ICG Montpellier | Institut Charles Gerhardt CTMM

UMR 5253 - Institut de Chimie Moléculaire et des Matériaux de Montpellier

18-Electron Rule: Myth or Reality ?

An NBO Perspective

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Interaction Experiment/Theory

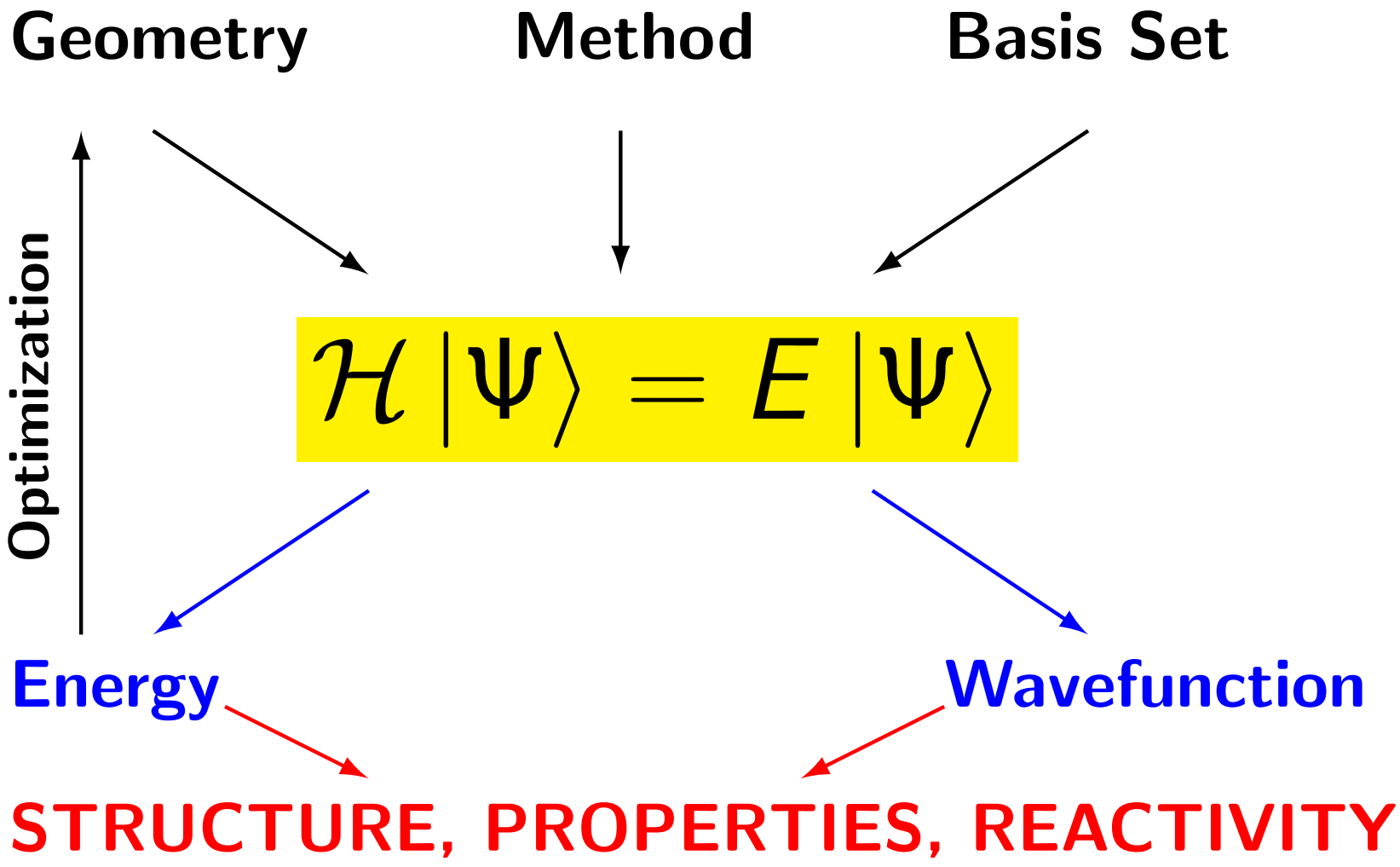
Experimental Chemists have Questions

- Where are the Nucleophilic and Electrophilic Sites in a Molecule ?
- How Strong are the Bonds within a Molecule ?
- What is the Nature of the Bonds between the Atoms ?
- Why is this Molecule more Stable than this Other ?
- How can we Describe the Interaction between two Reacting Molecules ?

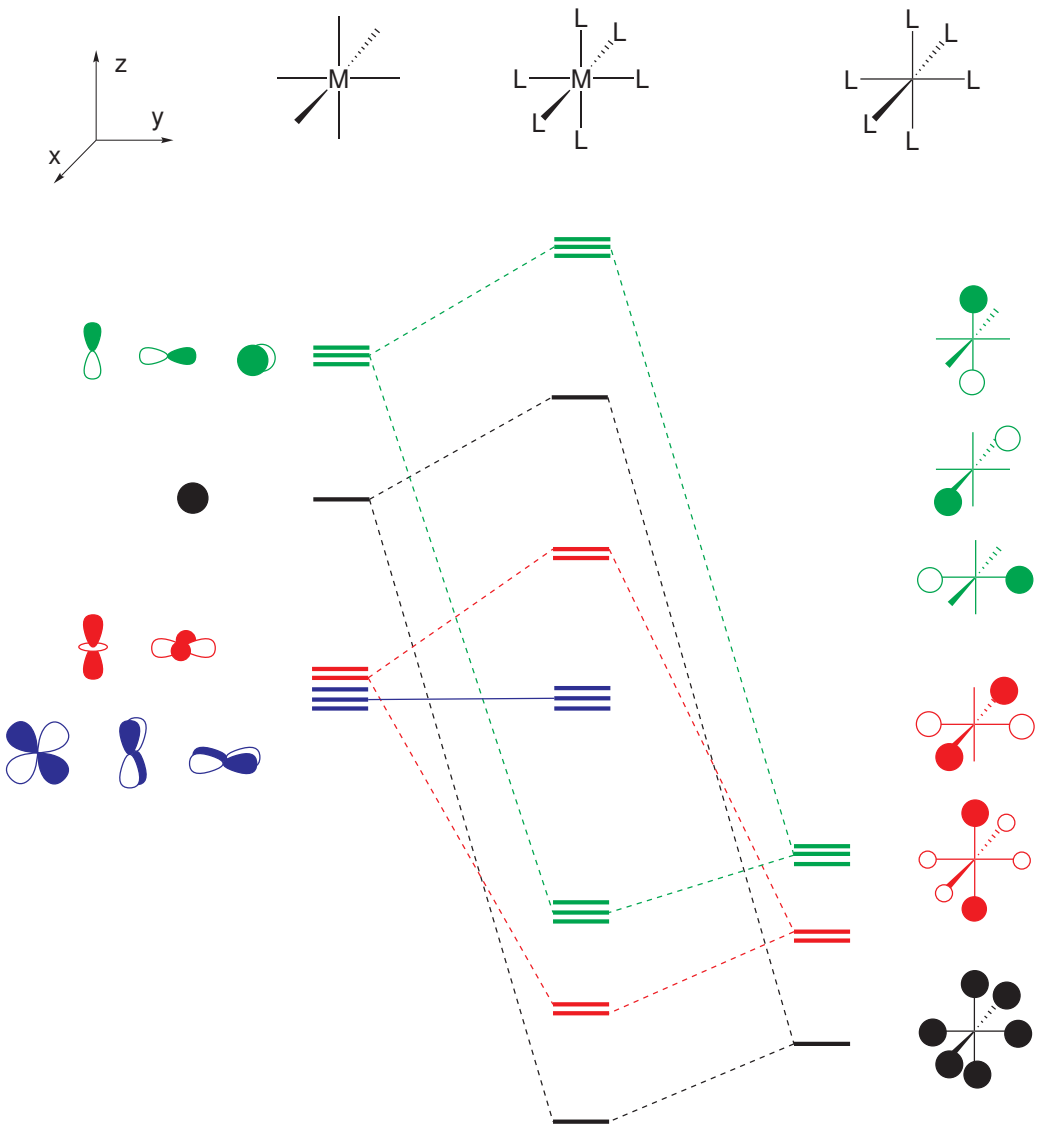
They use Concepts to Rationalize the Results

- Lewis structure, Resonance, Hyperconjugation
- Electonegativity, Hybridation

Computational Chemistry



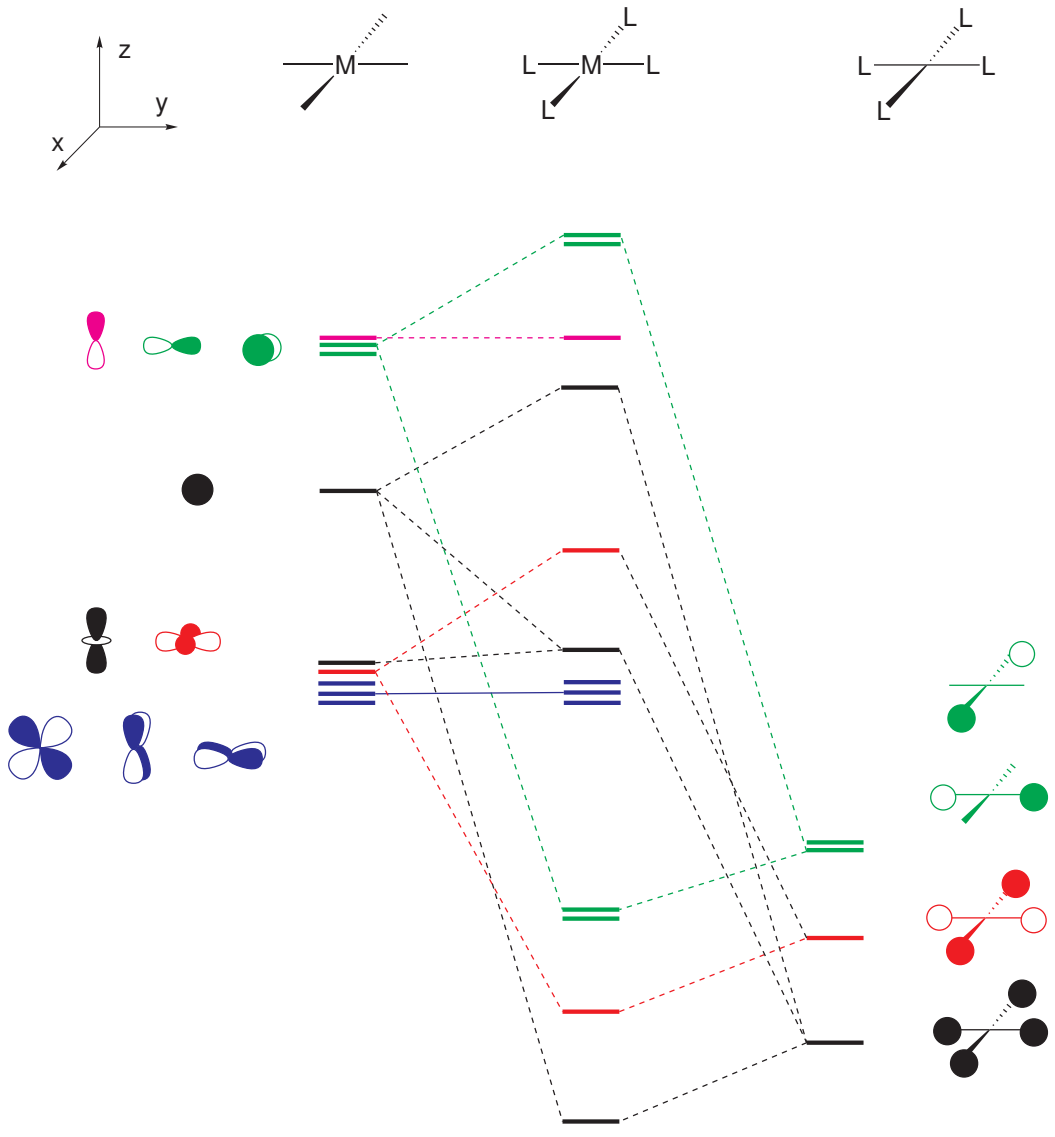
Complex with octahedral geometry



3 non bonding orbitals :
up to 6 d electrons possible.

18 electrons rule!

Complex with square planar geometry



3 non bonding orbitals :
up to 6 electrons possible.

1 quasi non bonding orbital :
up to 2 electrons possible.

stable with 16 electrons!

Natural Bonding Orbitals: Concept

Use Information in Wavefunction to Build a Lewis Structure

- Electronic Configuration for the Atoms in the Molecule :

  Natural Atomic Orbitals (NAO)

- Mixing of Natural Atomic Orbitals to Build Hybrids :

  Natural Hybrid Orbitals (NHO)

- Covalent Bond as Overlap between Hybrids :

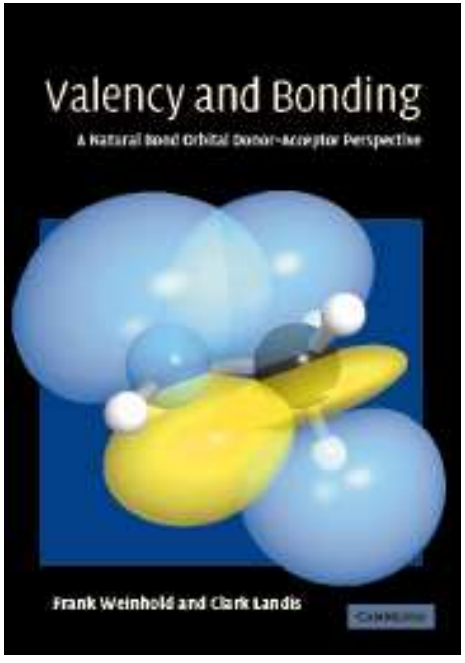
  Natural Bond Orbitals (NBO)

- Departure From Stricktly Localized Lewis Structure :

  Natural Localized Molecular Orbitals (NLMO)

Bibliography

NBO Web Site : **http://www.chem.wisc.edu/∼nbo5/**



Valency and Bonding

A Natural Bond Orbital Donor-Acceptor Perspective

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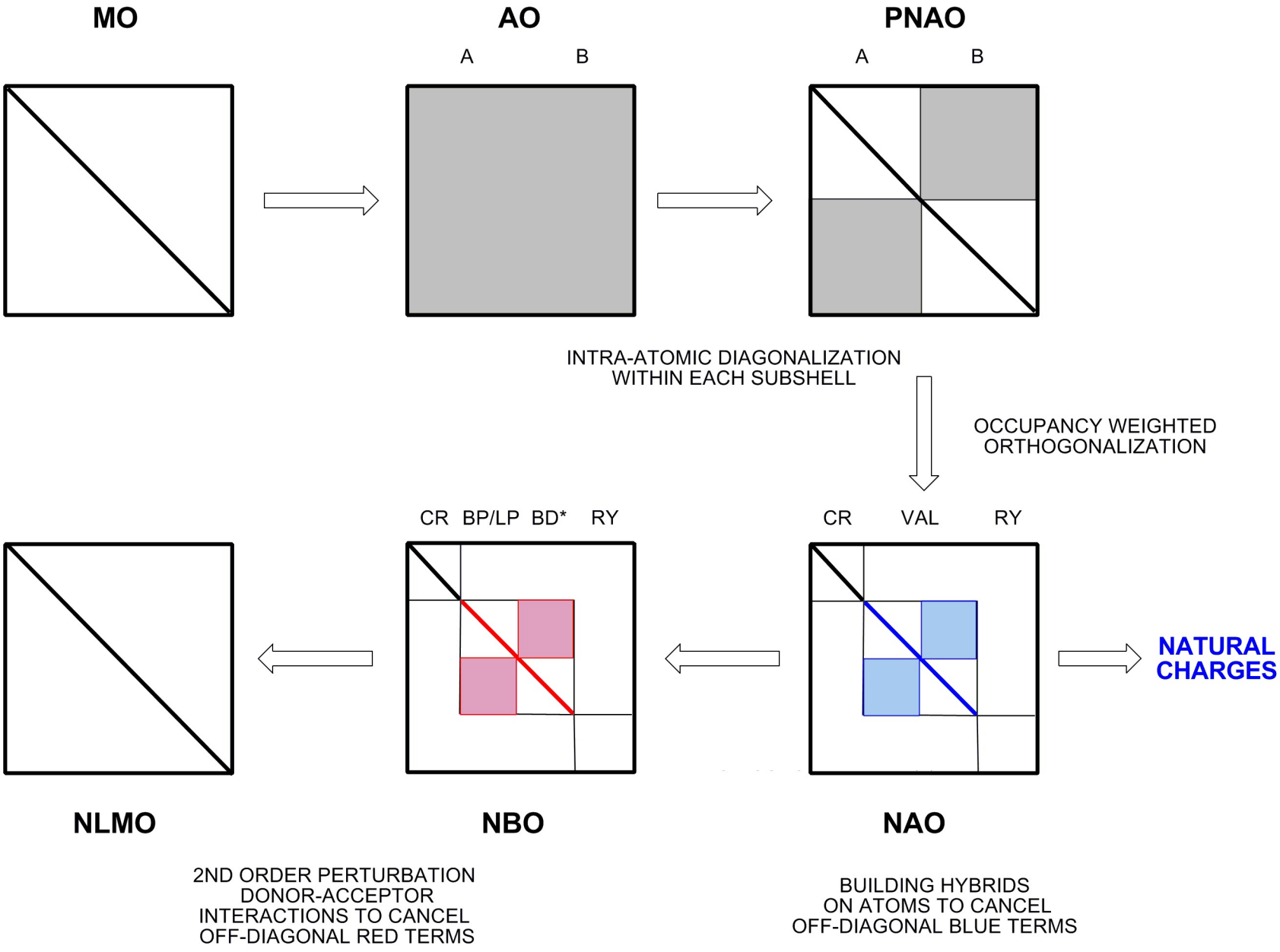
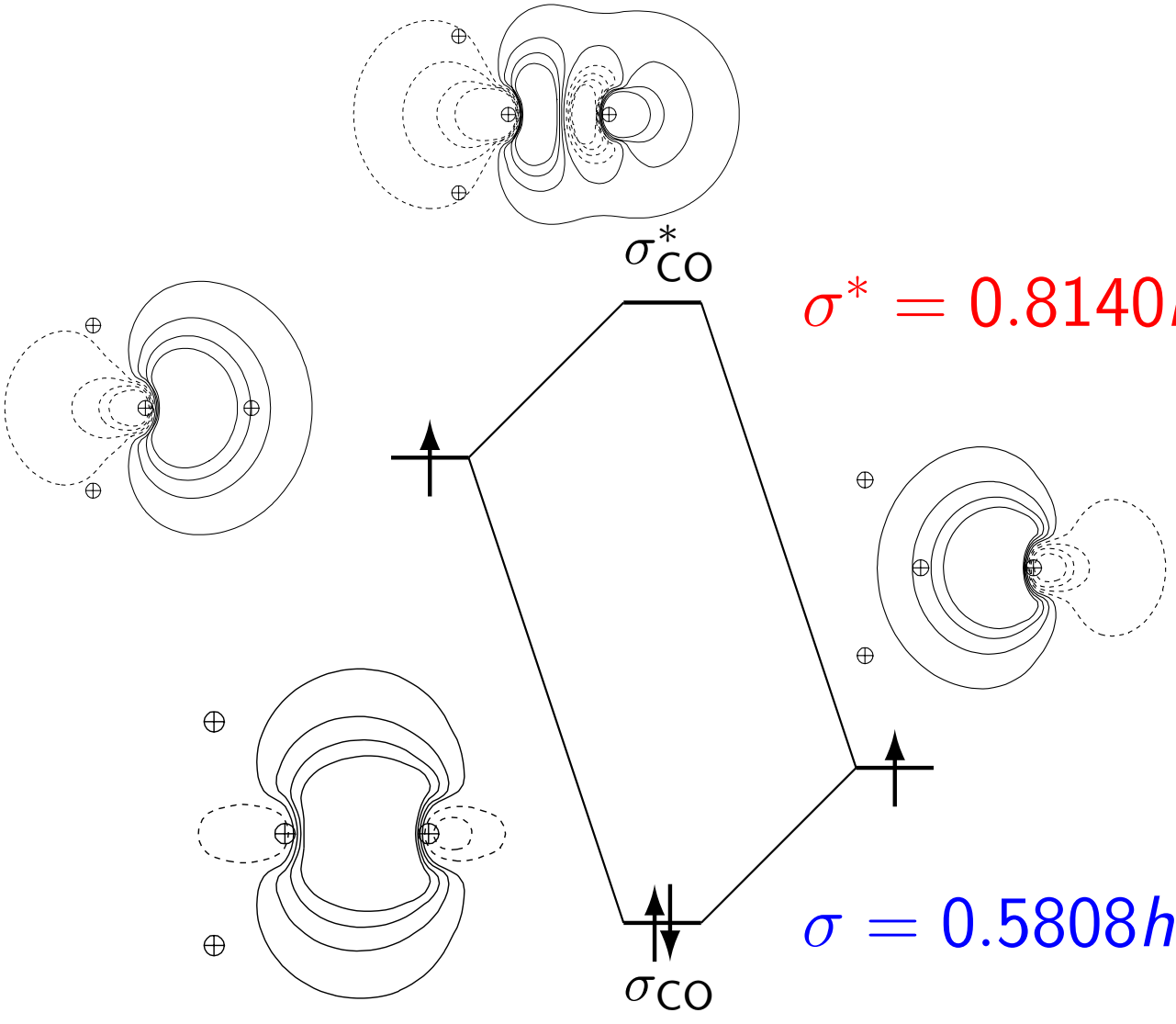
DOI: 10.2277/0521831288

NBO Procedure: Summary



Description of an NBO

The Overlap between two Hybrids to Create a Bonding Orbital Automatically Generates an Antibonding Orbital.

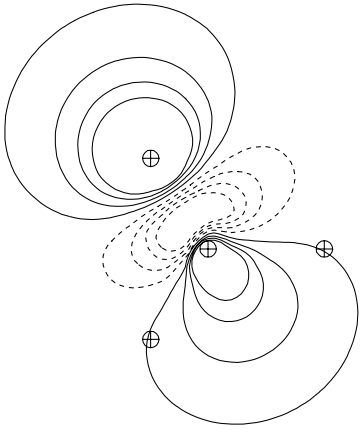


$$\sigma^* = 0.8140h_C - 0.5808h_O$$

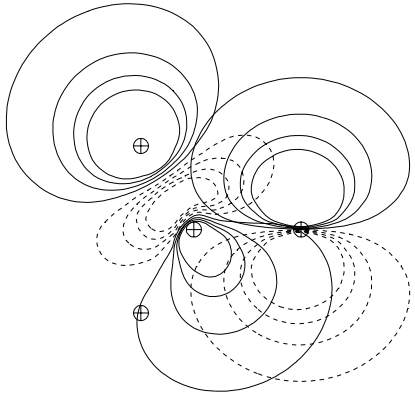
$$\sigma = 0.5808h_C + 0.8140h_O$$

Hyperconjugation Interactions

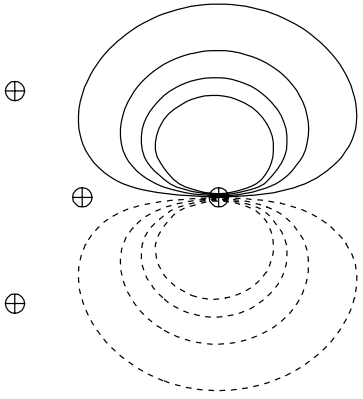
The Empty AntiBonds can Accept Electron Density from the Occupied Bonds : **Departure from Lewis Structure**



σ^*_{CH}

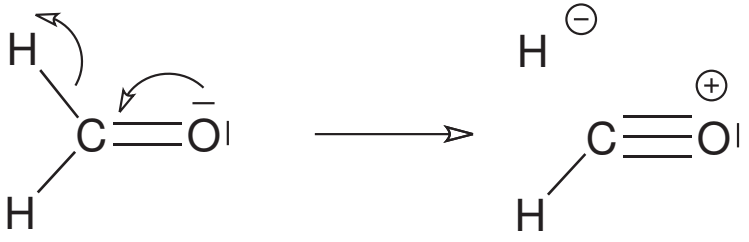


Overlap : 0.2126



LP_O

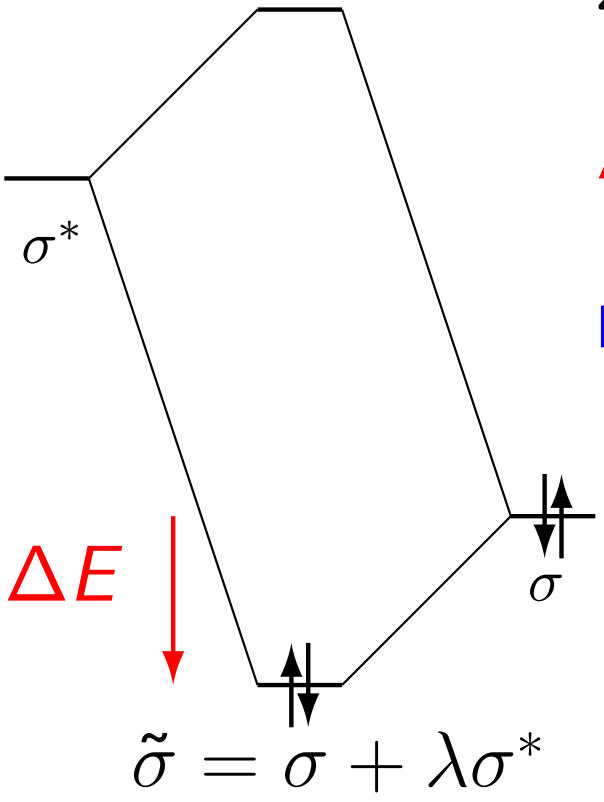
Resonance Forms :



How Stabilizing is this Resonance ?

Donor-Acceptor Interactions

The Departure from the Lewis Structure is Due to Donor-Acceptor Electron Transfers between Occupied and Vacant NBOs.



2nd Order Perturbation Theory

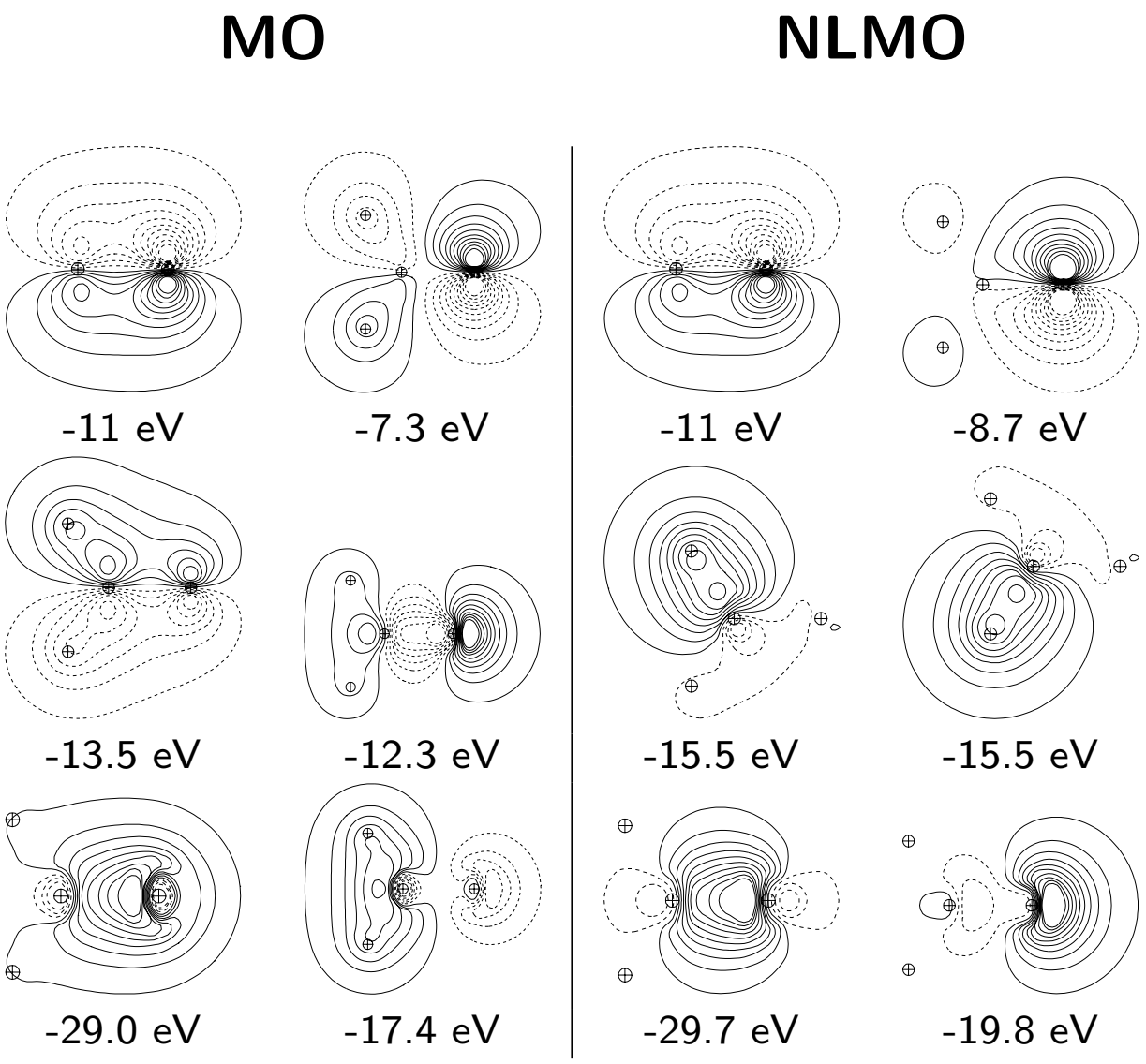
$$\Delta E = -2\frac{\langle\sigma|\,\mathcal{F}\,|\sigma^*\rangle^2}{\varepsilon_{\sigma^*} - \varepsilon_\sigma}$$

$\mathrm{LP}_0 \longrightarrow \sigma^*_{\mathrm{CH}} = 20.1$ kcal mol^{-1}

The Perturbed NBO Gives Access to **N**atural **L**ocalized **M**olecular **O**rbitals which Are Occupied stricktly by 2 Electrons

$\tilde{\mathrm{LP}}_0 = 0.9706\mathrm{LP}_0 + 0.1631\sigma^*_{\mathrm{CH}} + 0.1631\sigma'^*_{\mathrm{CH}}$

MO vs. NLMO


MO
NLMO
-11 eV
-7.3 eV
-11 eV
-8.7 eV
-13.5 eV
-12.3 eV
-15.5 eV
-15.5 eV
-29.0 eV
-17.4 eV
-29.7 eV
-19.8 eV

NBO and Transition Metal Complexes

Group 3-12 binary oxides, chlorides and alkyl compounds that are avalaible most cheaply and in largest quantities follow a simple relation.

$$|G_M - 6| + n_X V_X + e_u = 6$$

G_M : Group Number of the Metal
n_X : Number of X Ligands
V_X : Valency of the X Ligand
e_u : Number of Unpaired Electron

	3	4	5	6	8	9	10
chlorides	$ScCl_3$	$TiCl_4$	$NbCl_5$	WCl_5	$RuCl_3$	$RhCl_3$	$PdCl_2$
oxides	Sc_2O_3	TiO_2	Nb_2O_5	WO_3	RuO_2	Rh_2O_3	PdO
alkyls		$ZrMe_4$	$NbMe_5$	WMe_6	$Ru(Mes)_4$	$Rh(Mes)_3$	

Dodectet Rule

Each bond linkage to a **monovalent ligand X** is associated with a shared pair of electrons :

$$e_{bp} = 2n_X V_X$$

Each bond linkage to a **Lewis base L** is associated with a dative pair of electrons :

$$e_{dp} = 2n_L$$

For a closed shell compound with $G_M \geq 6$, the empirical rule gives :

$$G_M - n_X V_X + e_{bp} + 2n_L = 12$$

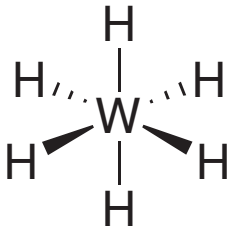
with the non-bonded lone pair electrons

$$e_{lp} = G_M - n_X V_x$$

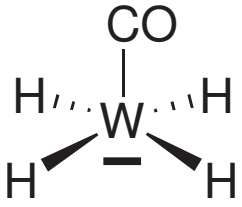
The dodectet rule holds : $e_{bp} + e_{lp} + e_{dp} = 12$

Case Study : $WH_x(CO)_y$

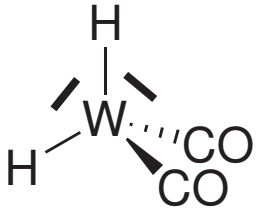
In each case, NBO gives a Lewis structure that obeys the dodectet rule.



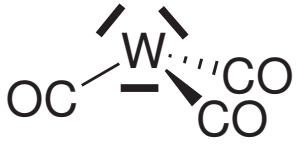
$e_{bp} = 12$
$e_{lp} = G_M - 6 = 0$
$e_{dp} = 0$



$e_{bp} = 8$
$e_{lp} = G_M - 4 = 2$
$e_{dp} = 2$



$e_{bp} = 4$
$e_{lp} = G_M - 2 = 4$
$e_{dp} = 4$



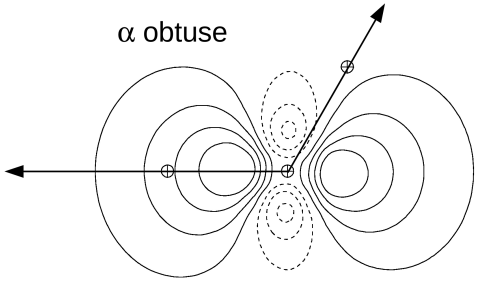
$e_{bp} = 0$
$e_{lp} = G_M - 0 = 6$
$e_{dp} = 6$

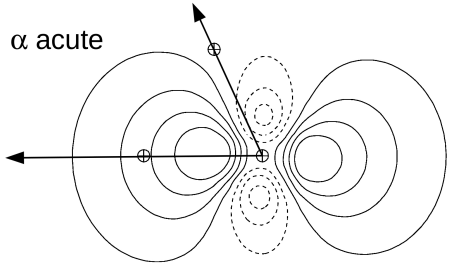
Only one s and five d orbitals are necessary to build the hybrids on the metal able to accomodate 6 pairs of electrons.

sd Hybridation

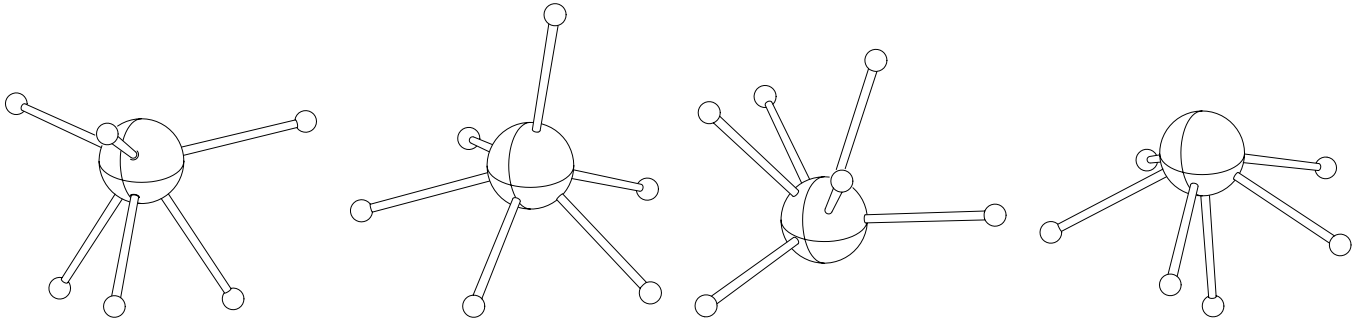
Geometry Dictated by Hybridation between s and d Orbitals

	α_{accute}	α_{obtuse}
sd	90.0	90.0
sd^2	90.0	90.0
sd^3	70.53	109.47
sd^4	65.91	114.09
sd^5	63.43	116.57
sd^{10}	58.91	121.09
d	54.74	125.26





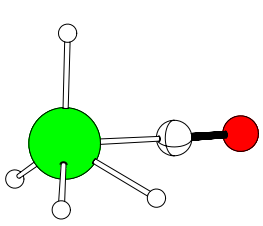
$\angle H - W - H = 62.4^\circ\ 67.0^\circ\ 114.6^\circ$



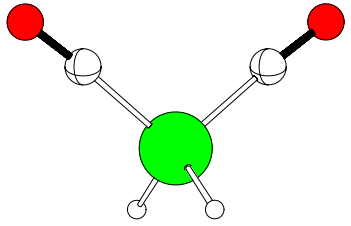
C_{3v}	C_{5v}	C_{3v}	C_{5v}
0.0	+0.2	+9.7	+17.4

Influence of a π-Accepting Ligand

The π-back-donation from a lone pair on the metal to a π-accepting orbital on the ligand induces changes in the preferred geometries.



0.0



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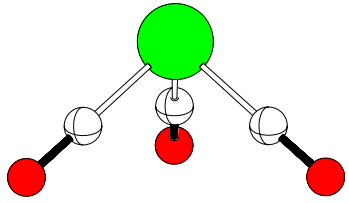

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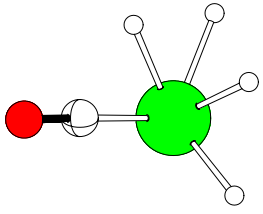
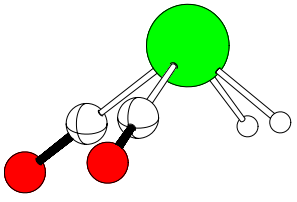
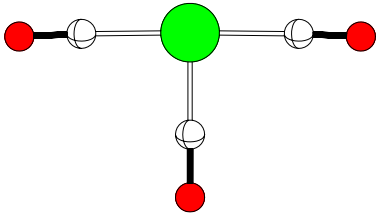


11.4



0.2



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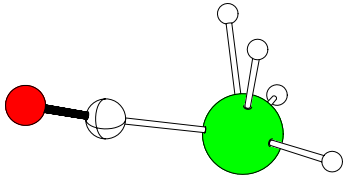

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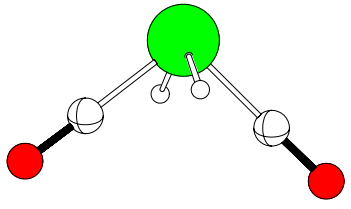
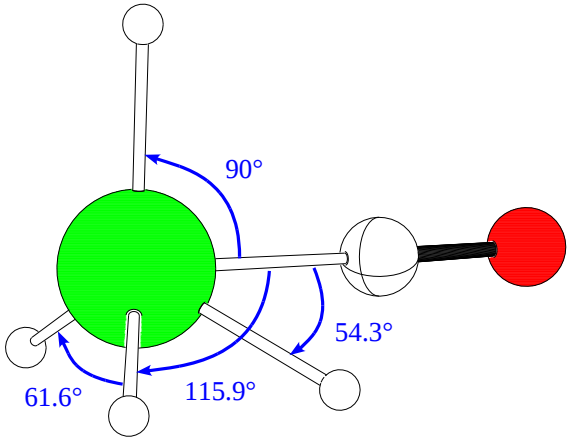


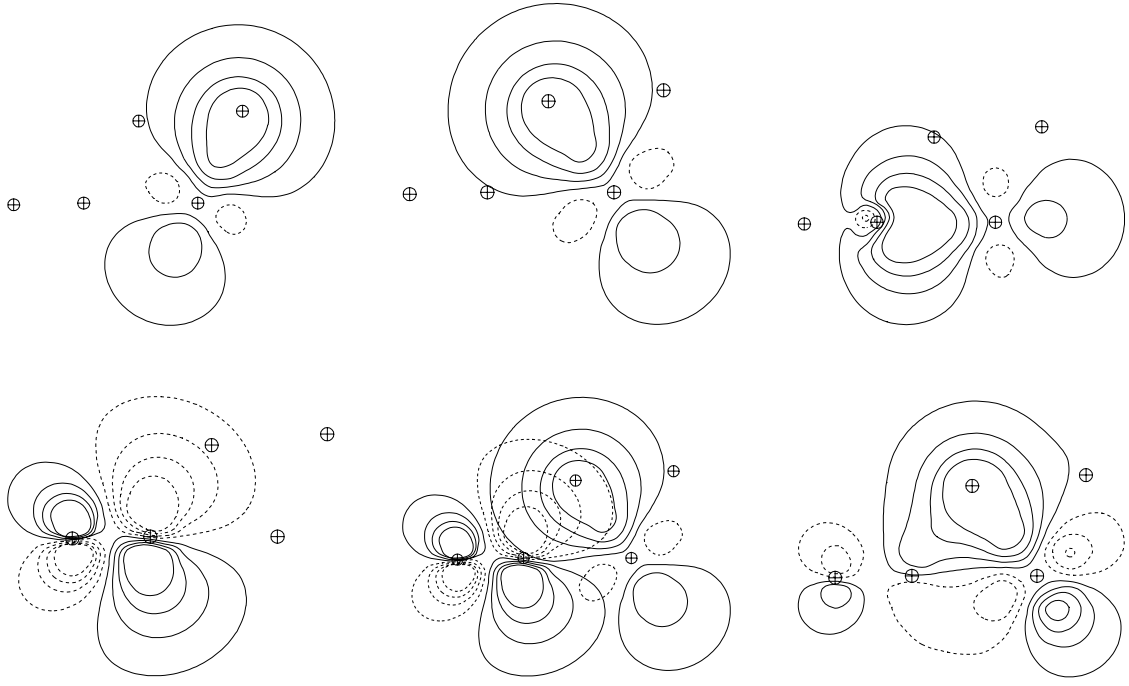
1.0

WH_4CO

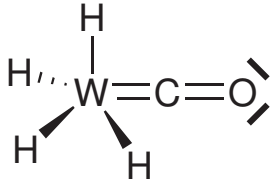
sd^4 Hybridation

65.9° and 114.1°

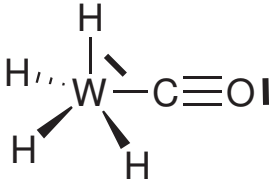




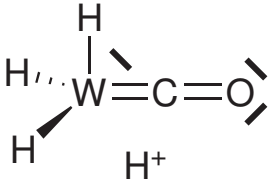
NLMO : $\tilde{\sigma}_{WH} = 0.92\sigma_{WH} - 0.33\pi^*_{CO}$



%NRT 37.9



37.0



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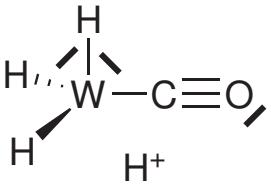
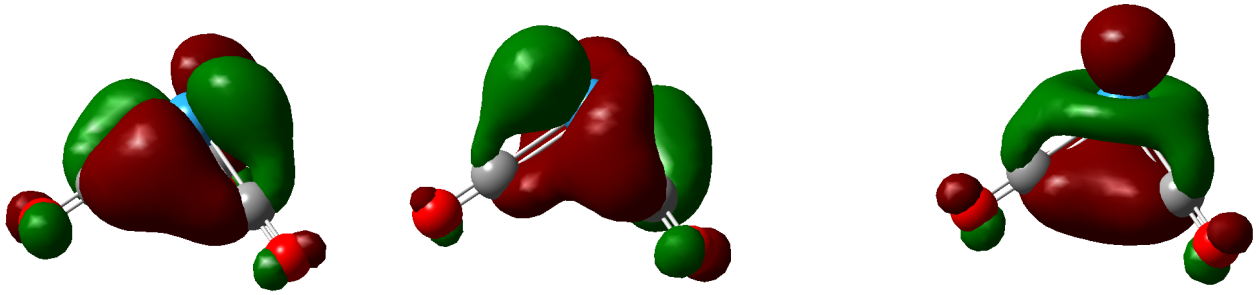


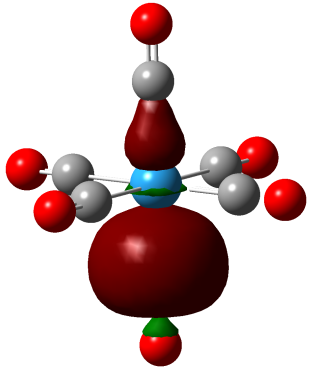
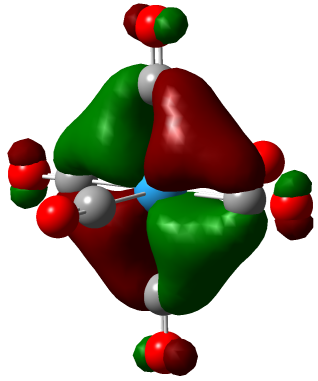
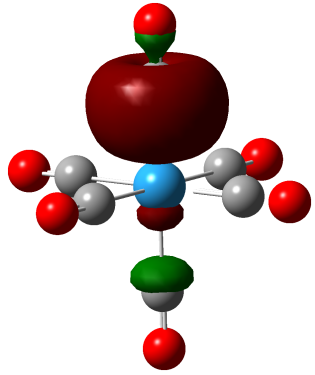
5.9

$W(CO)_3$ and $W(CO)_6$

$W(CO)_3$: Three Lone Pairs Involved in Back-Bonding

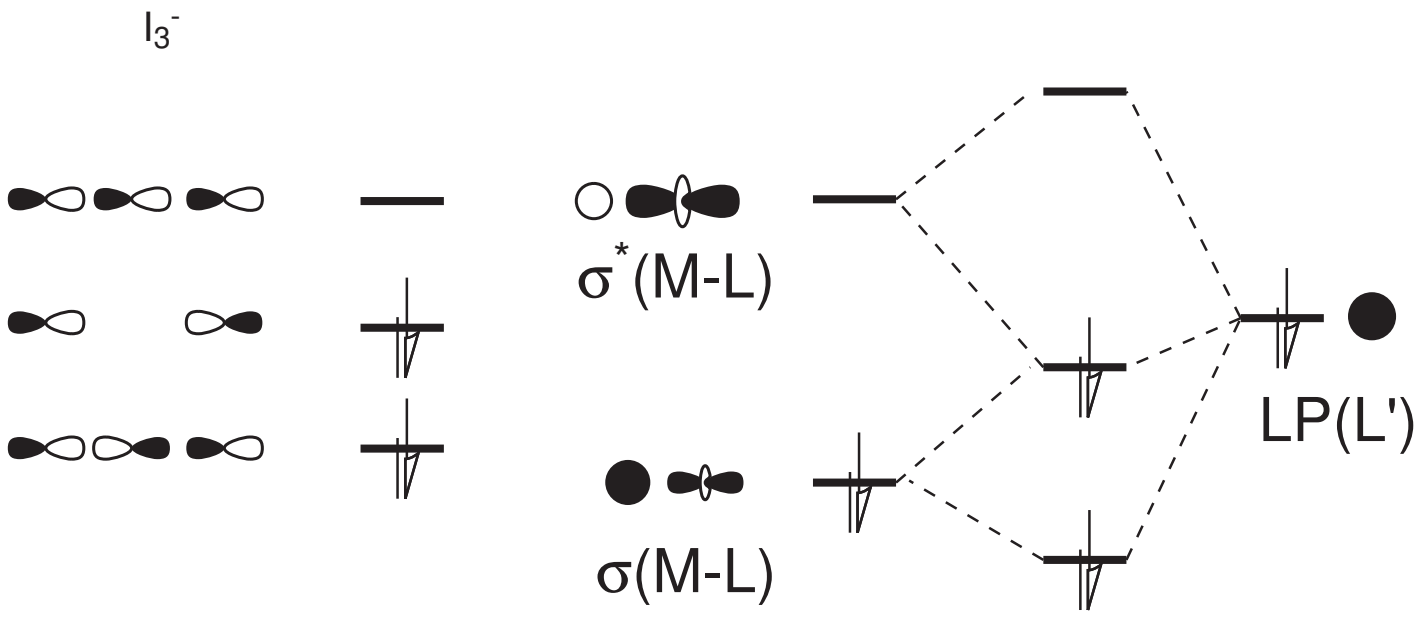


$W(CO)_6$ is Hypervalent (18-e) with 3-Centers 4-Electrons Bonds

	σ (W-C)	LP(W)	LP(C)
			
NBO	-0.527	-0.178	-0.204
NLMO	-0.638	-0.272	-0.600

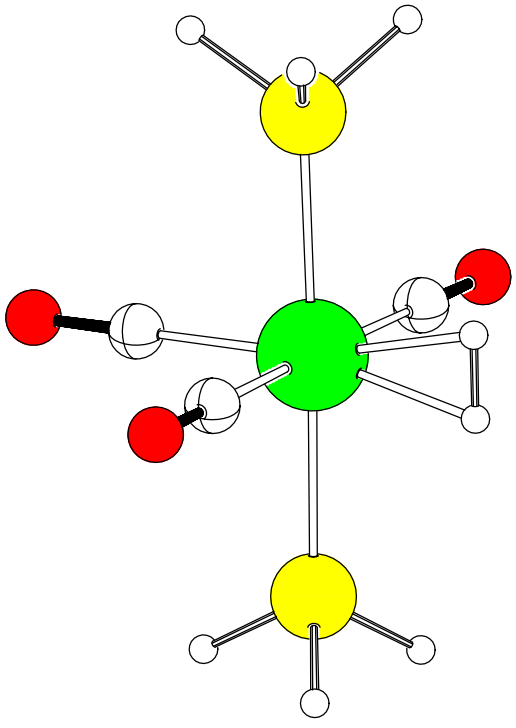
ω-Bonds

The vast majority of transition metal complexes are either octahedral or square planar with 18- or 16-electrons, respectively. The mechanism to override the 12-electron rule and to add extra ligands involves a particular type of bonding, the 3c-4e ω-bond introduce by Pimentel to describe bonding in hypervalent main group compounds.

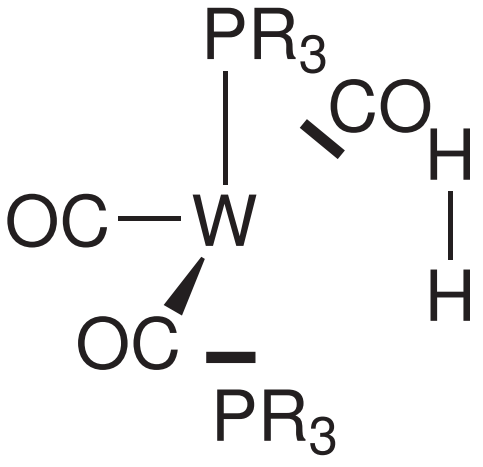


Kubas' Complex

The first dihydrogen complex $W(CO)_3(PR_3)_2(H_2)$ is a typical octahedral complex following the 18-electron rule.



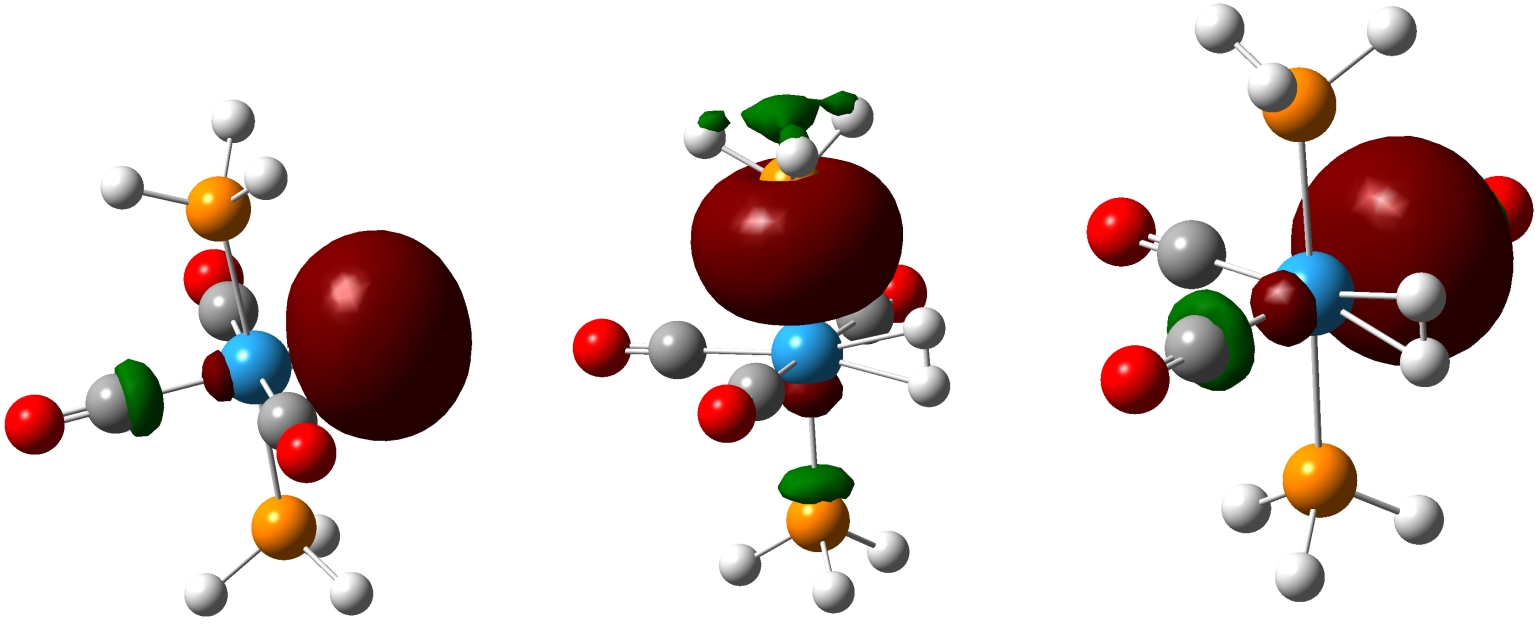
The Lewis structure proposed by NBO contains a $W(CO)_2(PR_3)$ 12-electron fragment and three entities (CO, PR_3, H_2) in interaction through 3-center 4-electron ω-bonds to reach an 18-electron configuration.



sd^2 Hybridation : three M-L bonds at 90°.

Analyzing Electron Transfer Upon Coordination

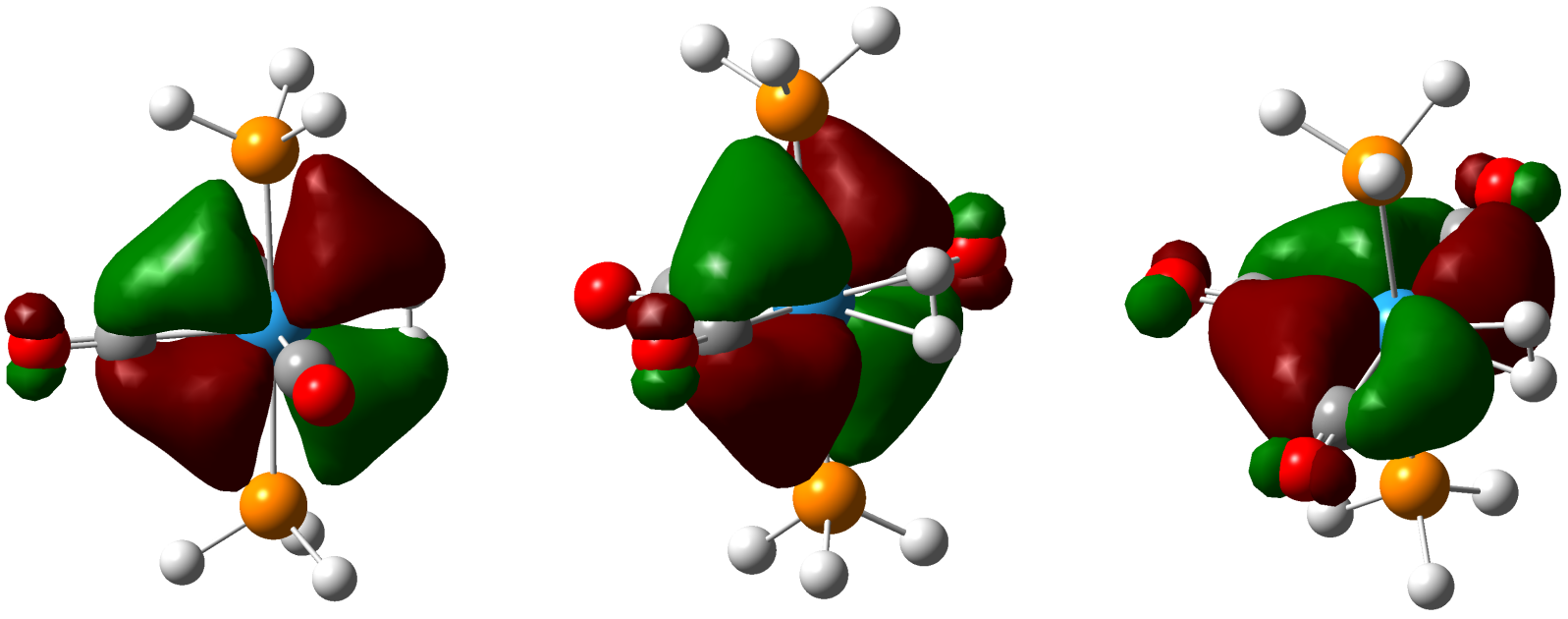
The composition of the NLMO allows to estimate the strength of σ-donation from the ligands.



$$\tilde{\sigma}(H_2) = 0.92\sigma(H_2) + 0.37\sigma^*(WC)$$
$$\tilde{LP}(P) = 0.86LP(P) + 0.46\sigma^*(WP)$$
$$\tilde{LP}(C) = 0.87LP(C) + 0.46\sigma^*(WC)$$

Analyzing Electron Transfer Upon Coordination

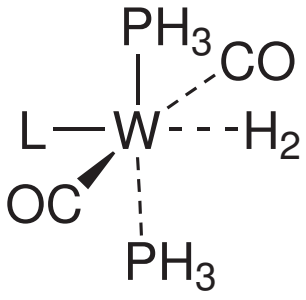
The composition of the NLMO allows to estimate the strength of π-back-donation from the metal.



$$\tilde{LP}(W) = 0.90LP(W) + 0.3\pi^*(CO) + 0.2\sigma^*(H_2)$$
$$\tilde{LP}(W) = 0.87LP(W) + 0.3\pi^*(CO) + 0.3\pi'^*(CO)$$
$$\tilde{LP}(W) = 0.85LP(W) + 0.32\pi^*(CO) + 0.28(\pi'^*(CO) + \pi''^*(CO))$$

Analyzing Trans Influence

The composition of the $\tilde{\sigma}(H_2)$ and $\tilde{LP}(W)$ NLMOs allows to estimate the strength of σ-donation and π-back-donation.



CO H–H = 0.853 Å

$\tilde{\sigma}(H_2) = 0.92\sigma(H_2) + 0.37\sigma^*(WC)$

$\tilde{LP}(W) = 0.90LP(W) + 0.3\pi^*(CO) + 0.2\sigma^*(H_2)$

NHC H–H = 0.930 Å

$\tilde{\sigma}(H_2) = 0.895\sigma(H_2) + 0.418\sigma^*(WC)$

$\tilde{LP}(W) = 0.86LP(W) + 0.18\pi^*(CN) + 0.28\sigma^*(H_2)$

PH_3 H–H = 0.943 Å

$\tilde{\sigma}(H_2) = 0.886\sigma(H_2) + 0.432\sigma^*(WC)$

$\tilde{LP}(W) = 0.91LP(W) + 0.29\sigma^*(H_2)$

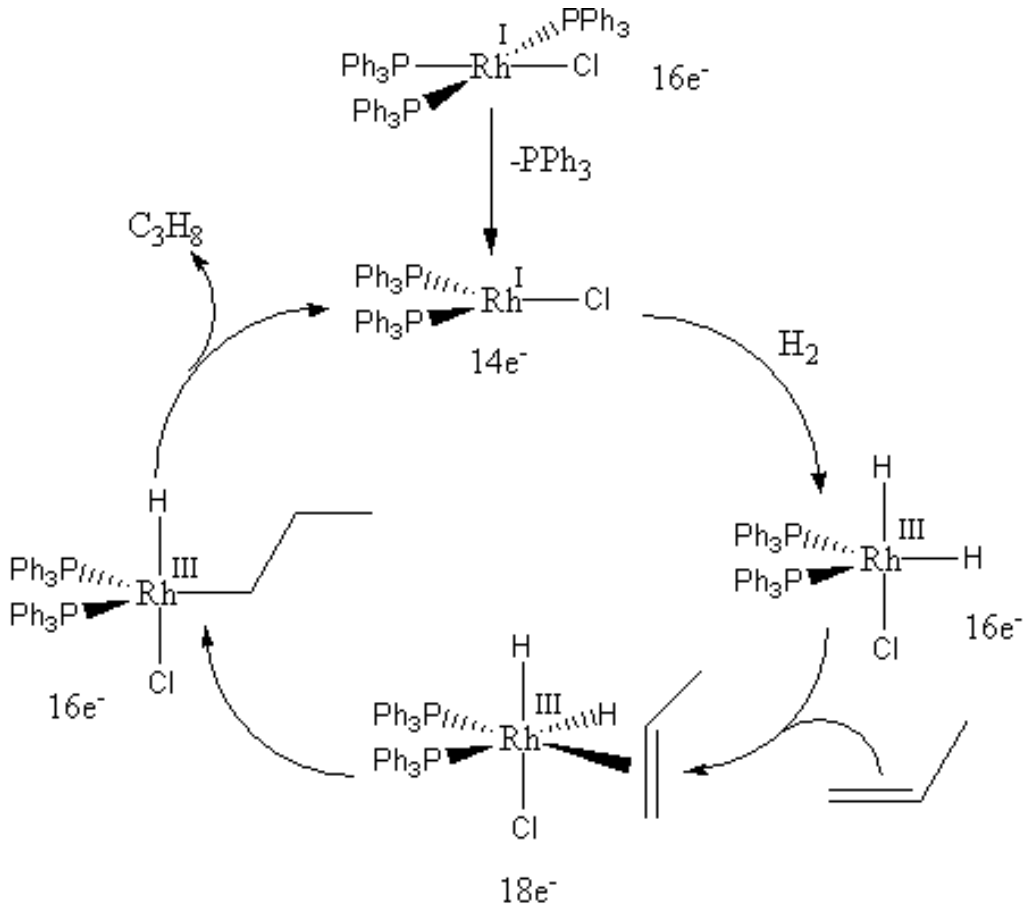
Observed H–H bond distance results from both σ-donation and π-back-donation.

Guidelines

- In general, an octahedral ML_6 d^6 complex will have a structure where the strong σ-donors are creating a C_{3v} like ML_3 12-electron fragment with mutual 90° angles.
- The three remaining ligands are engaged in non-symmetric ω-bonds and the composition of the NLMOs gives access to the extent of charge transfers from the ligand to the metal and from the metal to the ligand.
- The best situation for the structure is obtained when the weakest ligand is trans to the strongest one.
- The same situation holds for ML_4 d^8 complexes with a C_{2v}-like 12-electron building block.
- Again the same pattern is valid for ML_2 d^{10} systems with a 12-electron M-L unit as the Lewis structure.

Hydrogenation and Wilkinson's Catalyst

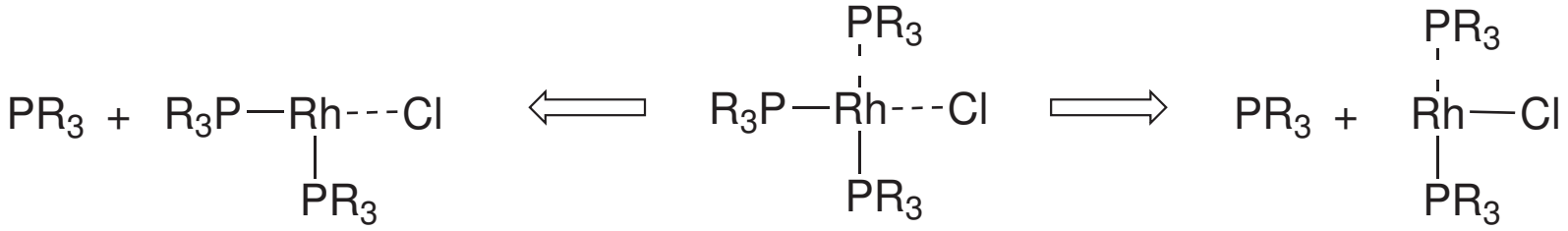
Many catalytic cycles are drawn with particular emphasis on the number of electrons but not on the relative positions of the various ligands with different stereoelectronic properties.



Catalytic hydrogenation of propylene

Phosphine Dissociation

Wilkinson's catalyst is hypervalent with 16-electron and upon phosphine dissociation another hypervalent complex is formed (14-electron).



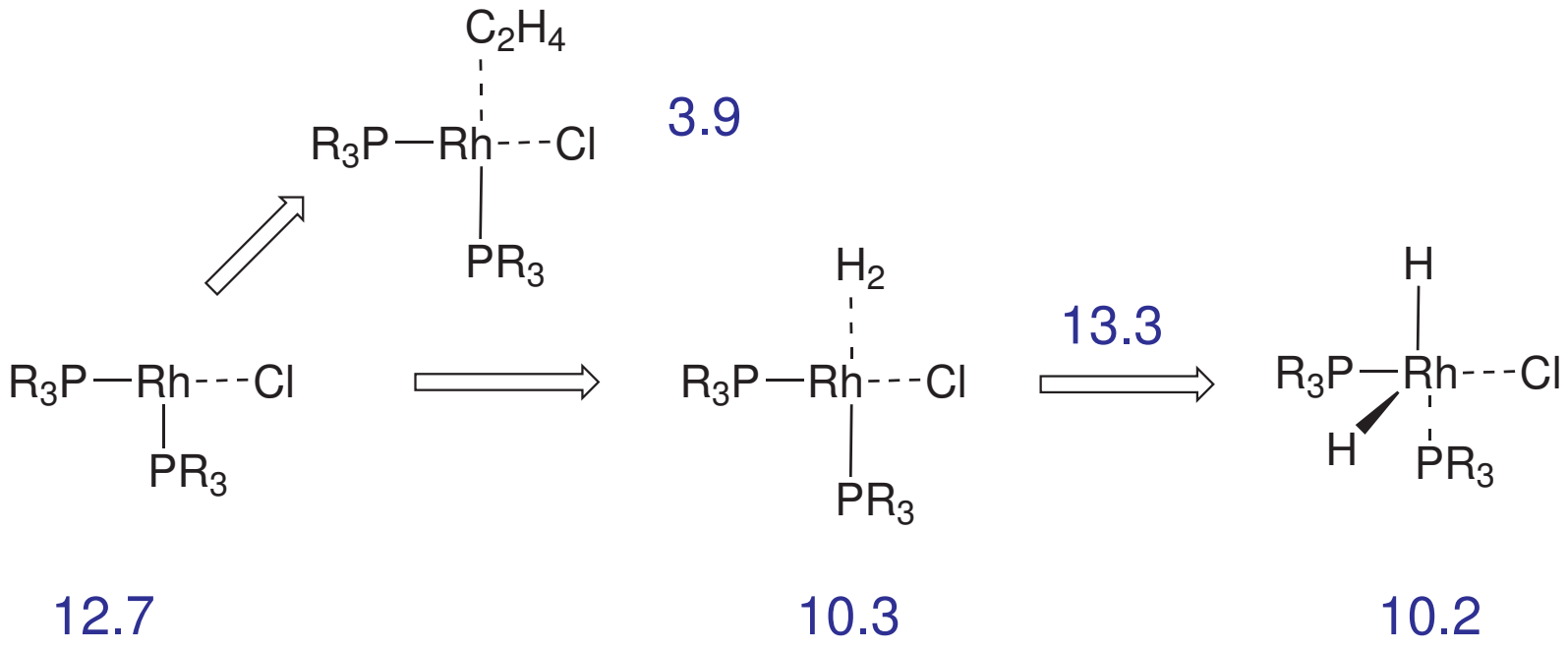
12.7 0.0 25.9

The ML_3 intermediate has a T-geometry and not a Y-shape.

The phosphine engaged in an ω-bond dissociates.

Dihydrogen Activation

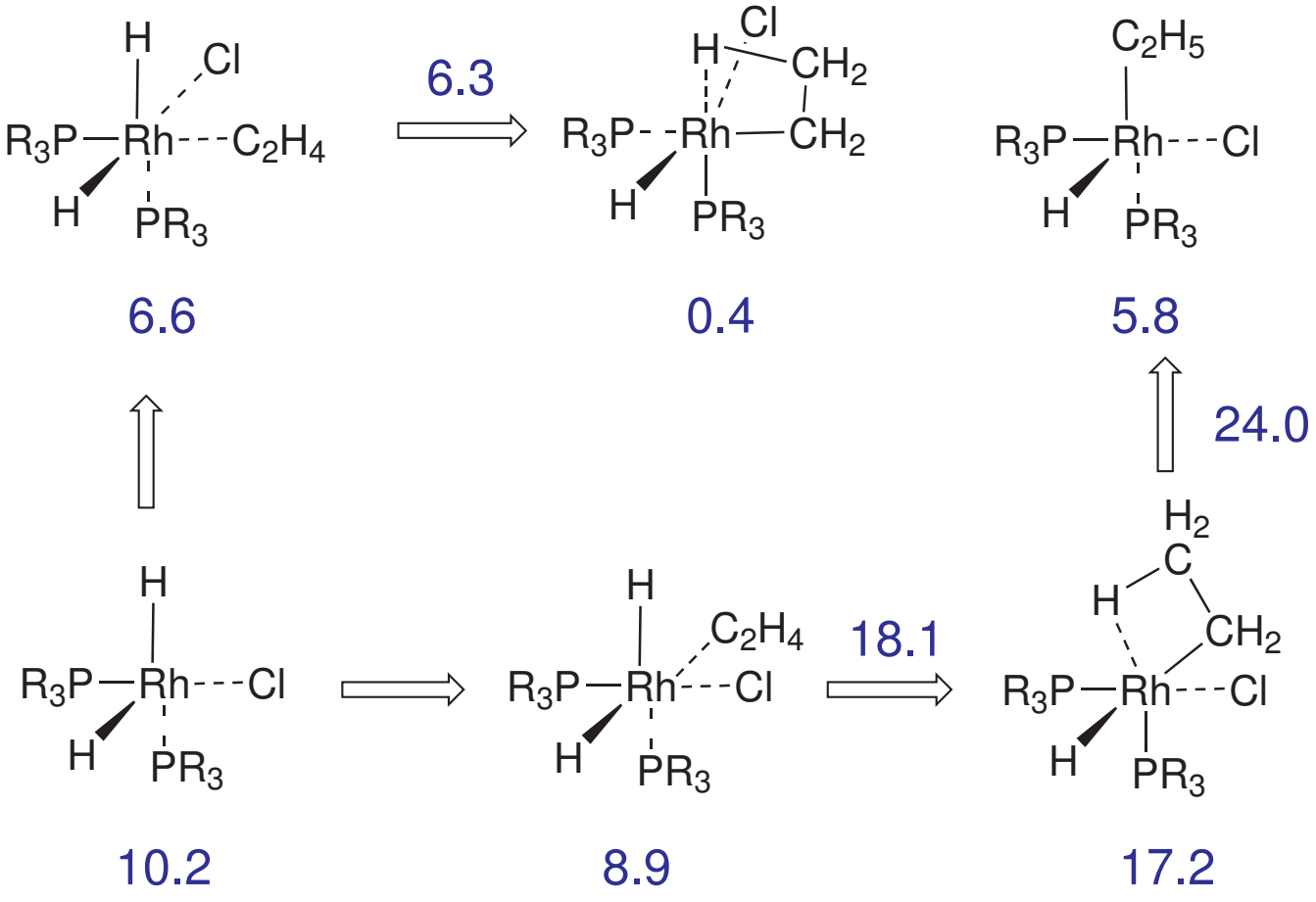
The vacant site trans to P does not allow too strong ethylene coordination and affords an easy pathway for H_2 oxidative addition.



The ML_5 intermediate is not a trigonal bipyramid.

The oxidative addition is easy because the nature of the M-P bond trans to H can change smoothly.

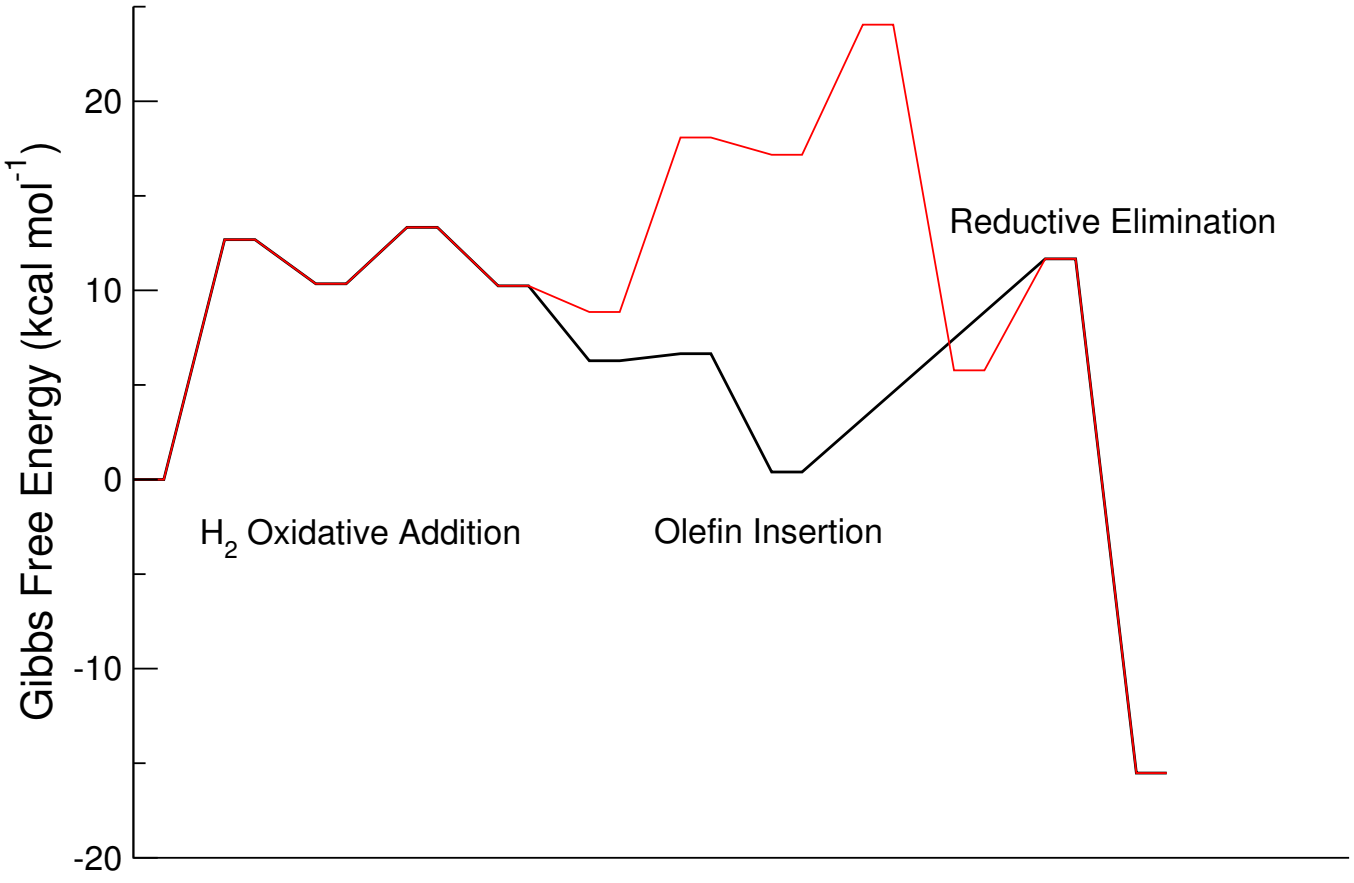
Olefin Insertion



The catalyst needs to adapt the relative position of the ligands to open a low energy pathway.

Best to avoid situations with two strong donor ligands mutually trans.

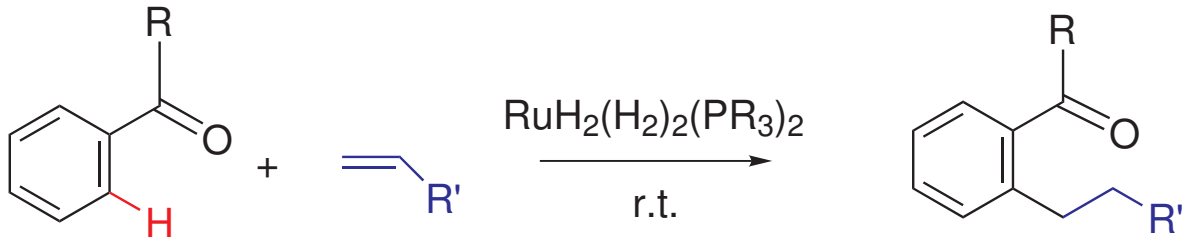
Overall Catalytic Cycle



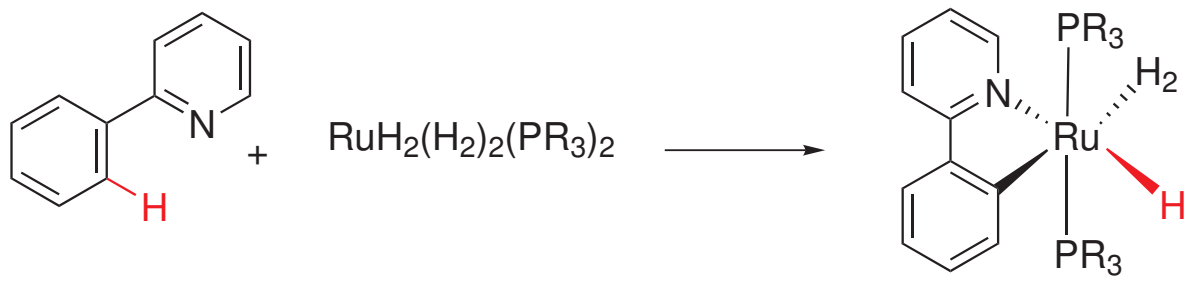
The easiest pathway preserves a situation where the three strongest ligands in each steps are creating a pseudo C_{3v} ML_3 fragment with the three remaining ligands engaged in ω-bonds.

Muraï's Reaction

Selective C–C coupling in *ortho* of the carbonyl group.
$Ru(H_2)_2(H)_2(PR_3)_2$ allows to work in mild conditions, contrary to the catalyst developped by Muraï, $Ru(CO)(H)_2(PPh_3)_3$.

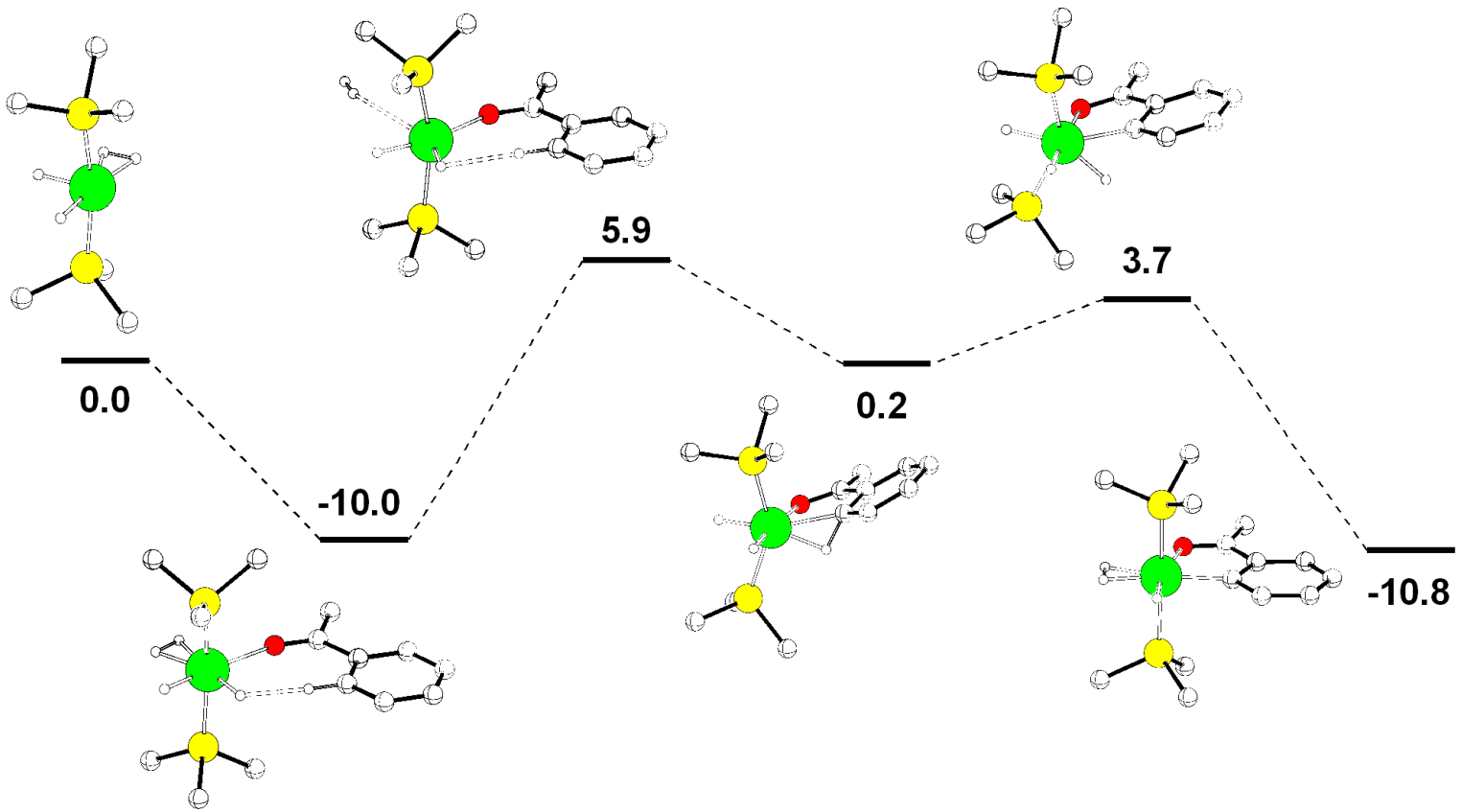


Substituting the carbonyl with pyridine impedes the C-C coupling but leads to the characterization of the C–H activation product.



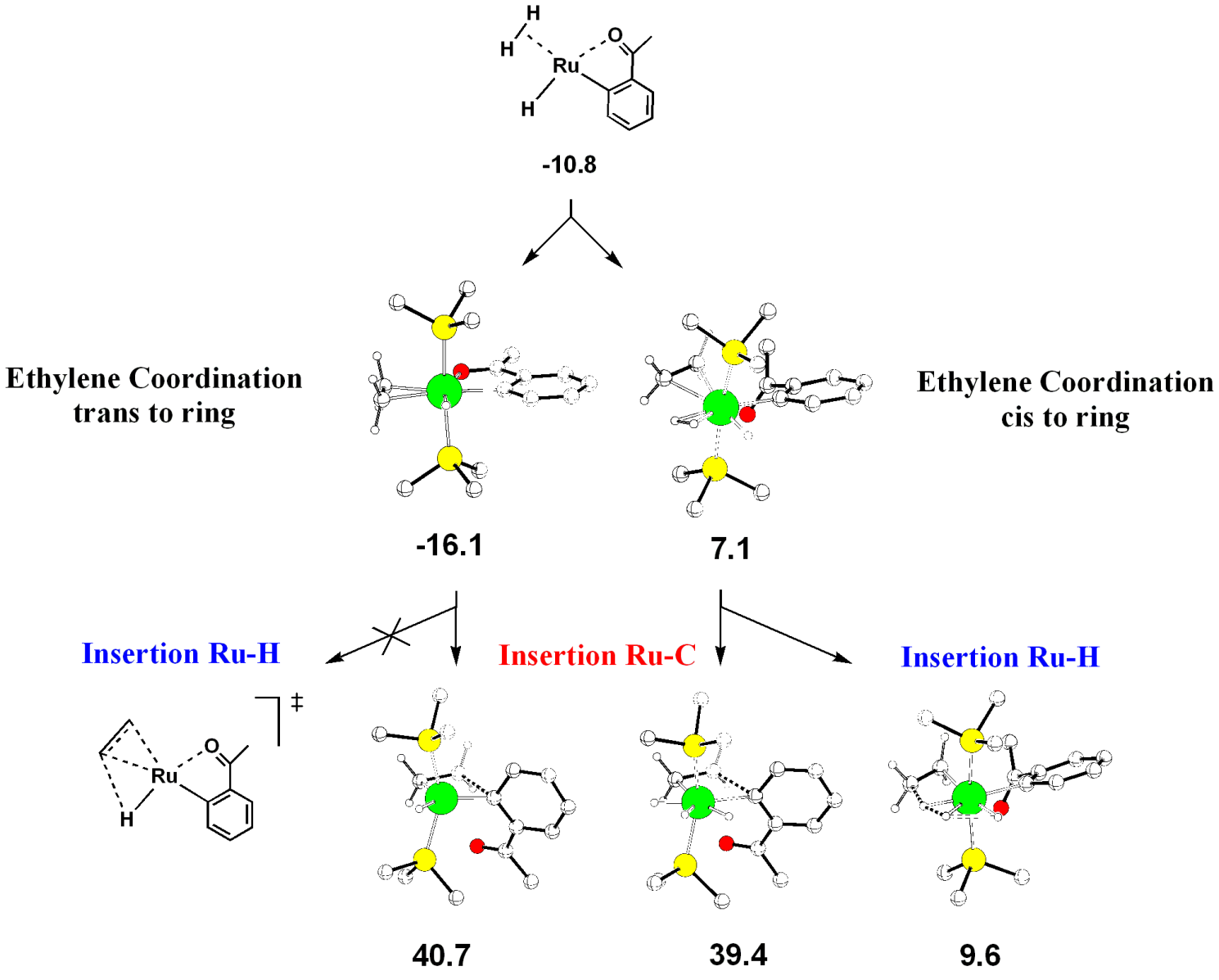
Ortho C-H activation with chelation

Formation of the agostic interaction more difficult than actual C–H cleavage.



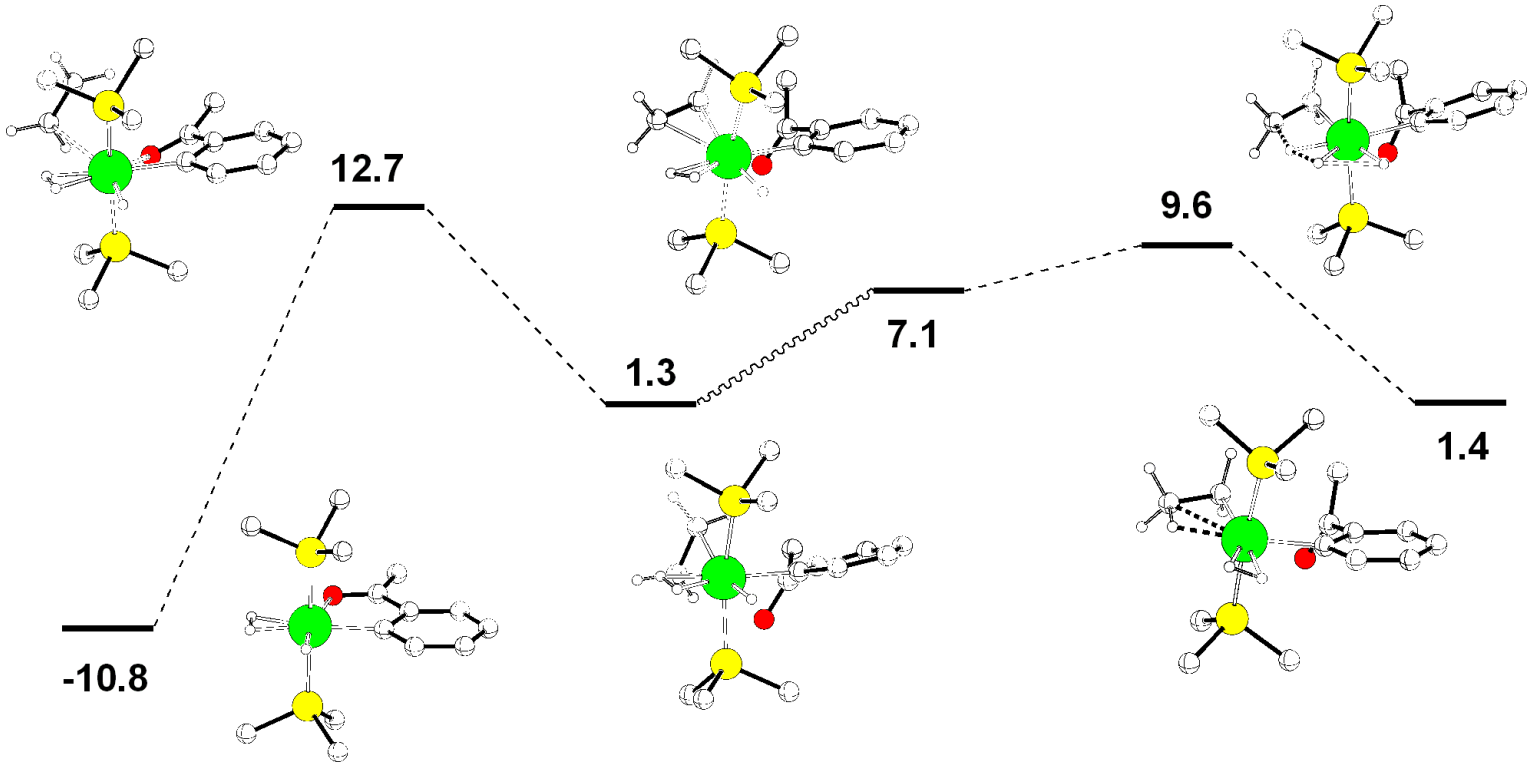
σ-CAM mechanism preserves the optimal relative position of the ligands

Ethylene Insertion into Ru–H or Ru–C ?



Ethylene Insertion

Coordination cis to aromatic ring is mandatory to achieve low barrier for insertion into Ru-H.

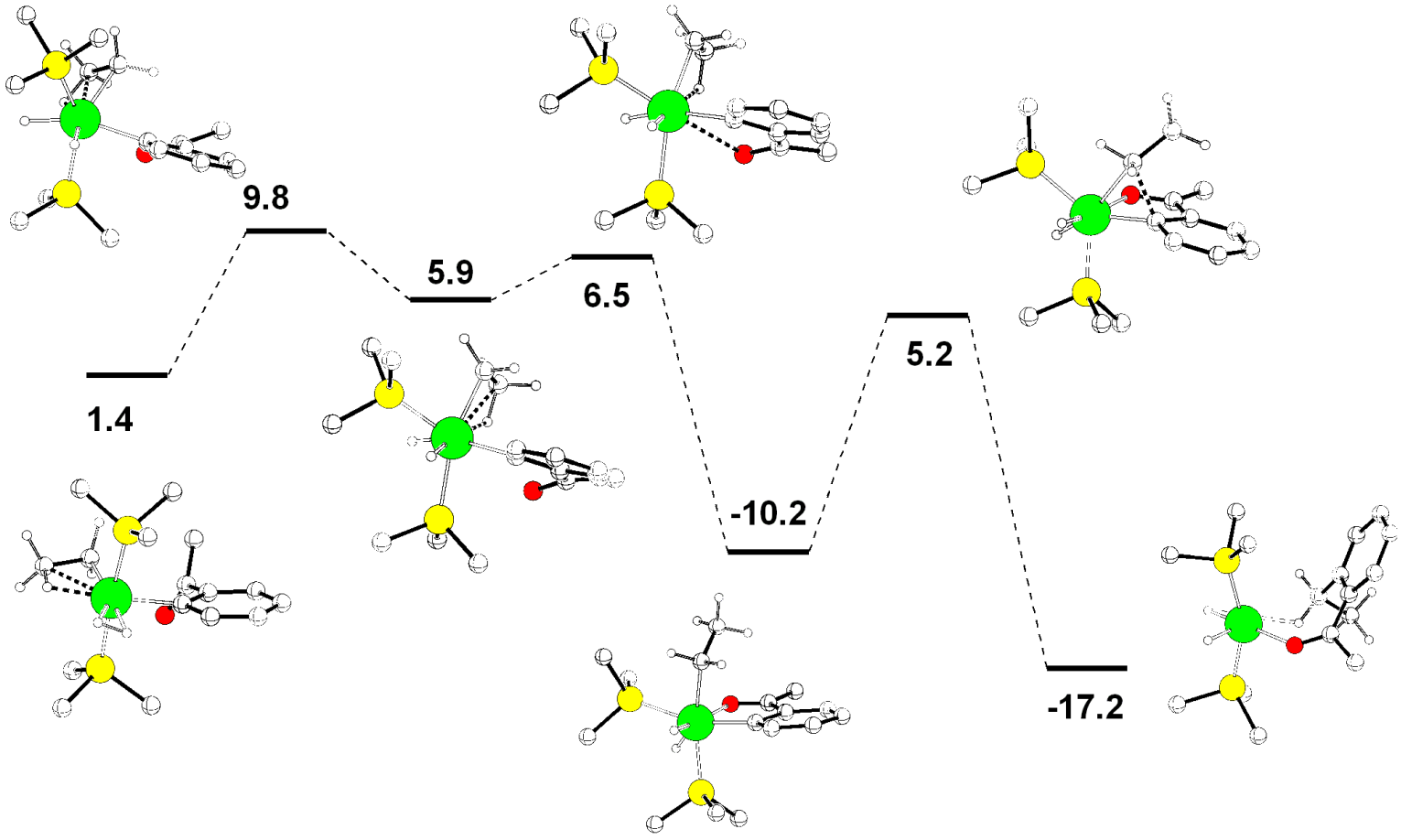


Insertion is associated with H transfer from H_2 to H.

Here again the typical ML_3 fragment of strong donors is maintained.

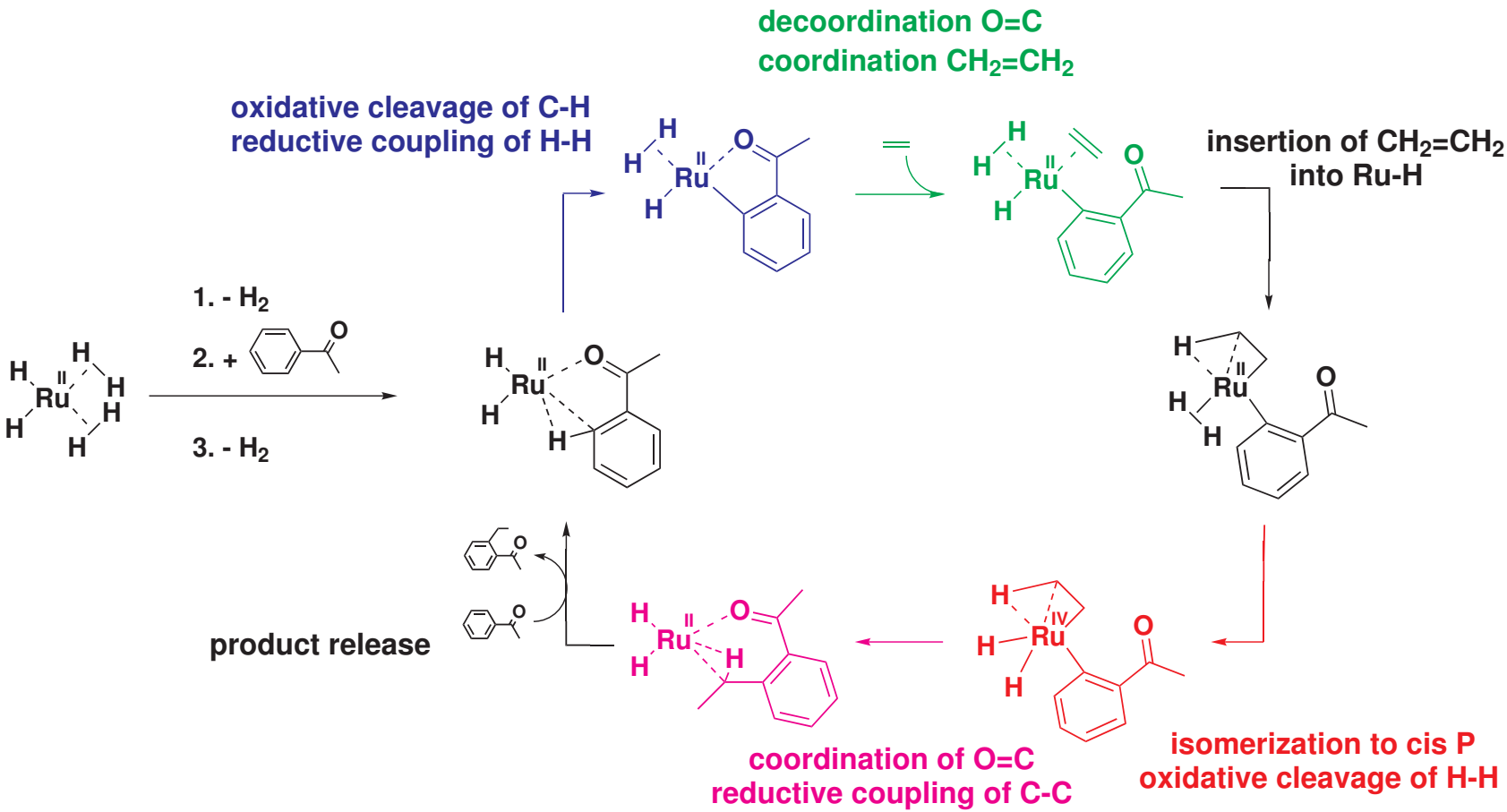
C-C Coupling

Isomerization to cis phosphines is necessary to achieve a geometry adapted to C-C coupling.



H–H cleavage is necessary to keep the cis phosphine complex at low energy

Catalytic Cycle



Conclusions

- Transition metals use essentially s and d orbitals to create bonds with the ligands: **sd^n hybridation**
- A stable configuration is reached when 6 pairs of electrons surround the metal: **dodectet rule**
- Hypervalency is easily obtained through donation from a lone pair into a M-X antibond: **ω-bond**.
- 18-electron or 16-electron complexes are hypervalent and the relative positions of the strong donor ligands follow the dodectet rule : **sd^2 or sd hybridation**.
- Dodectet rule also explains the mutual position of the ligands along a catalytic cycle.