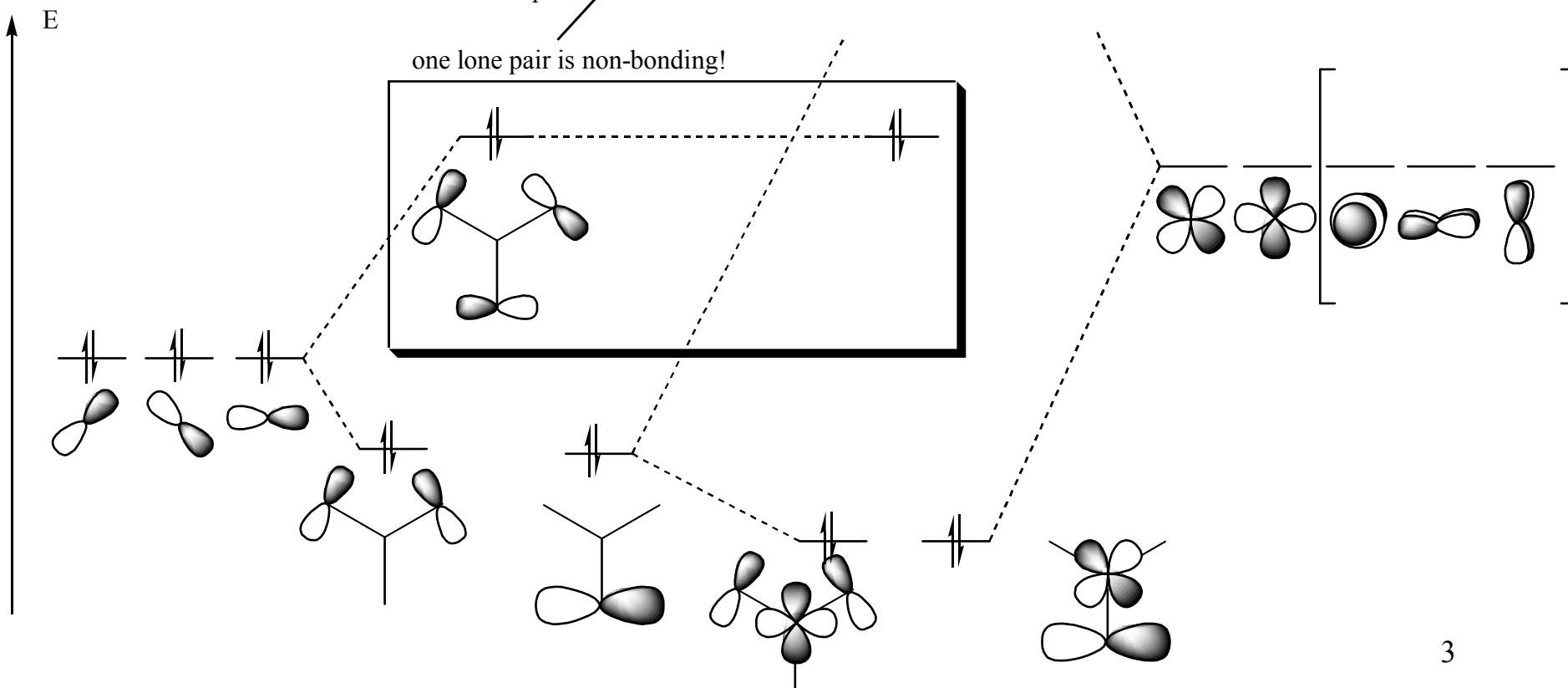
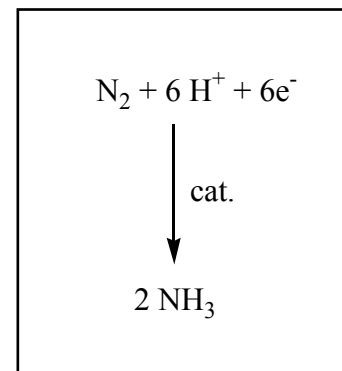


Symmetric restrictions

1.

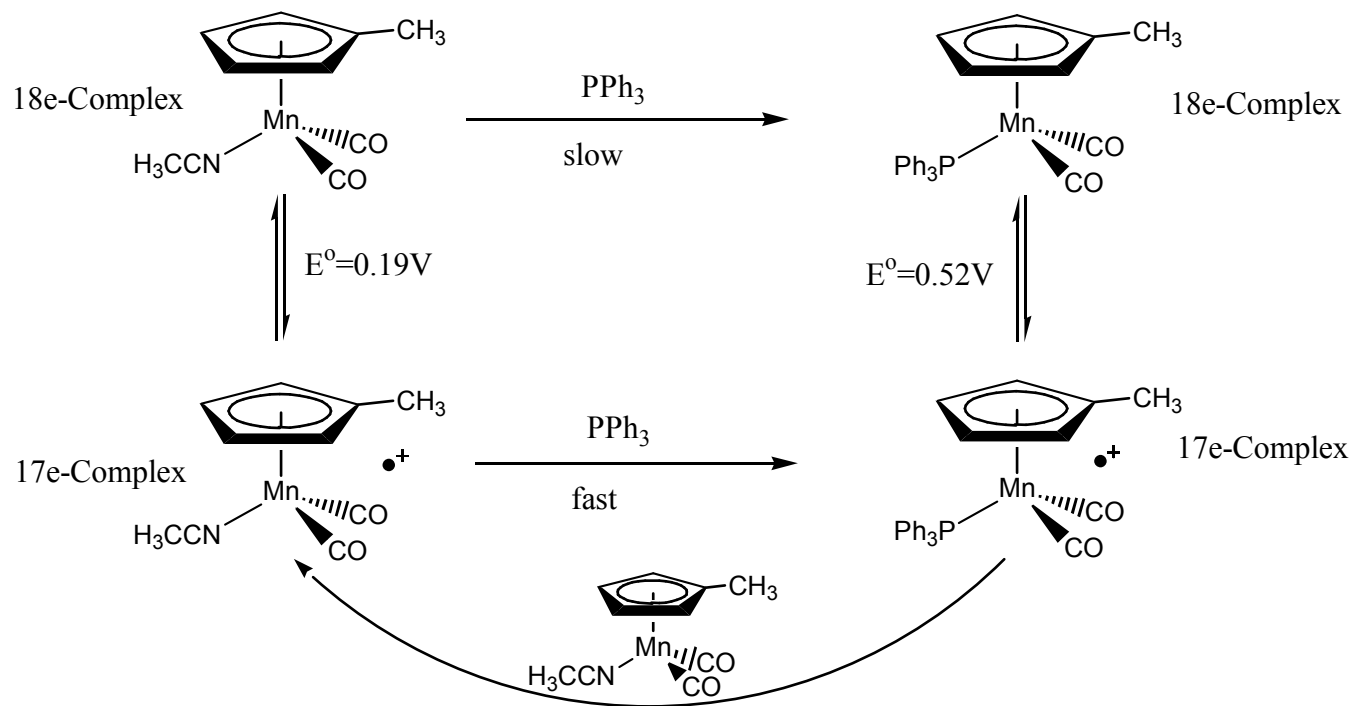


15e-complex
rather than
17e-complex



Electron-transfer-Catalysis

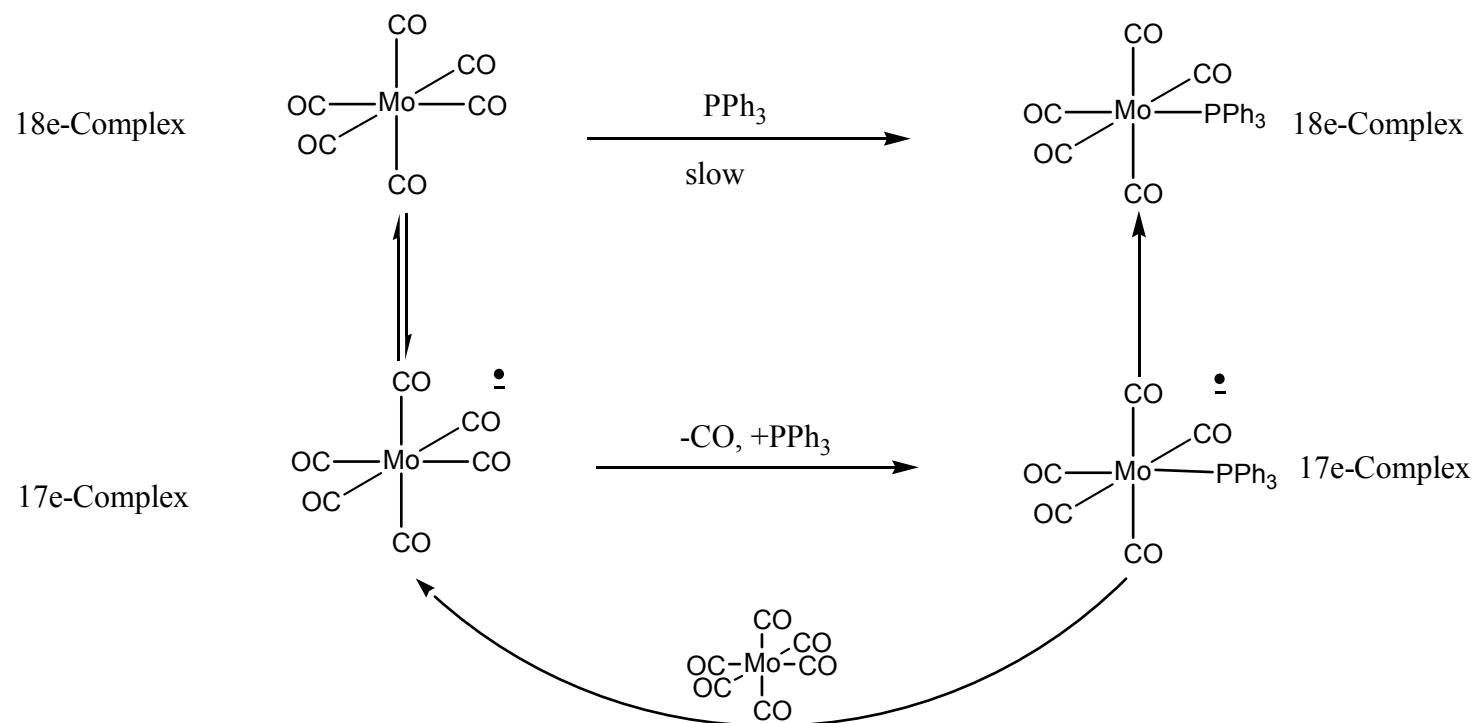
Electronic restrictions



The reaction works catalytically, because PPh_3 is a stronger π -acid than CH_3CN . Thus, the substituted complex becomes more precious than the starting compound.

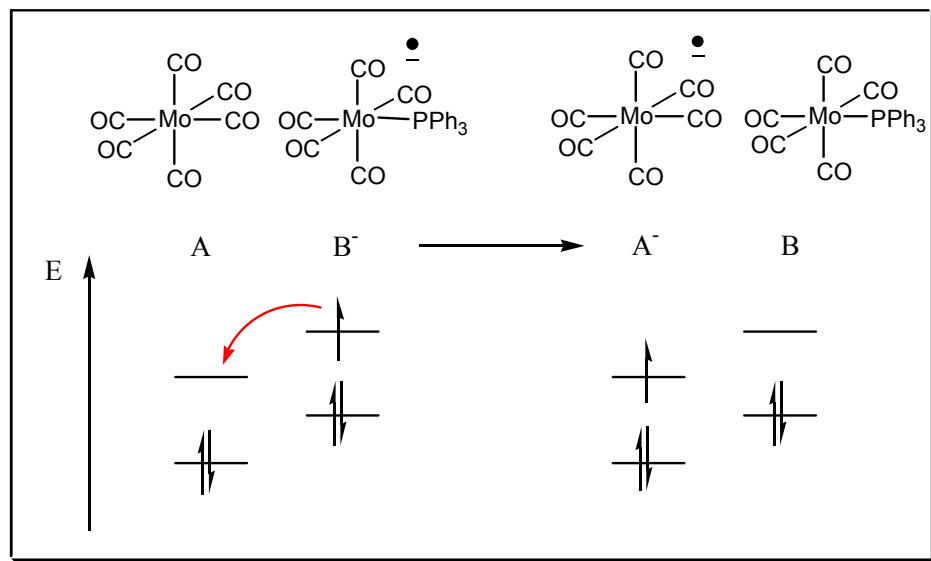
Electron-transfer-Catalysis

Electronic restrictions

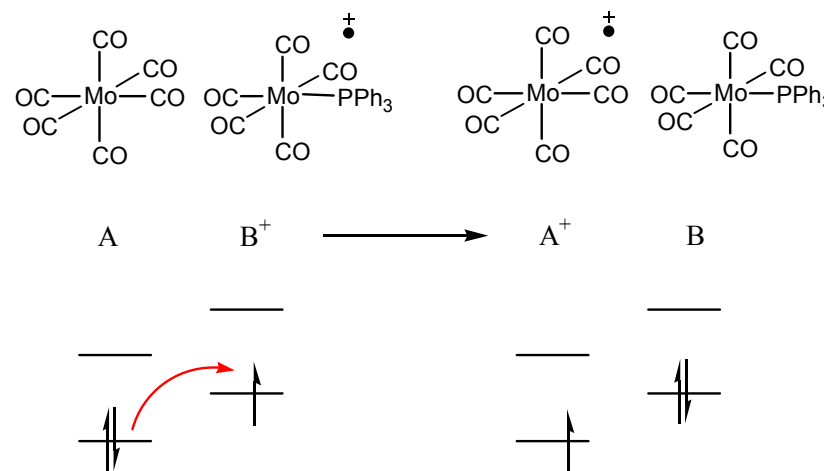


Electronic restrictions

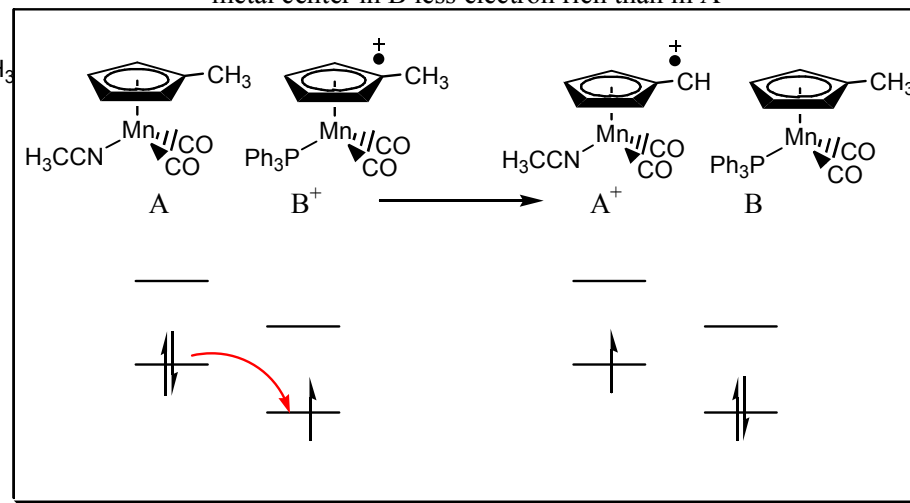
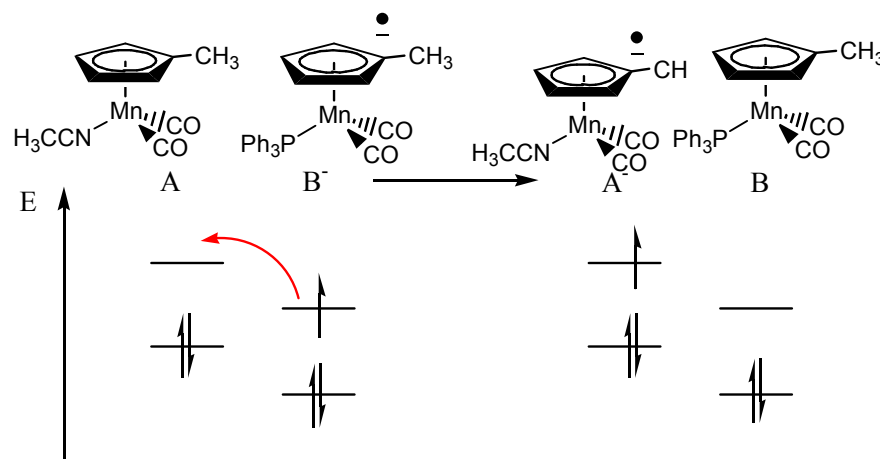
1.



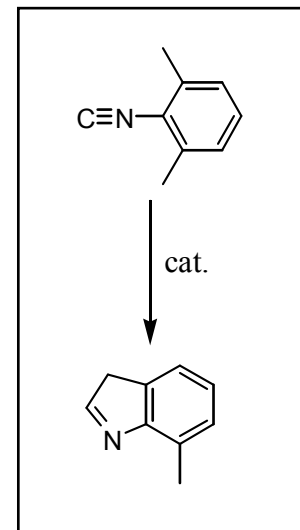
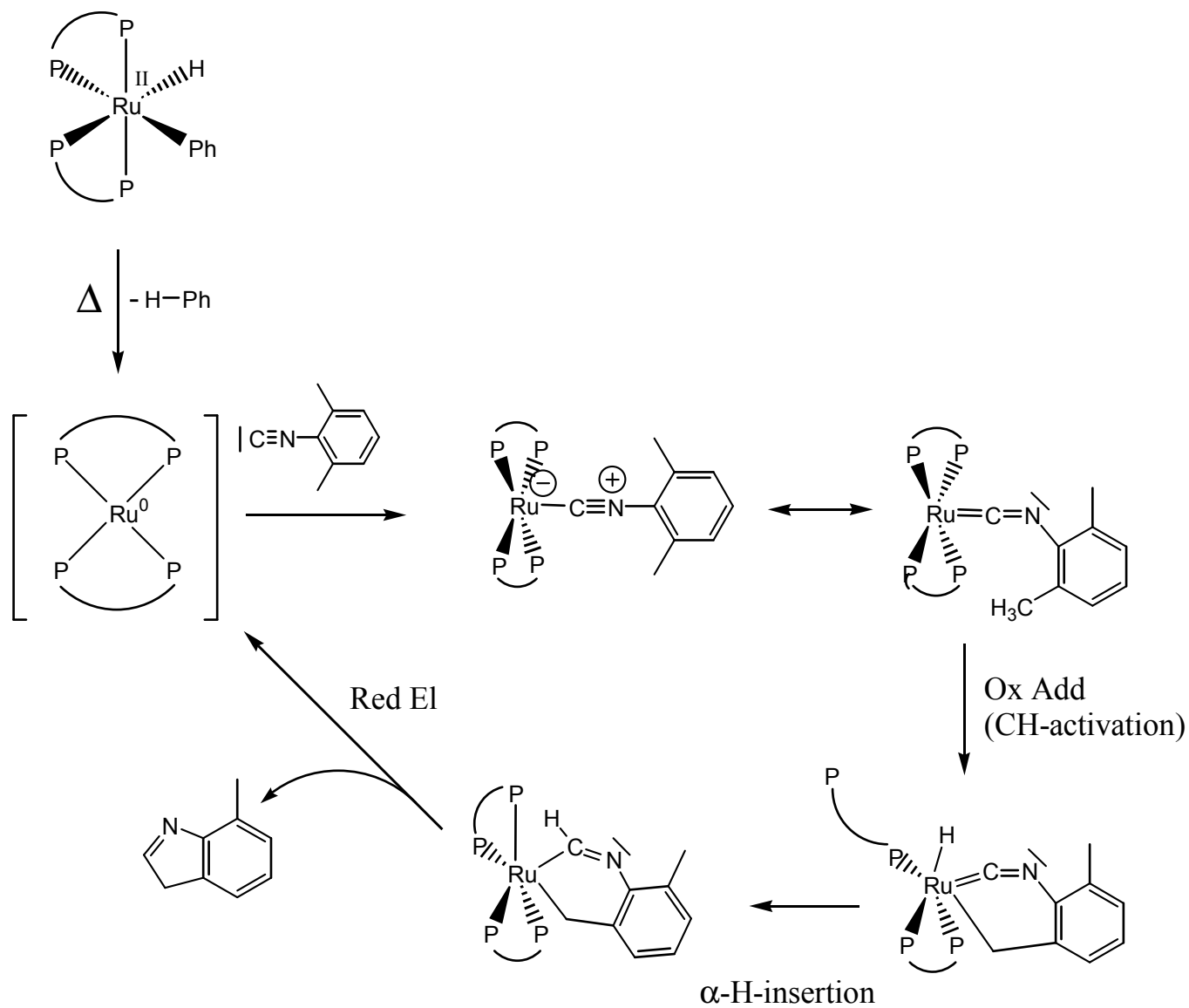
metal center in B more electron rich than in A



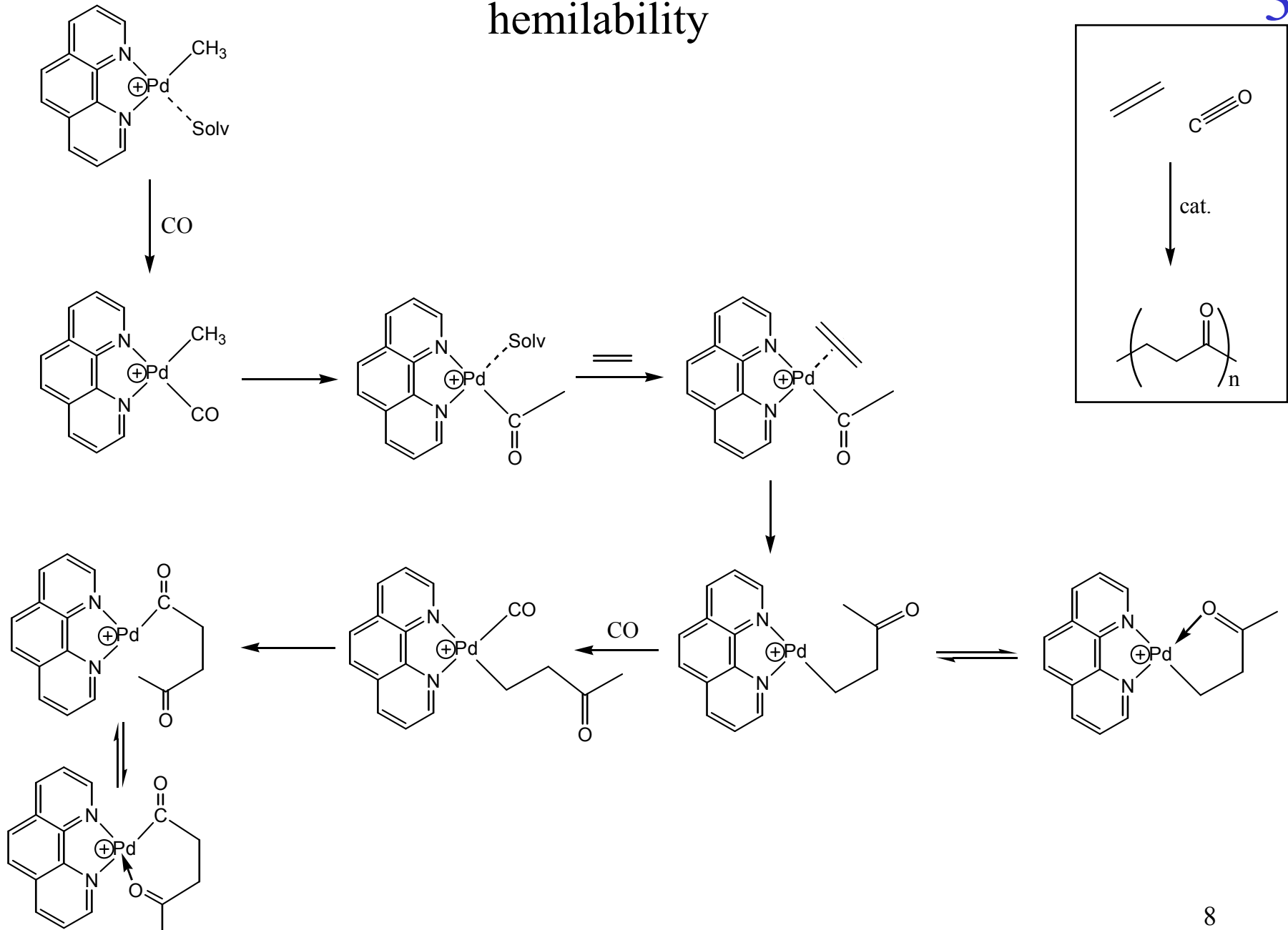
metal center in B less electron rich than in A



Reductive elimination

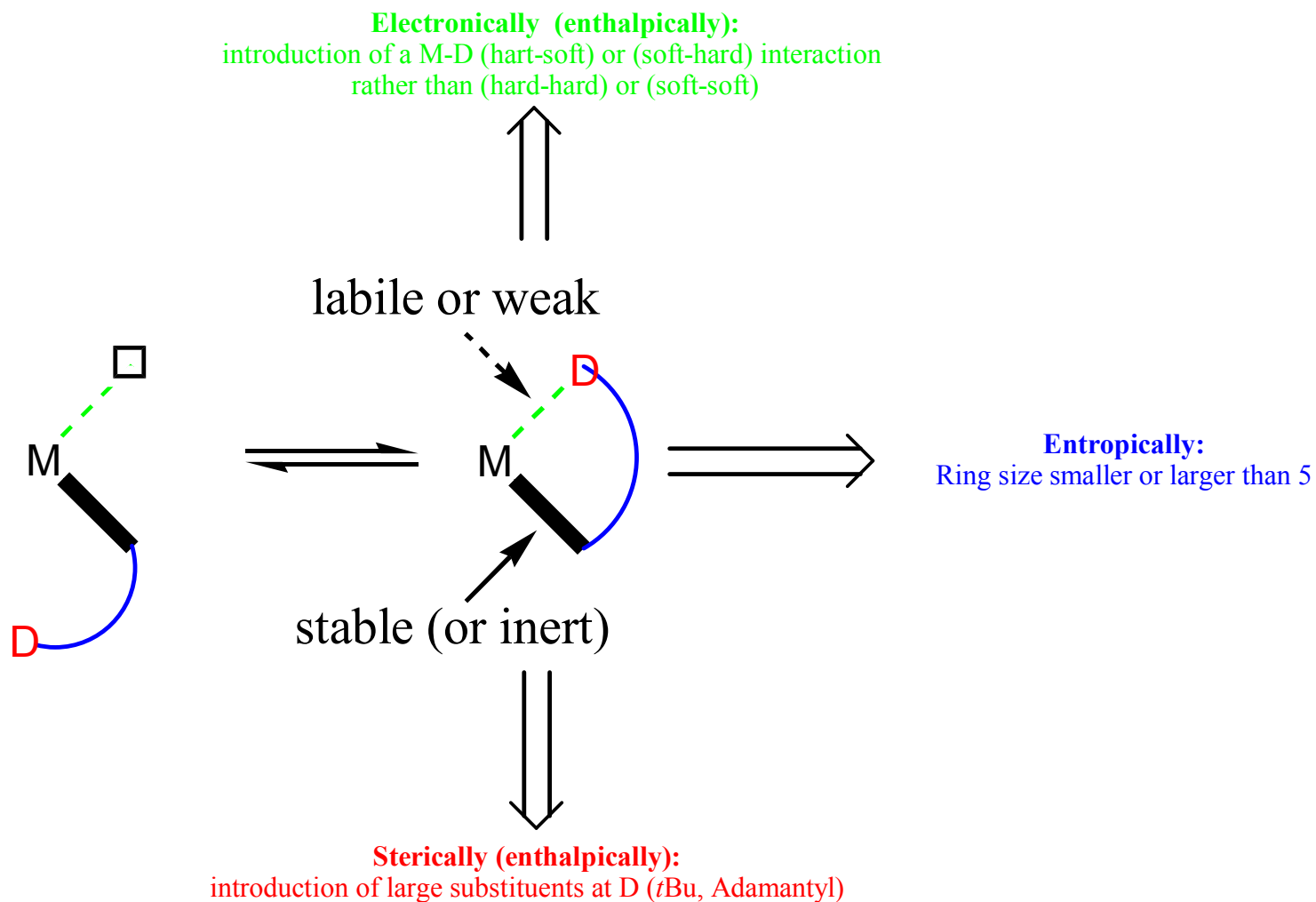


hemilability



Temporary free Coordination Sites (Hemilabile Ligands)

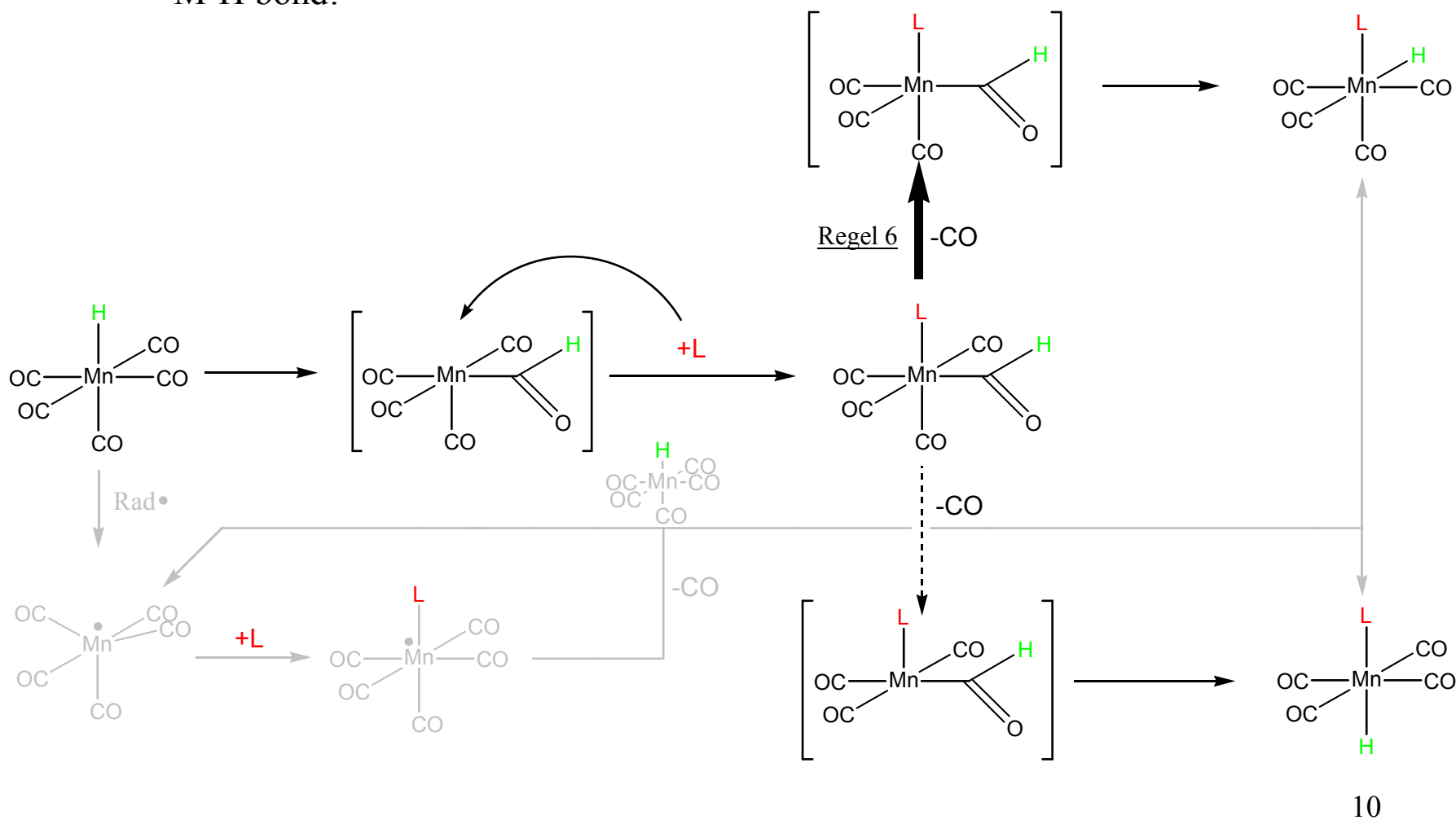
3.



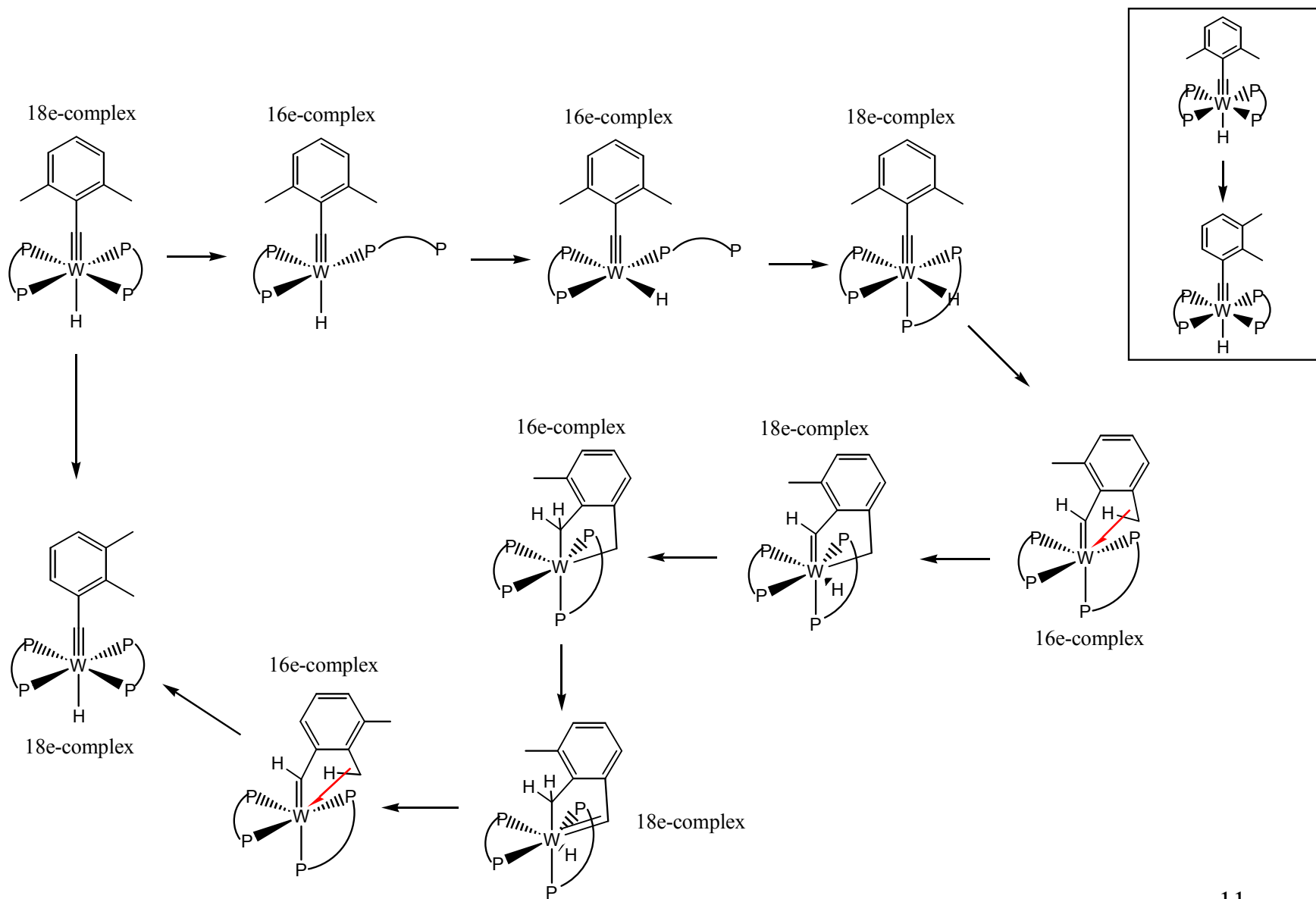
Temporary free Coordination Sites (M-H cis to CO)

Metal hydrides insert CO in contrast to M-Alkyls reversibly!

Metal hydrides often substitute easier than other similar complexes. They are sensitive to traces of radicals present, because those start a **radical reaction** by homolysis of the M-H bond!

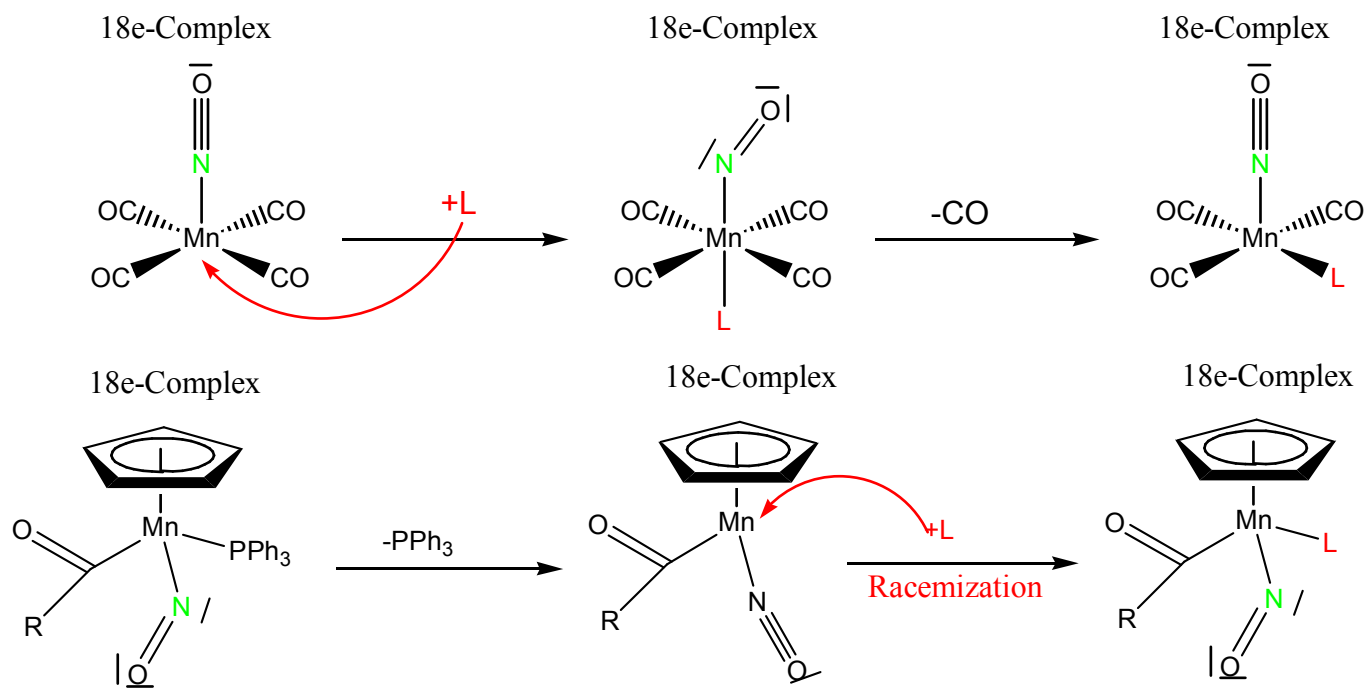
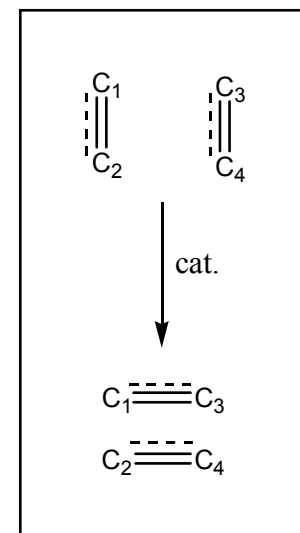
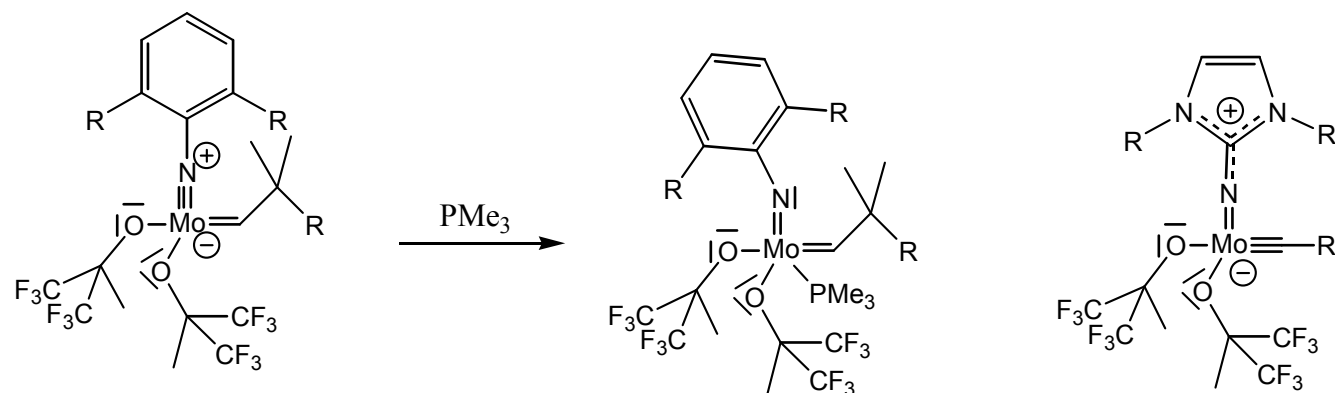


Neighboring group effect

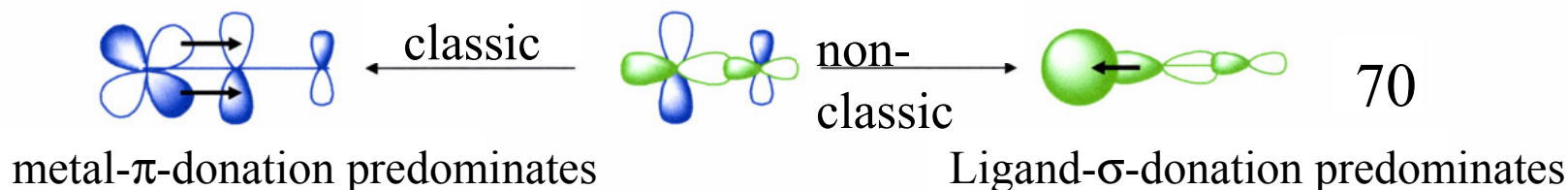
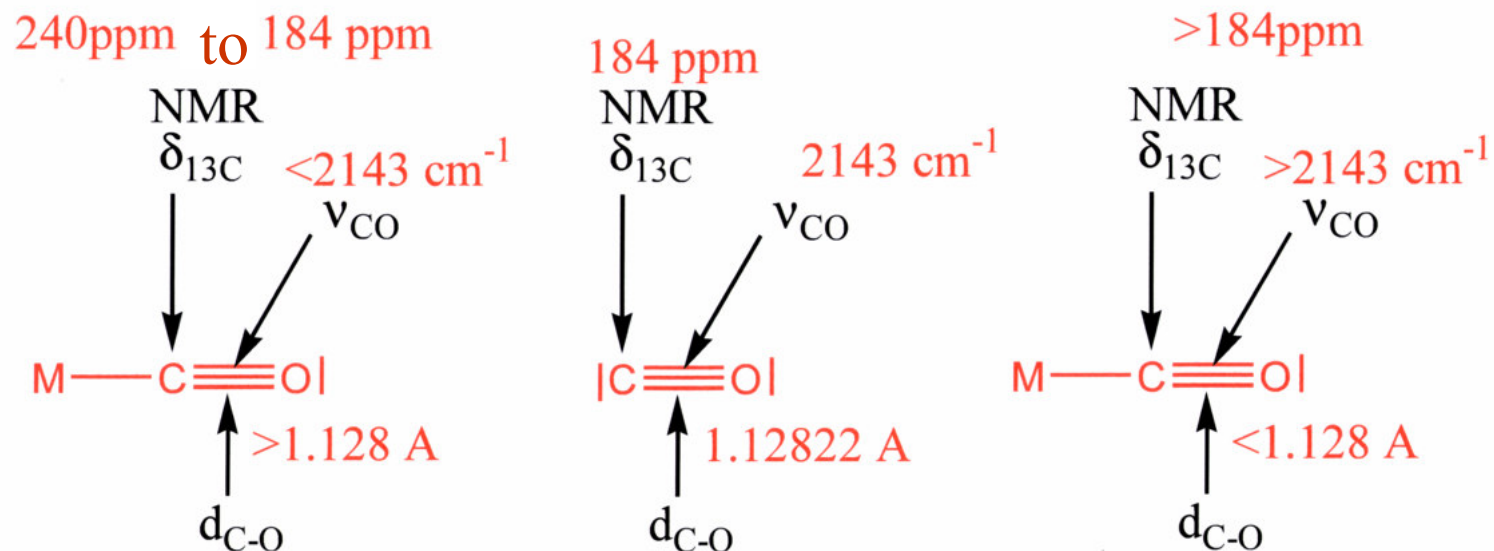


Dynamic lone pair

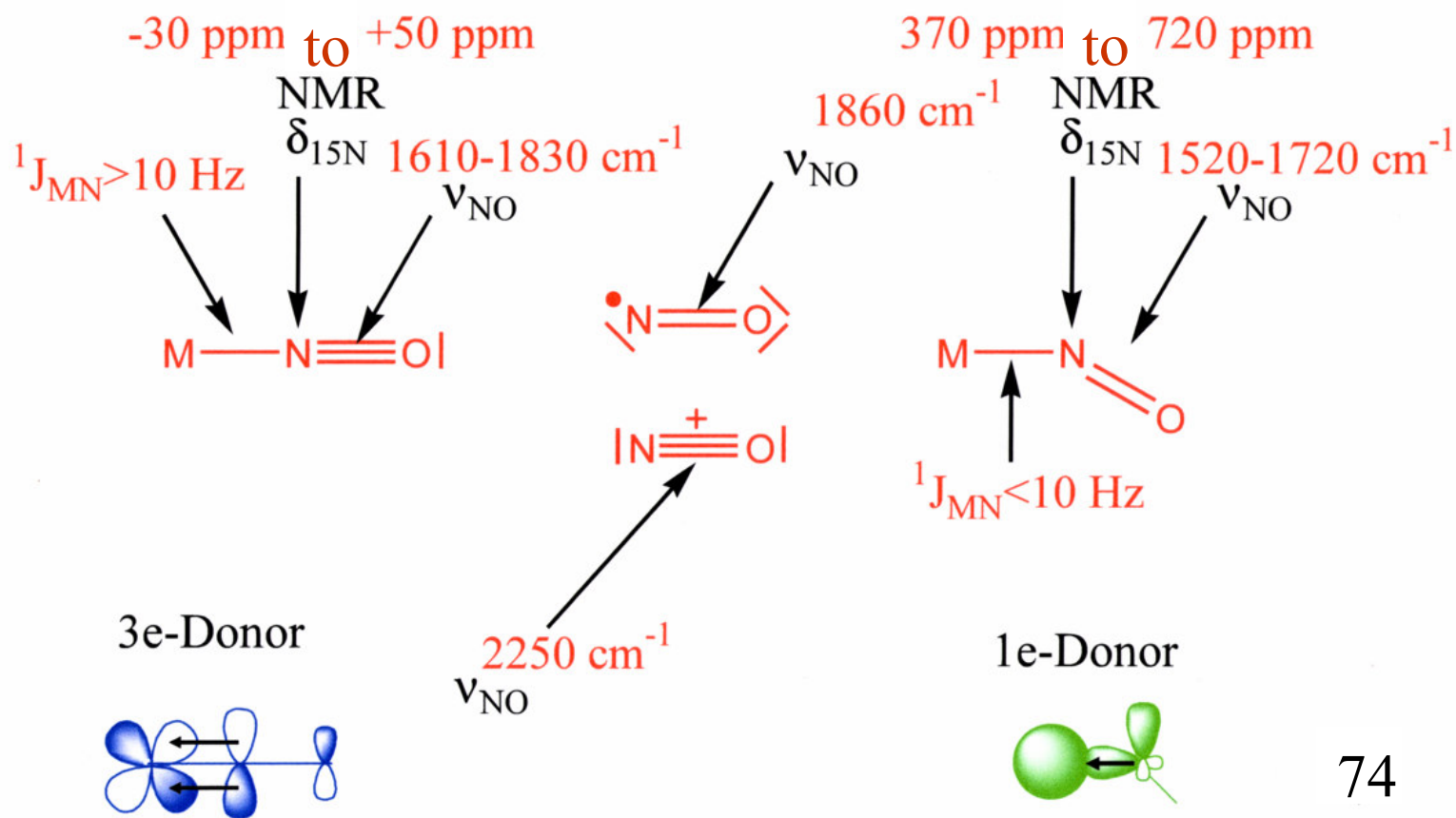
Formally an 18e-complex



Characterization of metal carbonyl complexes



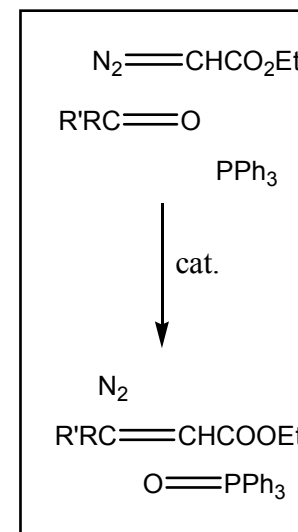
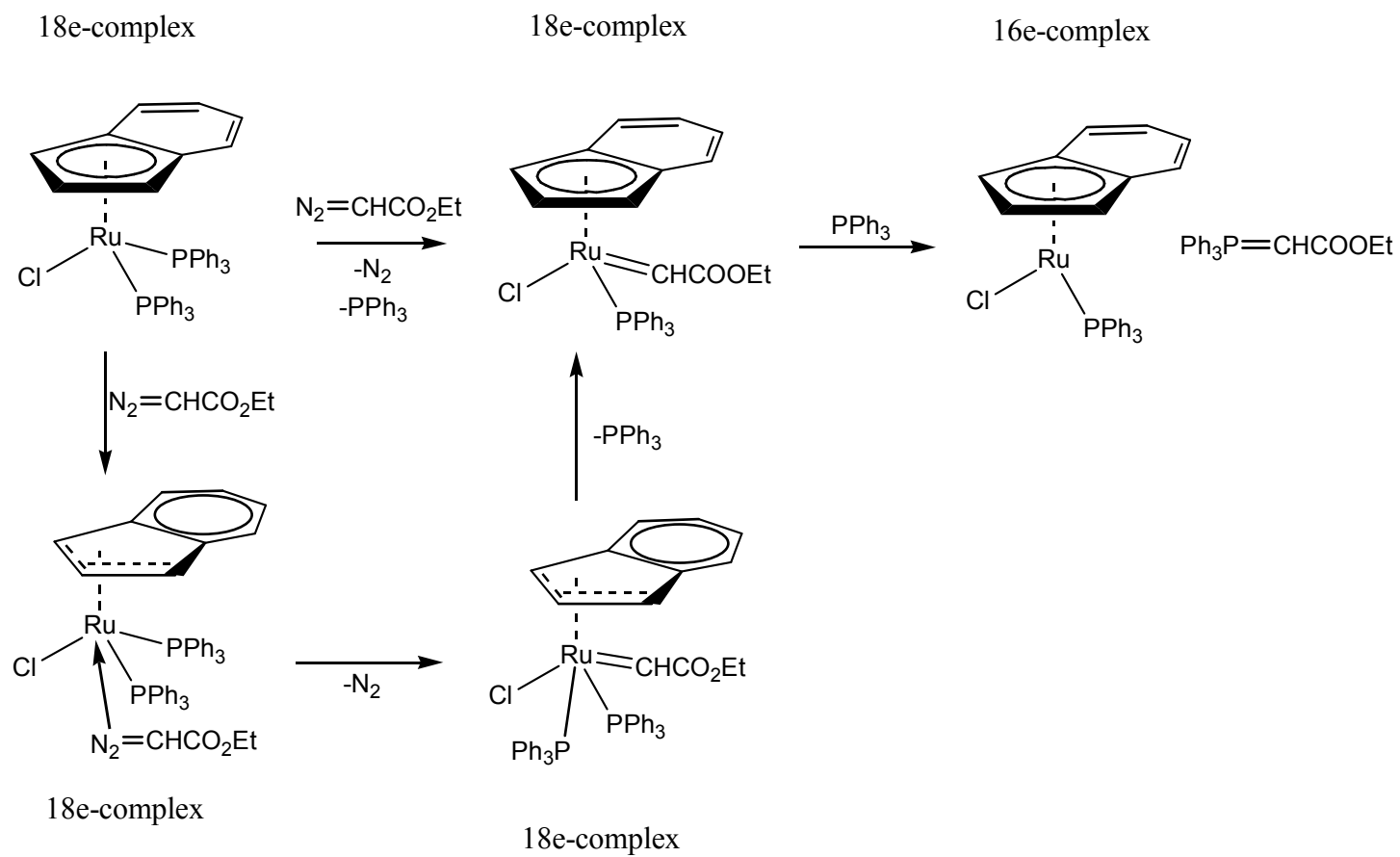
Characterization of metal nitrosyl complexes



Ligand- π -donation predominates

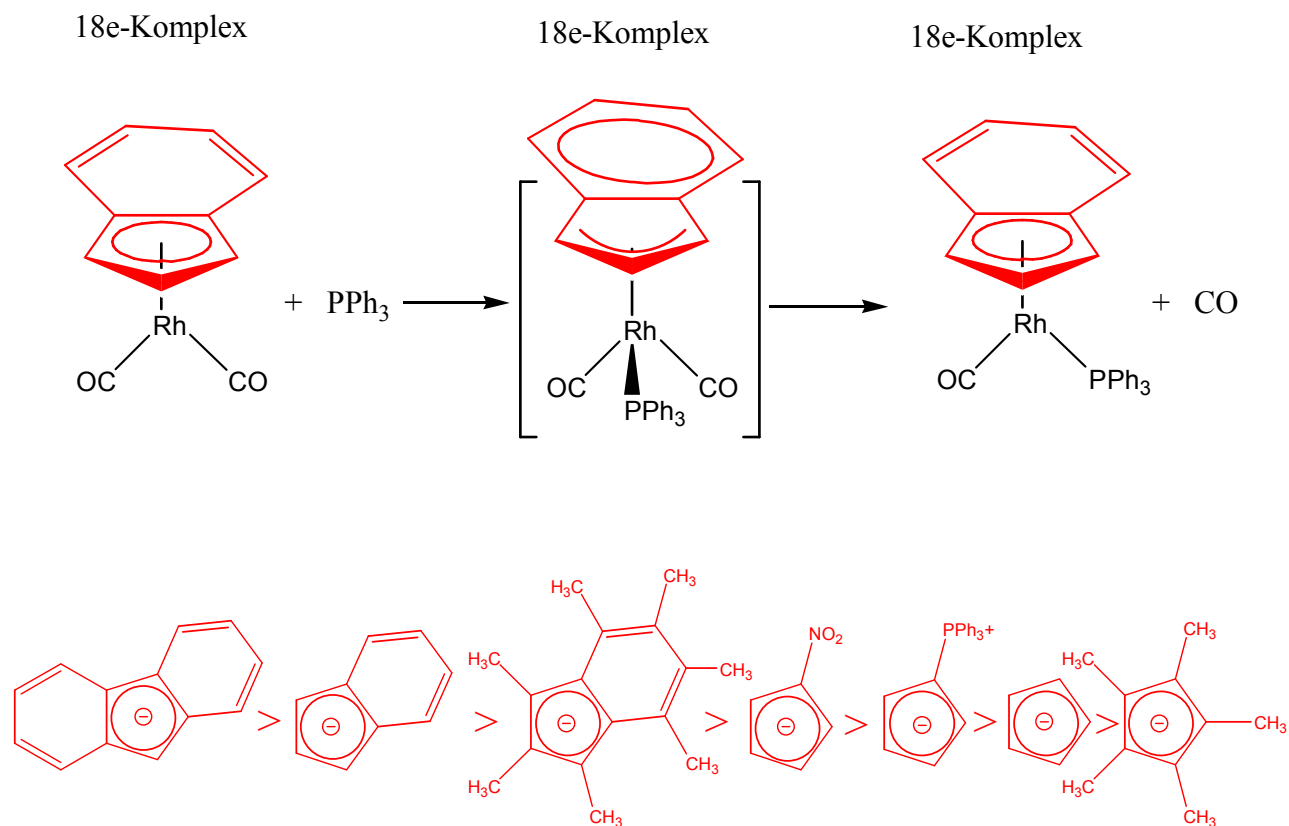
Ligand- σ -donation predominates

Indenyl effect

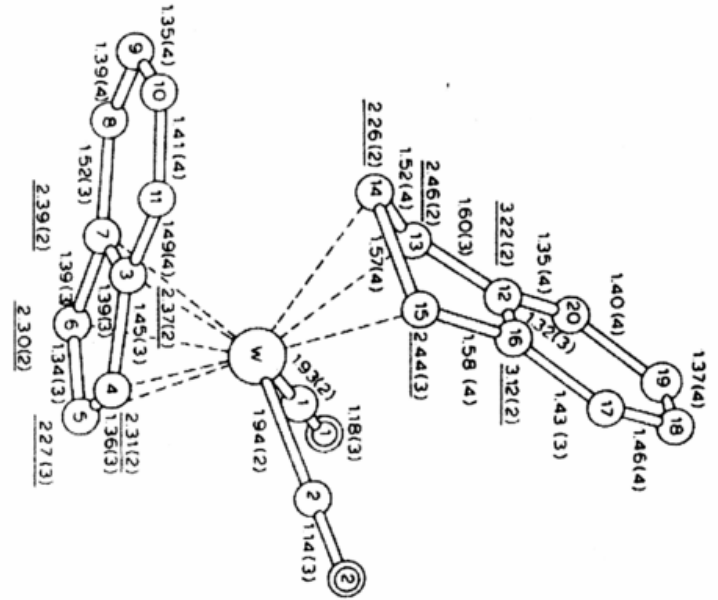
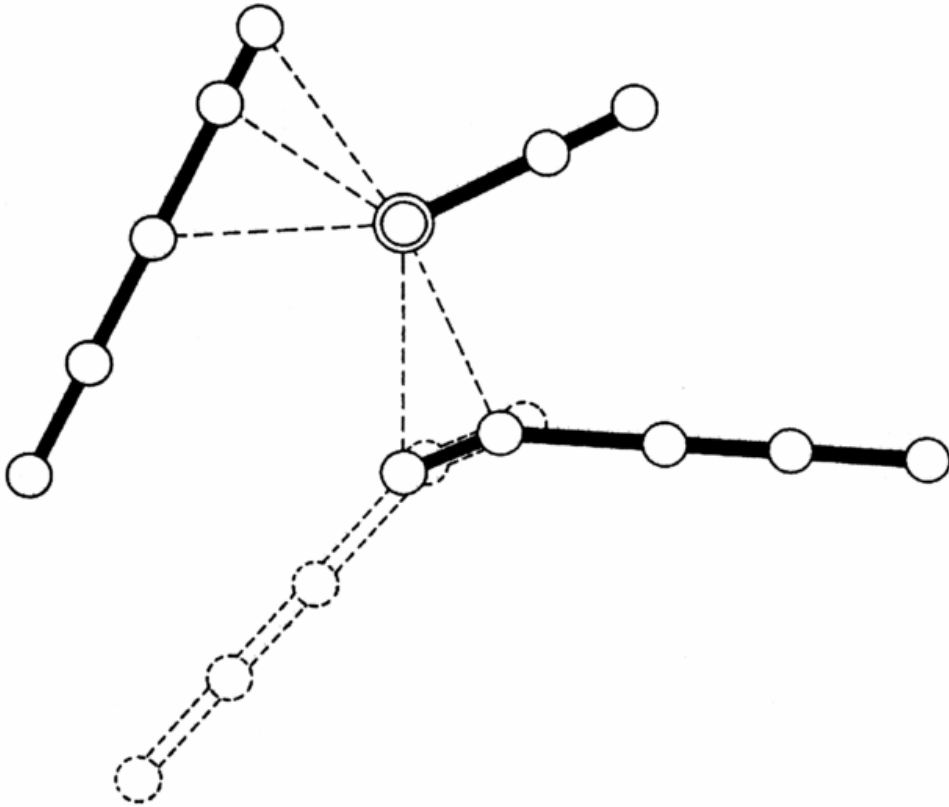


Temporary free Coordination Sites (Charged Polyenes)

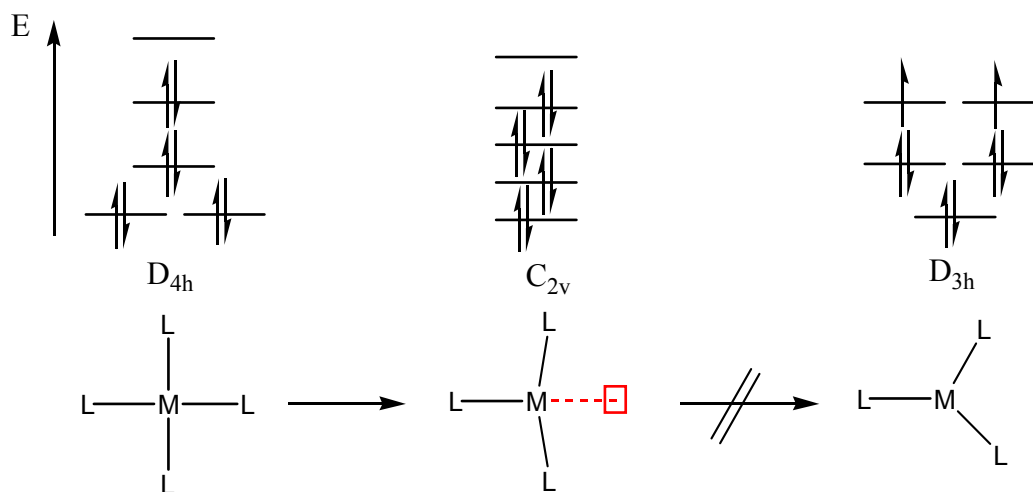
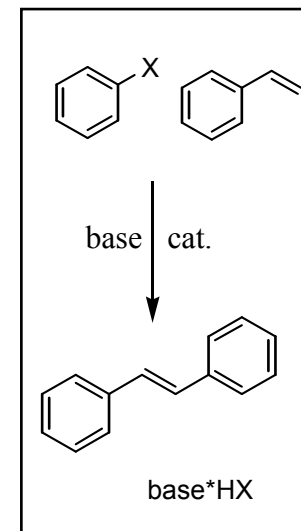
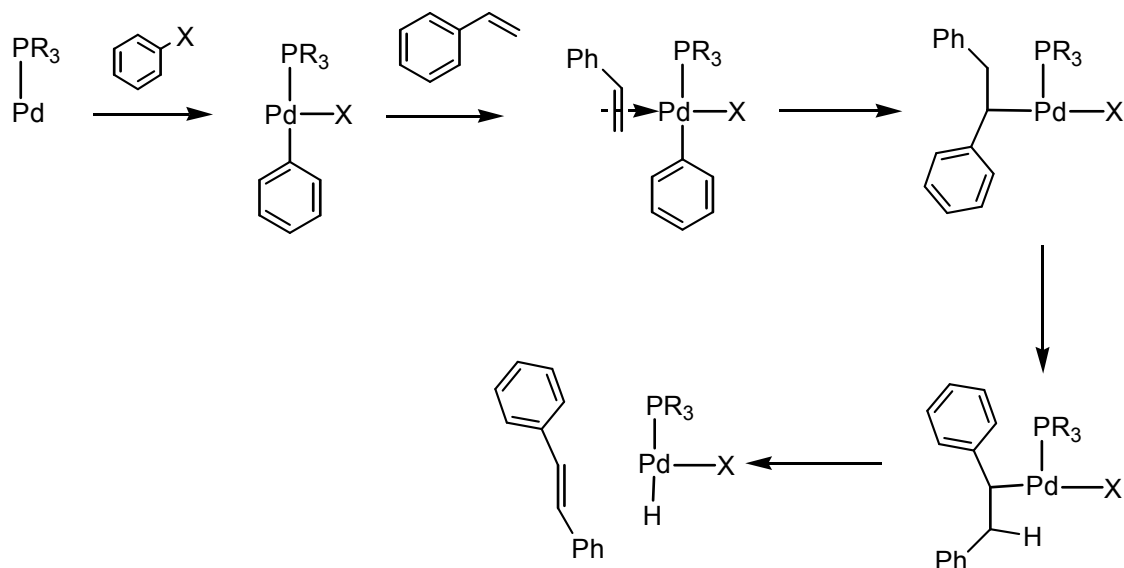
Electron-withdrawing and „rearomatizing“ substituents, annelated to the charged Polyene, facilitate the substitution at the Metal Center (Indenyl-Effect)!



Indenyl effect

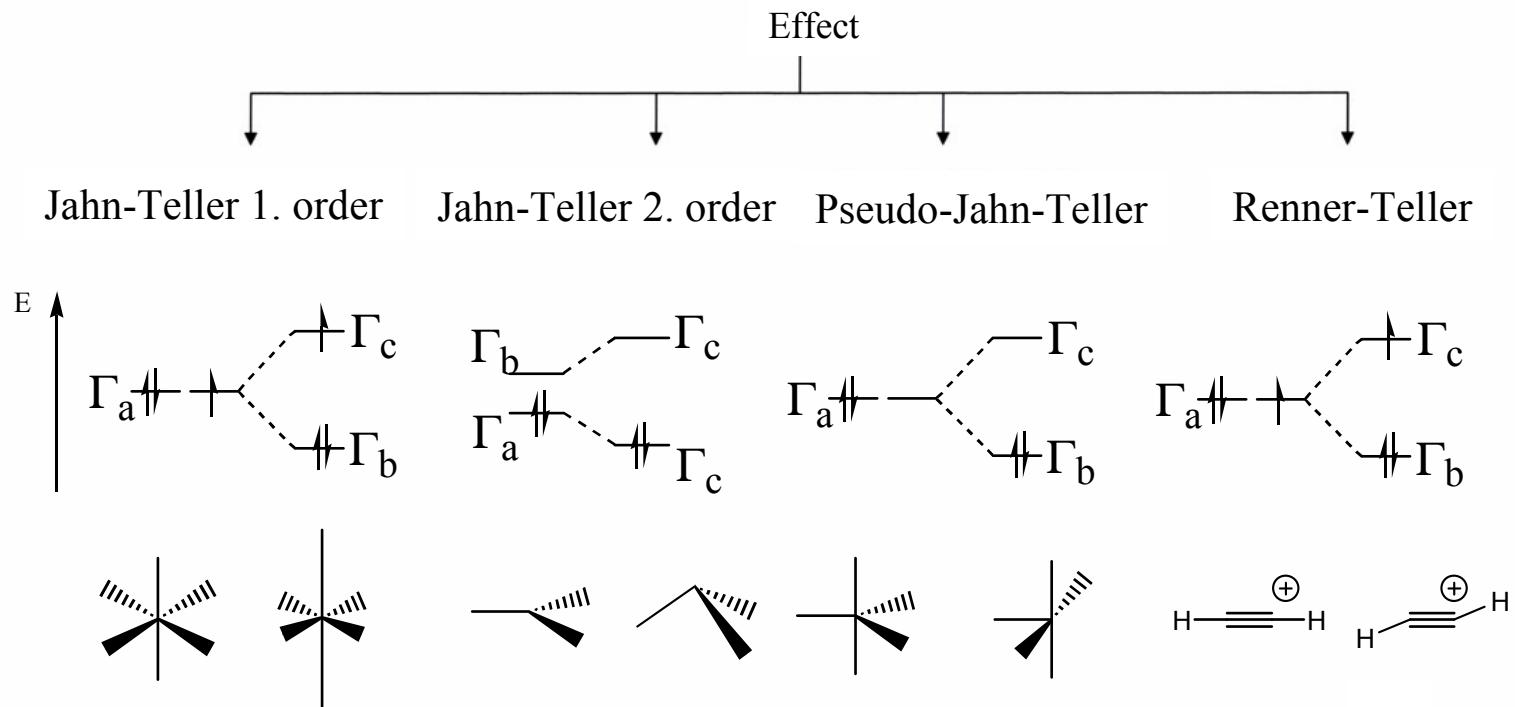


Pseudo-Jahn-Teller effect



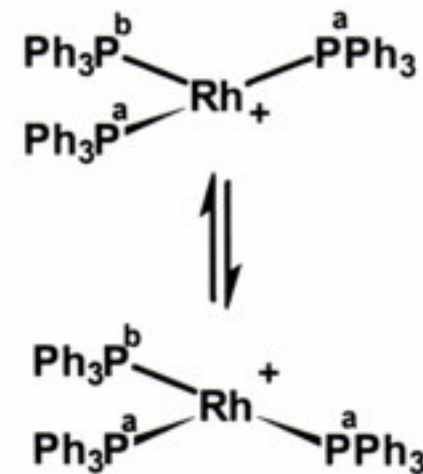
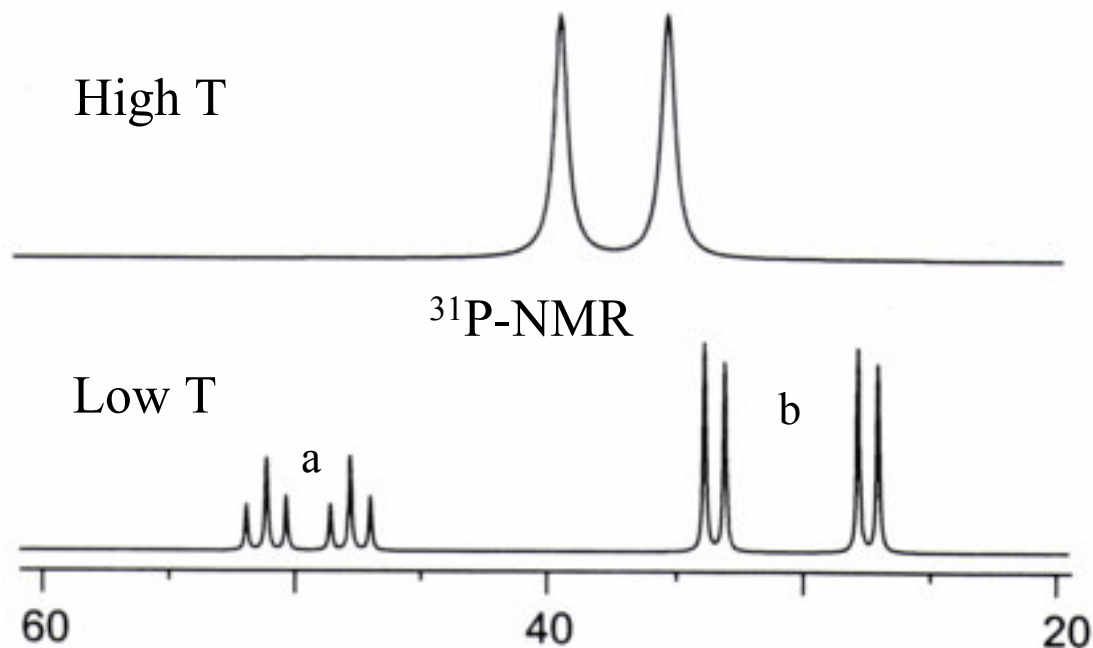
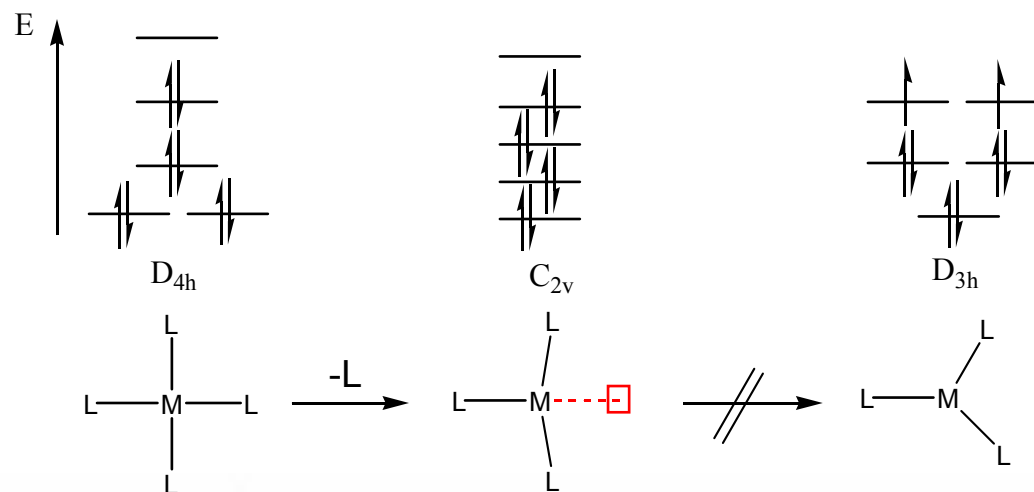
Desymmetrization effects

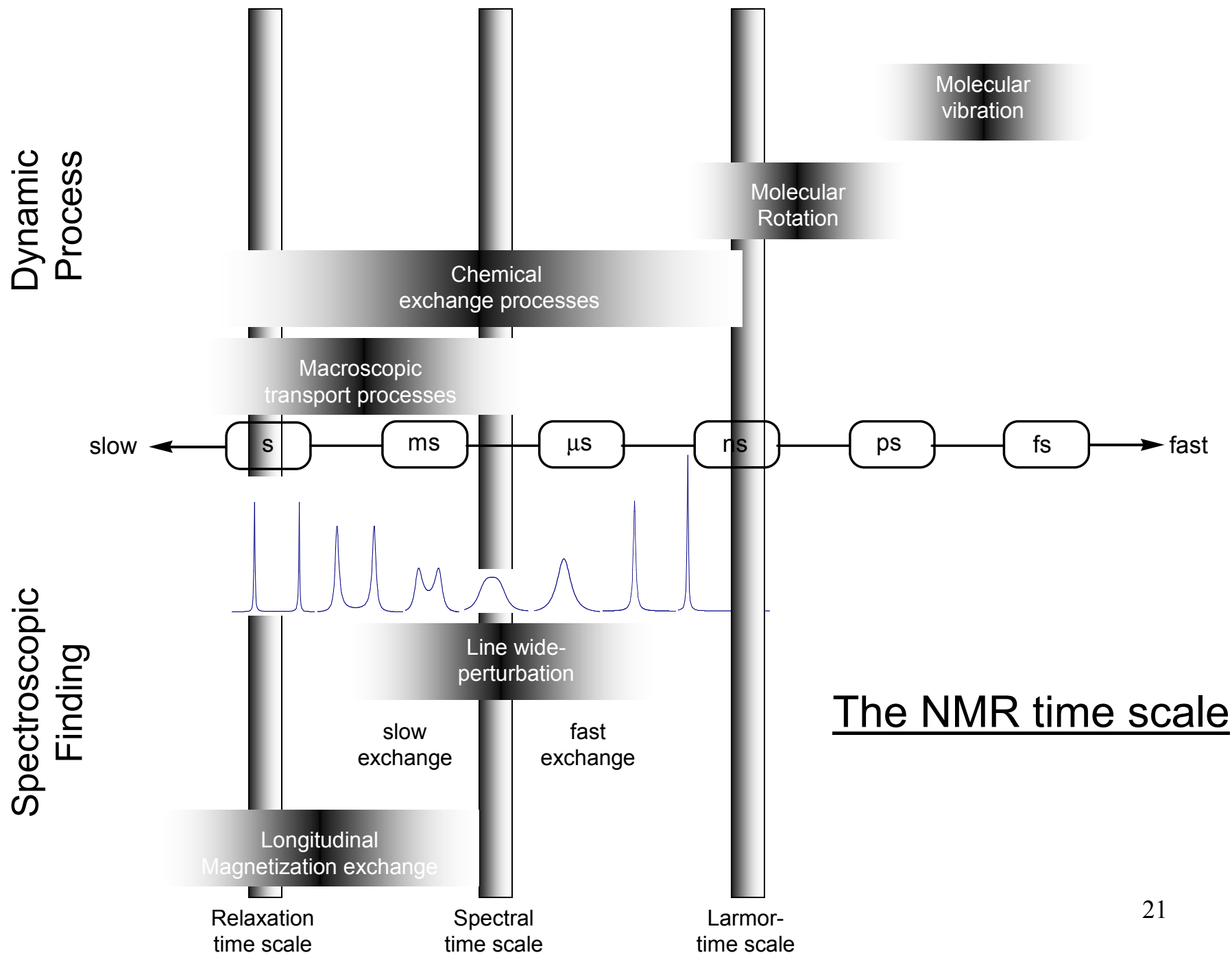
Coupling of electronic and vibrational structure (Vibronic)



Hidden Coordination Sites (Jahn-Teller-Effect)

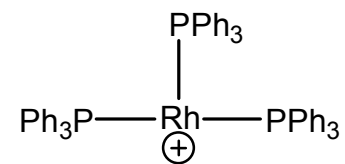
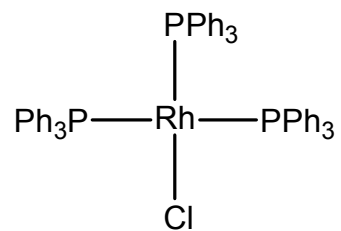
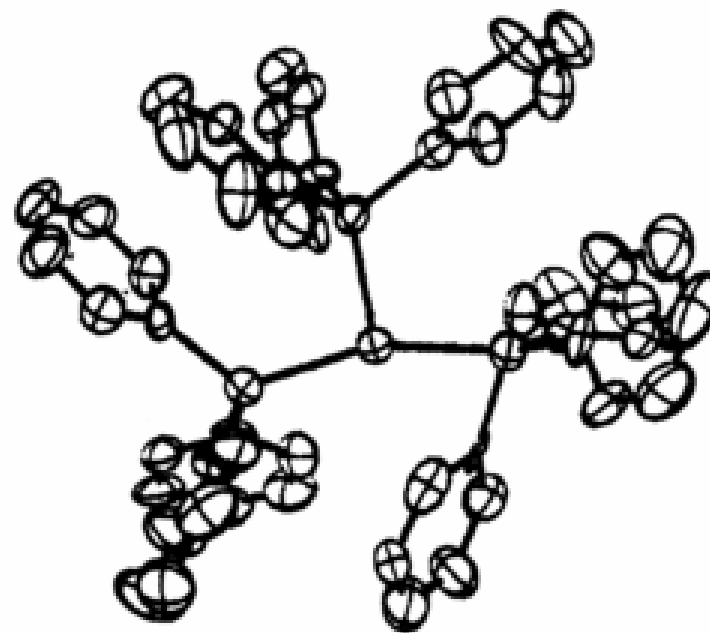
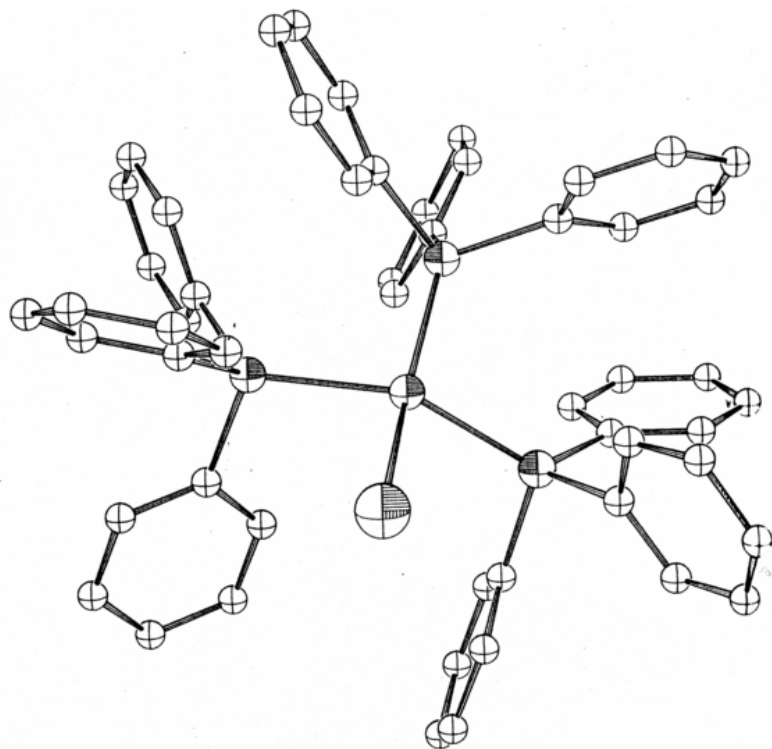
7.





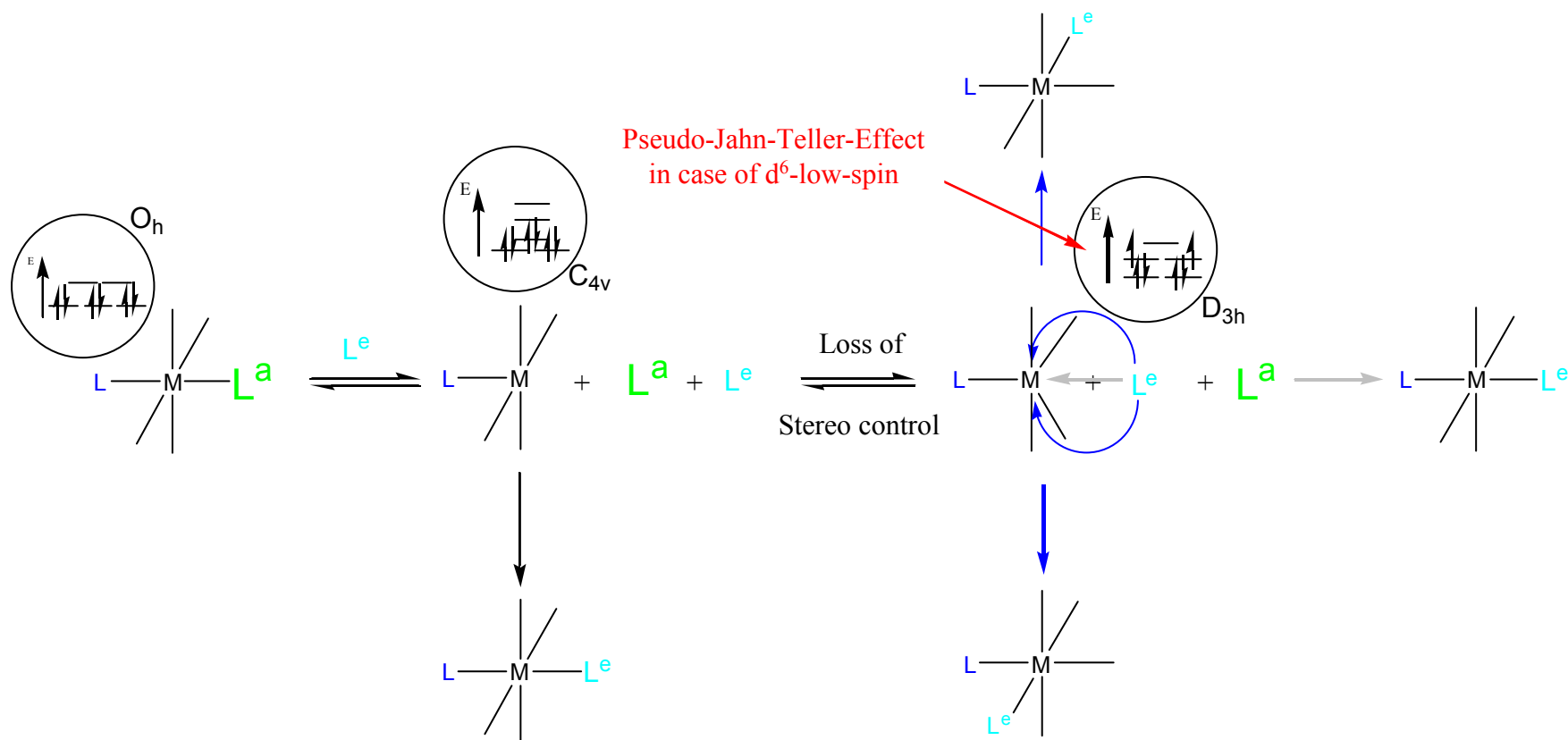
Pseudo-Jahn-Teller effect

7.



18e-Complexes

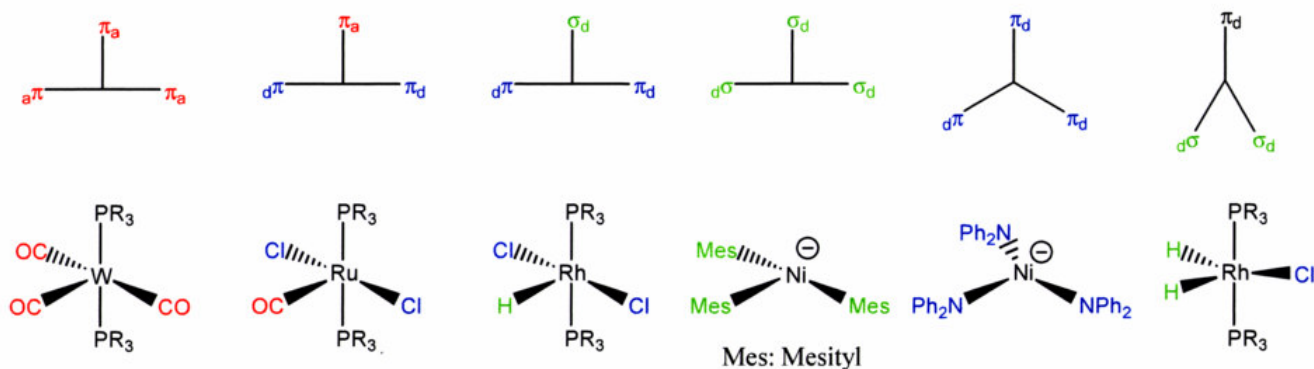
Pseudo-Jahn-Teller effect



Pseudo-Jahn-Teller effect

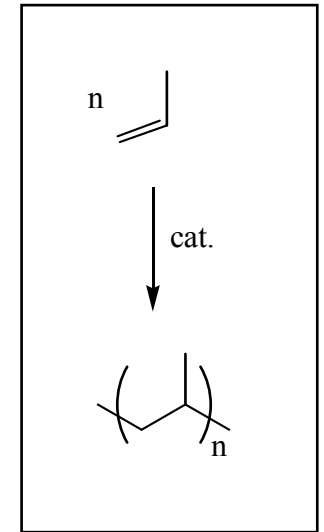
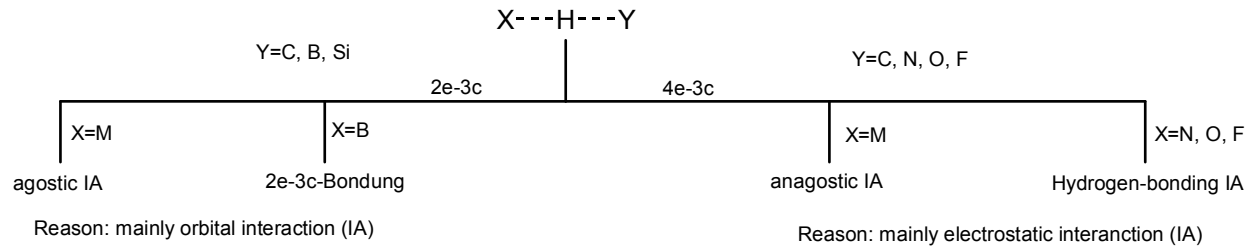
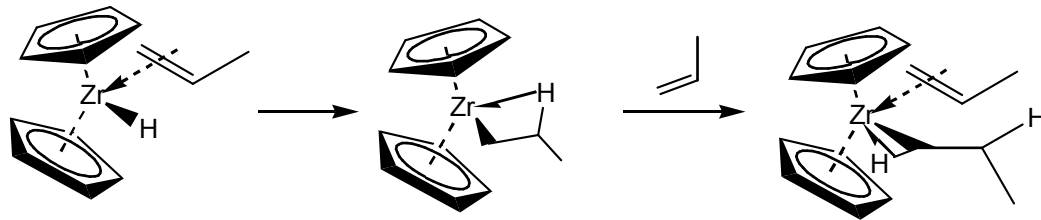
7.

T- or Y- shape?

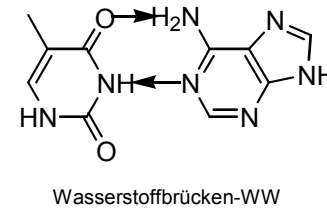
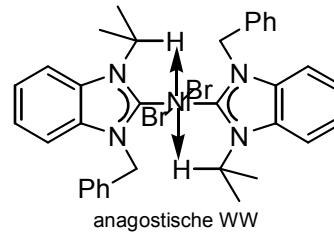
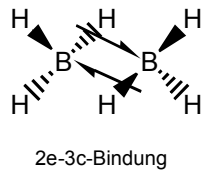
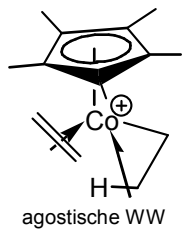
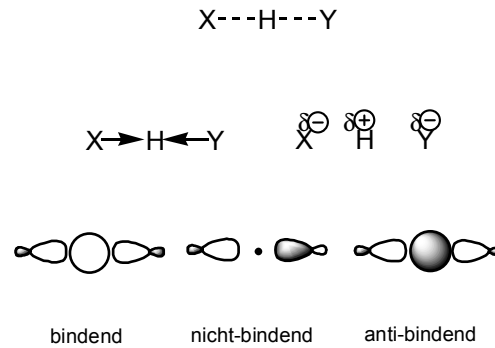
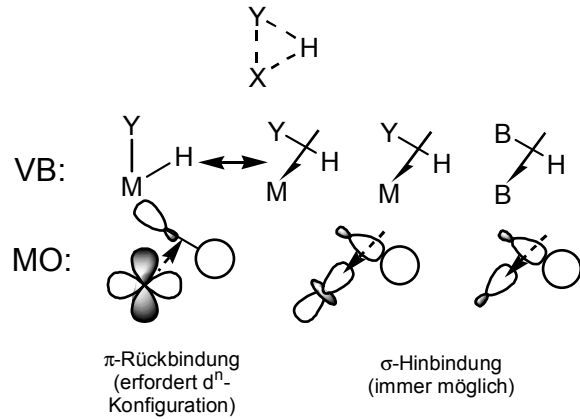


- π -donors maximize the angle to each other
- σ -donors and π -acceptors prefer 90° and 180° angles to each other

Agostic interactions

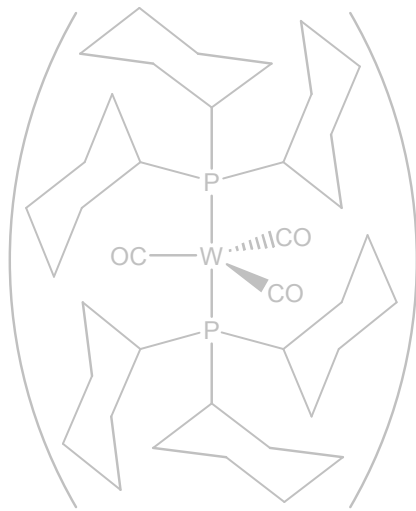


8.

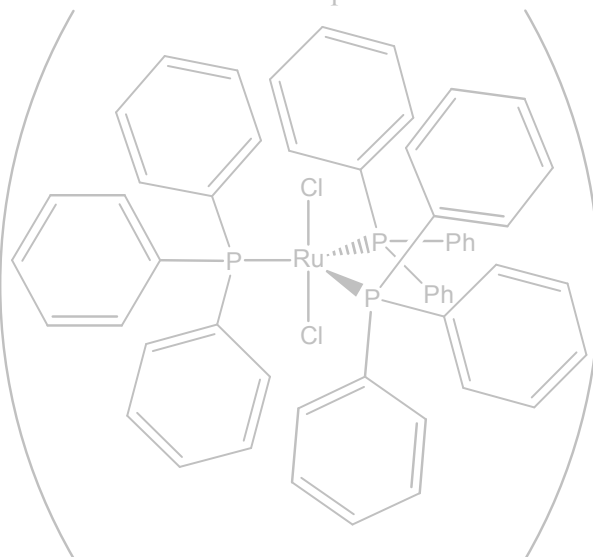


Hidden free Coordination Sites (agostic Hydrogens)

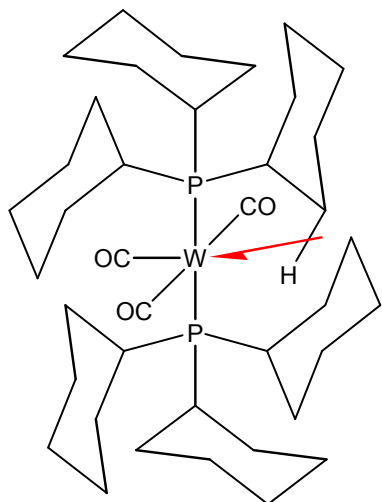
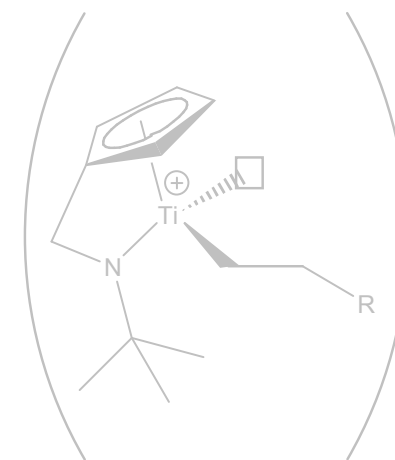
16e-Complex



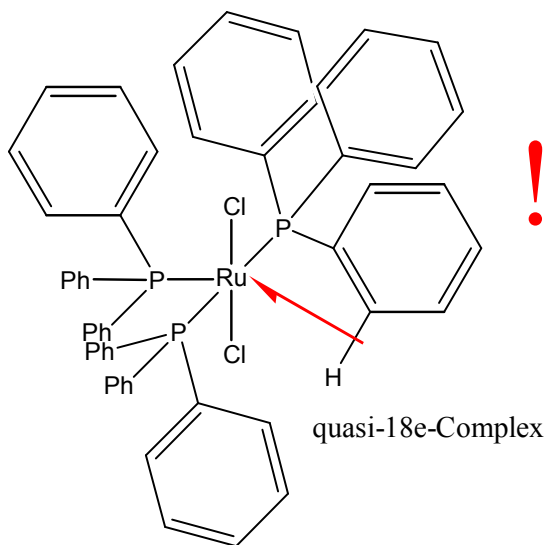
16e-Complex



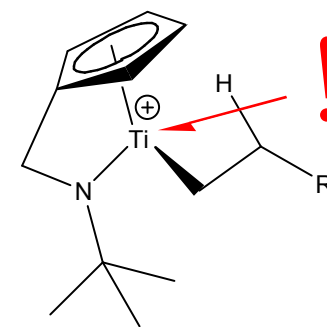
12e-Complex



quasi-18e-Complex

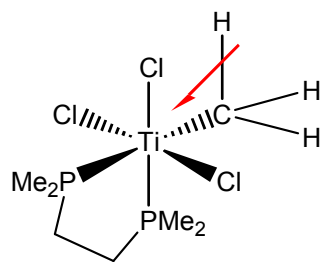
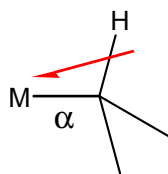
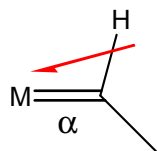
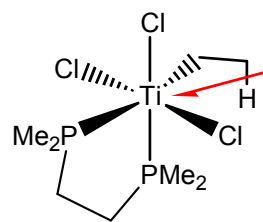
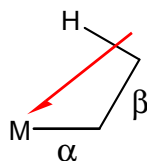
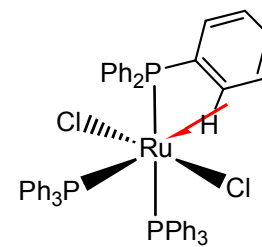
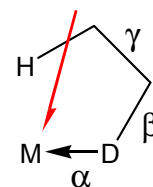


quasi-18e-Complex



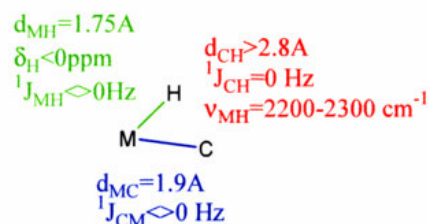
quasi-14e-Complex

Hidden free Coordination Sites (agostic Hydrogens, types)

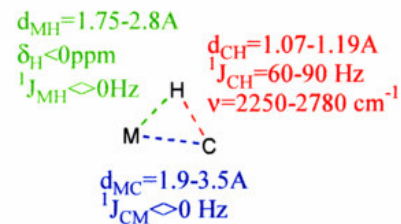
 α -agostic β -agostic γ -agostic

Agostic interaction (experim. evidence)

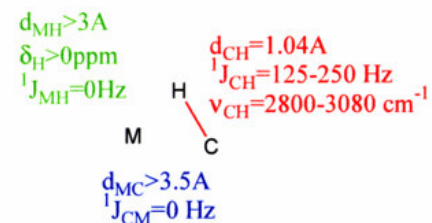
Rule: Necessary condition for an agostic interaction are electronic and coordinative undersaturation and steric availability of the metal center.



Oxidative addition



Agostic interaction

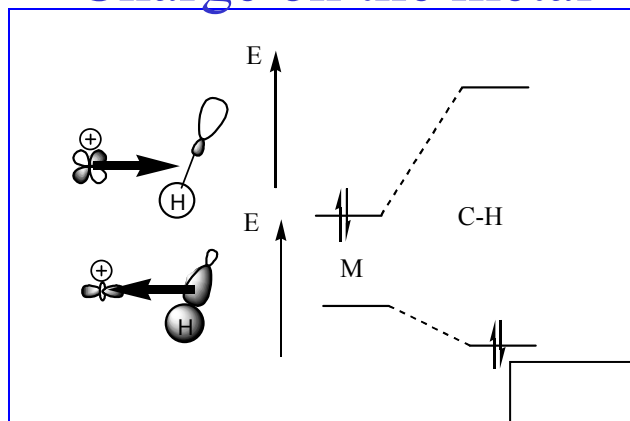


No interaction

	agostic	anagostic (preagostic)	H-bond
Bonding	3c-2e		3c-4e
CHM angle	90° to 130°	130° to 170°	160° to 180°
δ_H (NMR)	upfield shift	downfield shift	downfield shift
d_{MH}	1.8 to 2.2 Å	2.3 to 2.9 Å	2.65 to 3.5 Å
$^1J_{MH}$ Coupling	yes	no	

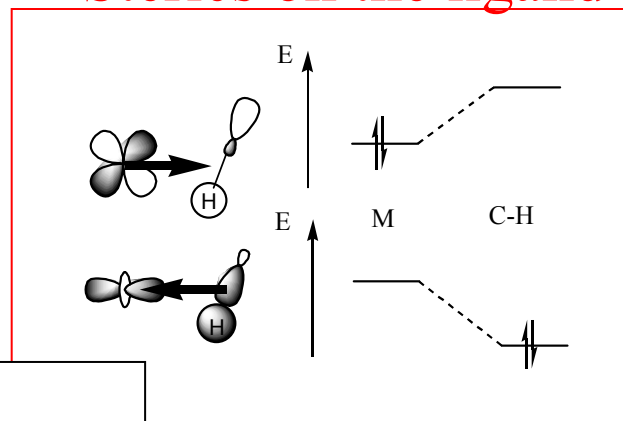
Agostic Interactions (influences)

Charge on the metal

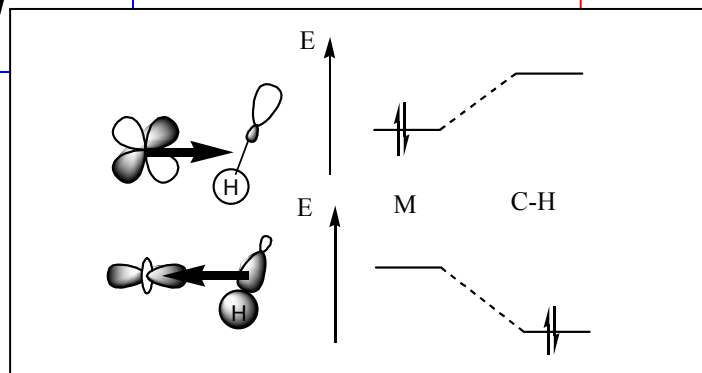


Positive charge at the metal center causes orbital contraction, which worsens the overlap abilities of this orbital. The metal center becomes more electrophile. The ligand to metal σ -bonding is stronger, while the metal to ligand π -back bonding is weaker. (The energy of the orbitals at the metal center is lowered by positive charge. In general positive charge at the metal center weakens the agostic interaction (important with Ziegler/Natta-Chemistry).)

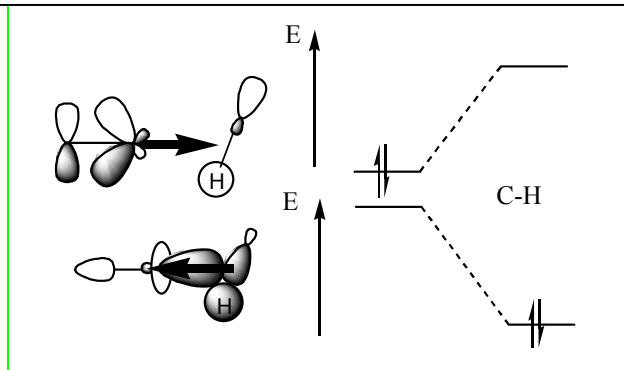
Sterics on the ligand



Sterically demanding substituents reduce the mobility of the C-H bond and freeze this bond. In general, this is positive for an agostic interaction. Overlap properties and energies of the orbitals are not influenced.



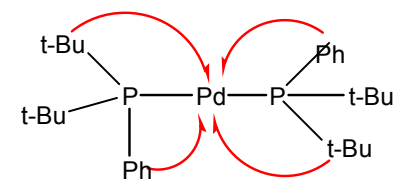
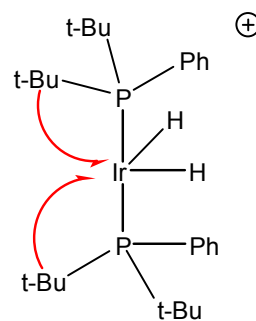
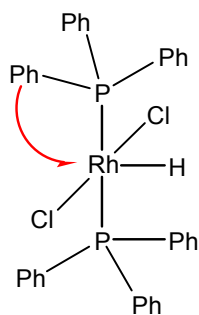
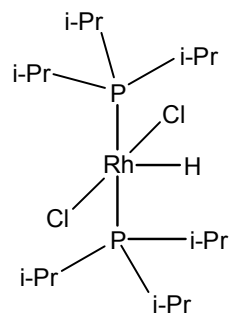
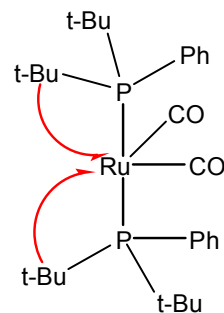
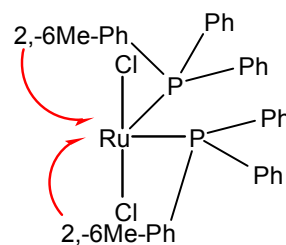
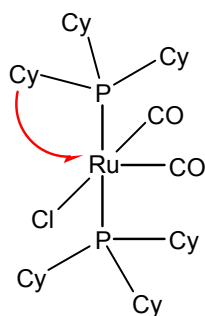
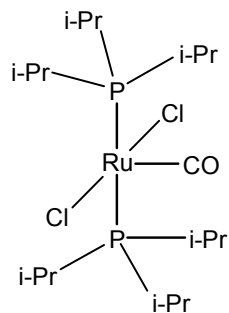
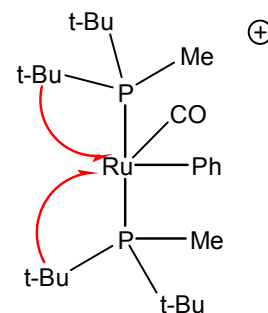
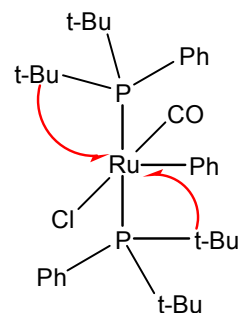
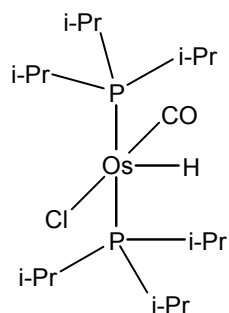
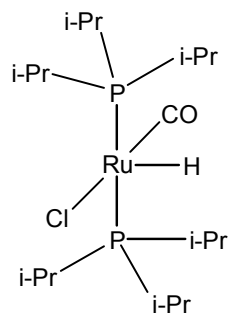
Strong σ -Donors polarise the HOMO towards them, and the LUMO away from them. This is advantageous for the ligand to metal σ -bond part of the agostic interaction, however the LUMO is raised energetically, which increases the energy gap between HOMO-C-H-Orbitals and Metal-LUMO-Orbitals. This weakens the interaction.



Strong π -acceptors polarise the HOMO towards them, and the LUMO away from them. This is disadvantageous for the metal to ligand π -back bonding part of the agostic interaction. The HOMO is lowered decisively in energy, which increases the energy gap between LUMO-C-H-Orbitals and Metal-HOMO-Orbitals and, thus, weakens this interaction as well.

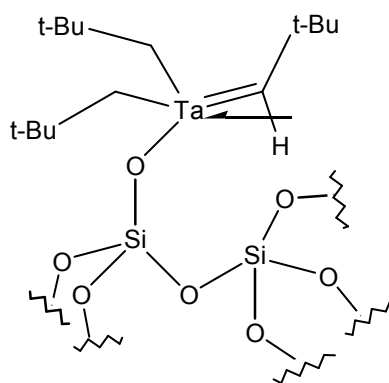
Orbital polarisation by trans-ligand

Agostic Interaction or No Agostic Interaction?

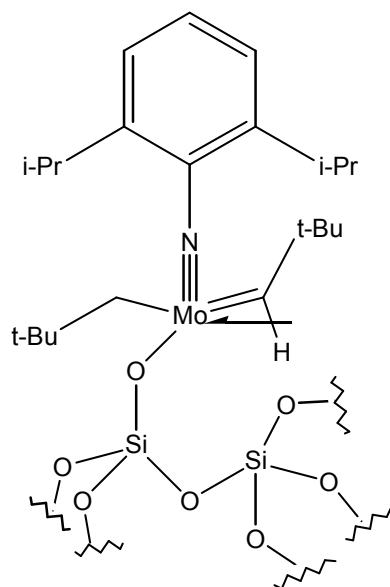


Agostic interactions

8.

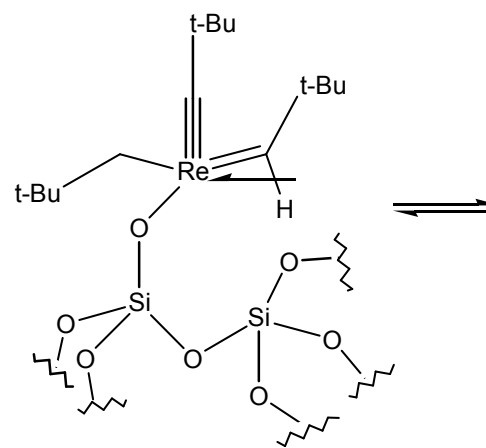


$^1J_{CH} = 80 \text{ Hz}$

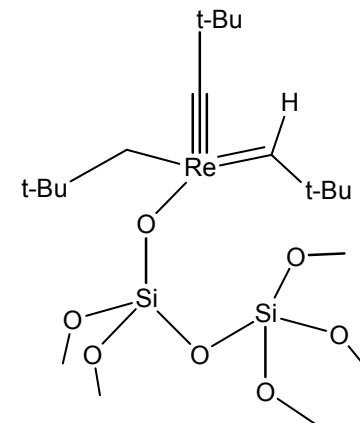


$^1J_{CH} = 110 \text{ Hz}$

$^1J_{CH_2} = 124 \text{ Hz}$



$^1J_{CH} = 109 \text{ Hz}$



$^1J_{CH} = 159 \text{ Hz}$

The Complete

Coupling of Coordination Sites

