College Toegepaste Quantumchemie 2017

KS-DFT – Chemische Binding – Reactiviteit

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Outline

Basic Models ——————————— Wed 4 Oct

1. KS MO theory and Activation Strain model

   ASM in action: **bond activation**

Structure, Bonding & Reactivity ——— Wed 11 Oct

2. Bite Angle and Bite-Angle Flexibility

3. **d** regime and **s** regime catalysts

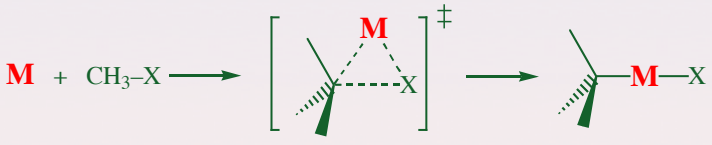
Part 2

Wed 11 Oct

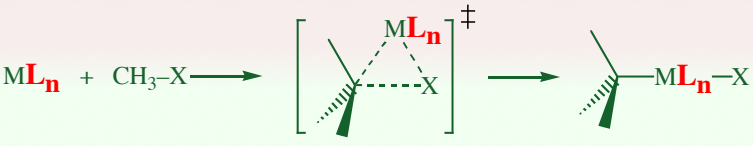
Fragment-oriented Design

of Catalysts for C–X Activation

1: Intrinsic reactivity:



2: "Improve" with ligands:



J. Chem. Theory Comput. **2005**, *1*, 286
J. Organomet. Chem. **2005**, *690*, 2191

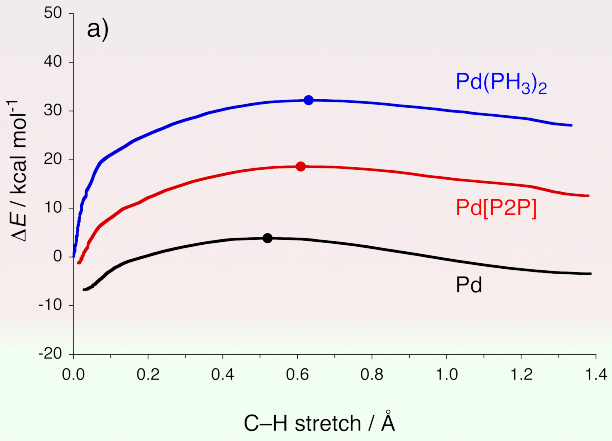
2 - Bite Angle & Bite-Angle Flexibility

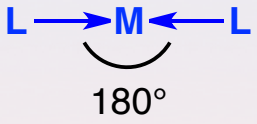
Bite Angle:
steric nature

Bidentate Ligands

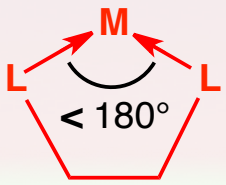
and the Steric Nature of the Bite Angle

Methane C–H activation:





- ligands raise barriers



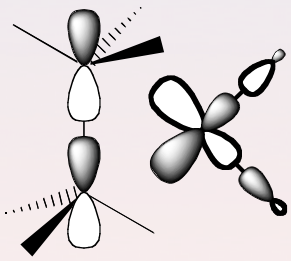
- smaller bite angle
  ➔ lower barrier

Chem. Eur. J. (communication) **2009**, *15*, 6112
ChemPhysChem. **2007**, *8*, 1170

Bidentate Ligands

and the Steric Nature of the Bite Angle

Bite-Angle Effect **according to literature**:



$\sigma^*_{C\text{-}X}$ "d_π"

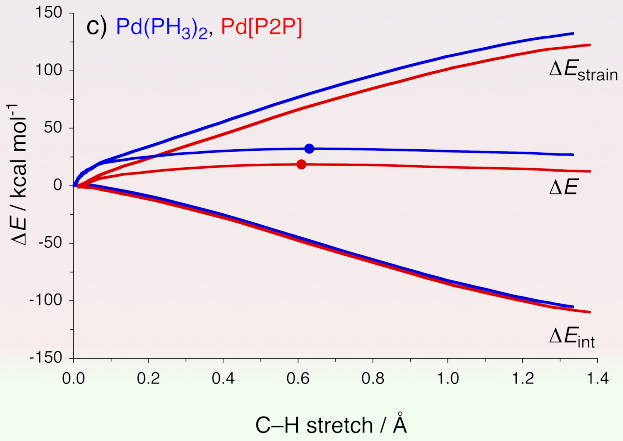
- ligands push *d* AOs up
  ➔ better HOMO–LUMO interaction
- this view is **not entirely exact**

Chem. Eur. J. (communication) **2009**, *15*, 6112
ChemPhysChem. **2007**, *8*, 1170

Bidentate Ligands

and the Steric Nature of the Bite Angle

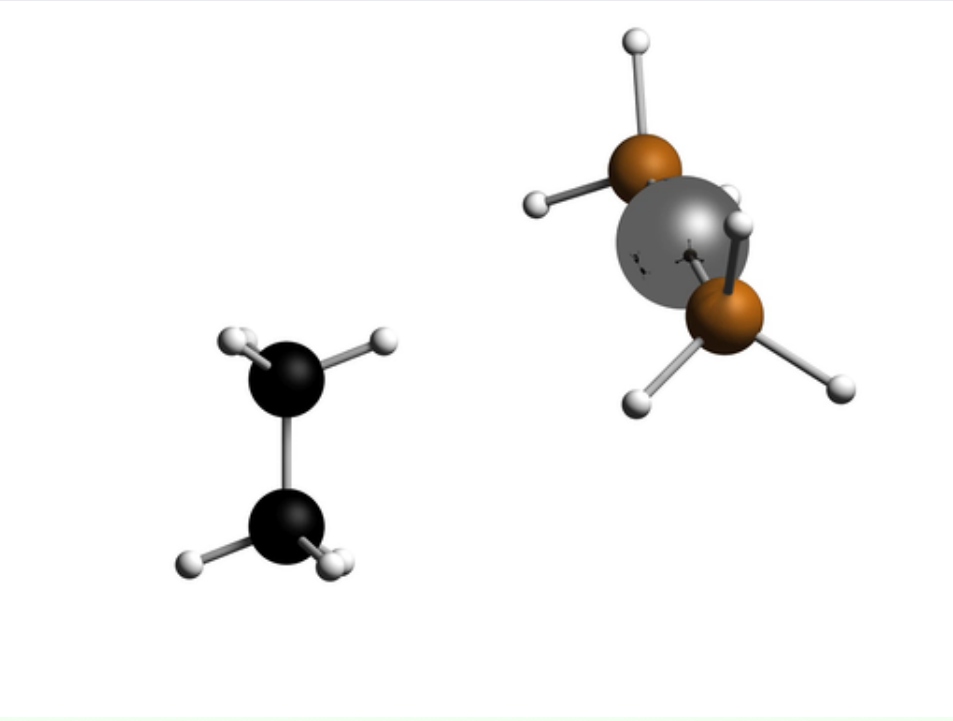
Bite-Angle Effect: **Activation Strain analyses**:



- HOMO–LUMO interaction only marginally improved

***Chem. Eur. J.* (communication) 2009, *15*, 6112**
ChemPhysChem. **2007**, *8*, 1170

Ligands



J. Organomet. Chem. **2005**, *690*, 2191

Bidentate Ligands

and the Steric Nature of the Bite Angle

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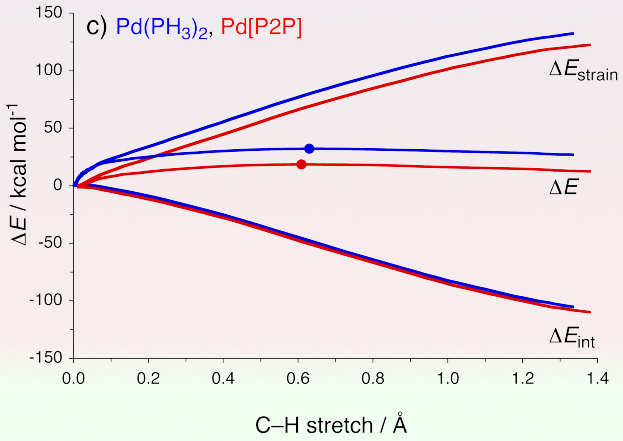
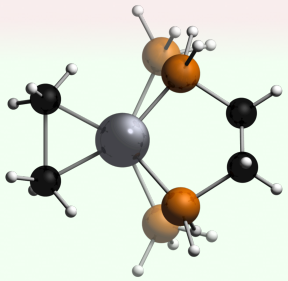


- HOMO–LUMO interaction marginally improved
- Instead:
  Strain reduced by building it into catalyst



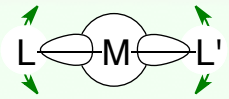
Chem. Eur. J. (communication) **2009**, *15*, 6112
Org. Biomol. Chem. **2010**, *8*, 3118
Nature Chem. **2010**, *2*, 417

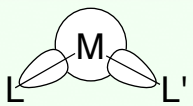
Variation M and L

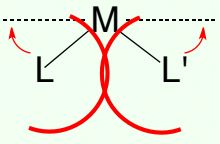
- Oxidative addition with **non-chelating** d^{10}-ML_2 complexes
- **Metal variation**: metals around Pd in the periodic table:
- **Ligand variation**: NH_3, PH_3 or CO

Co^-	Ni	Cu^+
Rh^-	Pd	Ag^+
Ir^-	Pt	Au^+

- **Text Books:** d^{10}-ML_2 is in general linear







ChemistryOpen **2013**, *2*, 106

Non-Linear d^{10}-ML_2

	L-M-L	ΔE_{lin}		L-M-L	ΔE_{lin}		L-M-L	ΔE_{lin}
$Co(NH_3)_2^-$	180	0	$Ni(NH_3)_2$	180	0	$Cu(NH_3)_2^+$	180	0
$Co(PH_3)_2^-$	132	6	$Ni(PH_3)_2$	180	0	$Cu(PH_3)_2^+$	180	0
$Co(CO)_2^-$	129	20	$Ni(CO)_2$	145	2	$Cu(CO)_2^+$	180	0
$Rh(NH_3)_2^-$	180	0	$Pd(NH_3)_2$	180	0	$Ag(NH_3)_2^+$	180	0
$Rh(PH_3)_2^-$	141	2	$Pd(PH_3)_2$	180	0	$Ag(PH_3)_2^+$	180	0
$Rh(CO)_2^-$	131	10	$Pd(CO)_2$	156	1	$Ag(CO)_2^+$	180	0
$Ir(NH_3)_2^-$	180	0	$Pt(NH_3)_2$	180	0	$Au(NH_3)_2^+$	180	0
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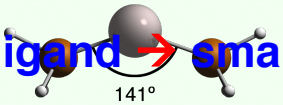

better π-accepting ligand → smaller bite angle

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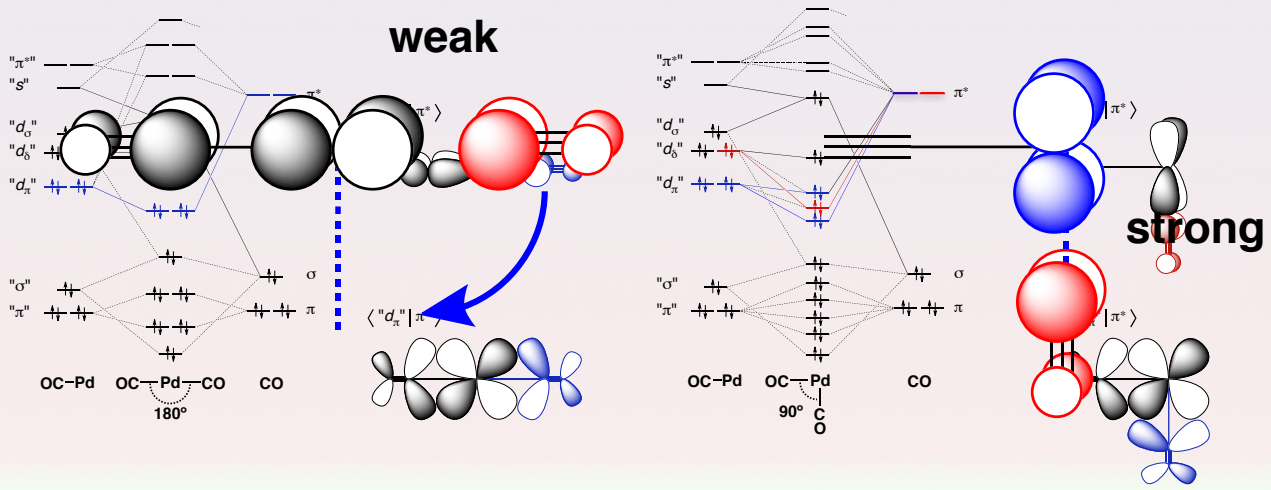
better π-backdonating metal → smaller bite angle

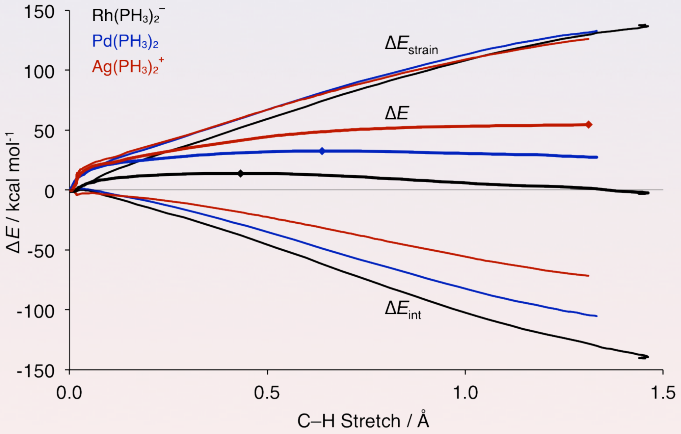
ML–L Bonding Analysis



bending provides access for π* to fresh *d* electrons

ChemistryOpen **2013**, *2*, 106

Application to H_3C–H Activation



smaller bite → less cat. strain

higher d → more stab. int.

design principles

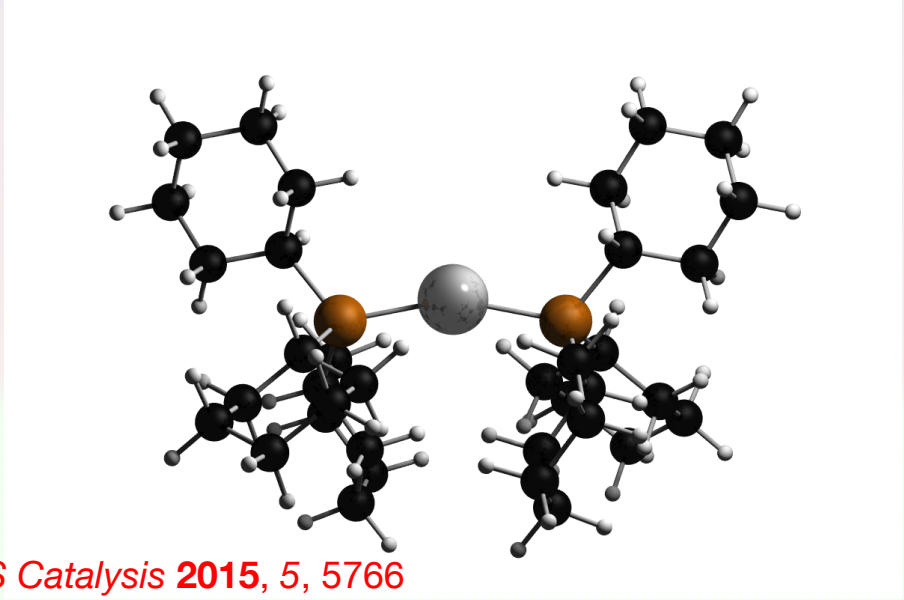
ChemistryOpen. **2013**, *2*, 106
WIRES Comput. Mol. Sci. **2015**, *5*, 324

Bite-Angle Flexibility:

"it is ***not*** about the angle"

Steric Attraction !

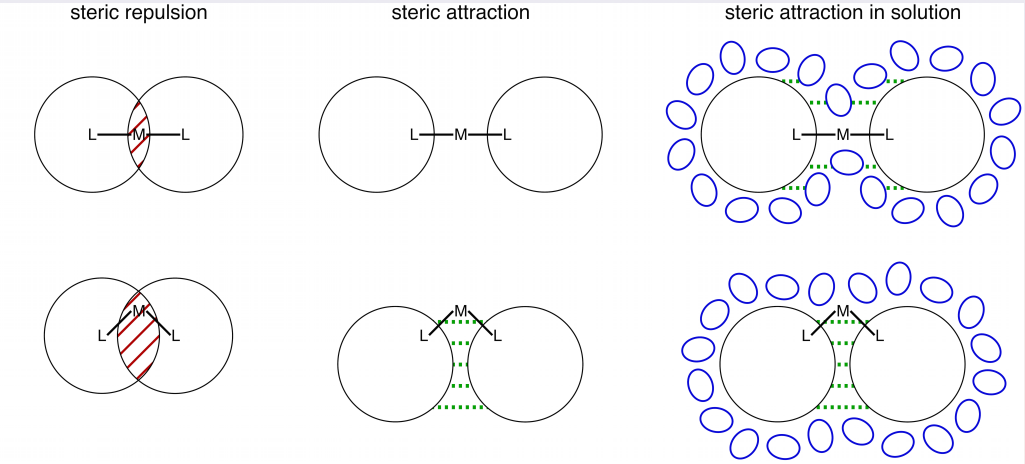
- Crank up steric bulk $Pd(PR_3)_2$
- Since $Pd(PH_3)_2$ is linear, all are... or not ??



- R = H: **Yes**
- R = Me: **Yes**
- R = iPr: **Yes**
- R = tBu: **Yes**
- R = Cy: **No**

ACS Catalysis **2015**, *5*, 5766
WIRES Comput. Mol. Sci. **2015**, *5*, 324

Steric Attraction !

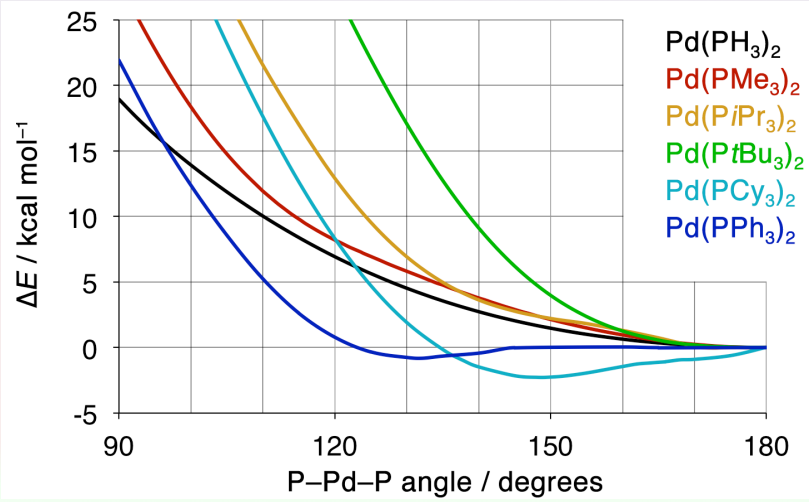


big <u>surfaces</u> stick together through Van der Waals forces

"Anisotropic Bulk" + Room = Steric Attraction

Bite-Angle Flexibility

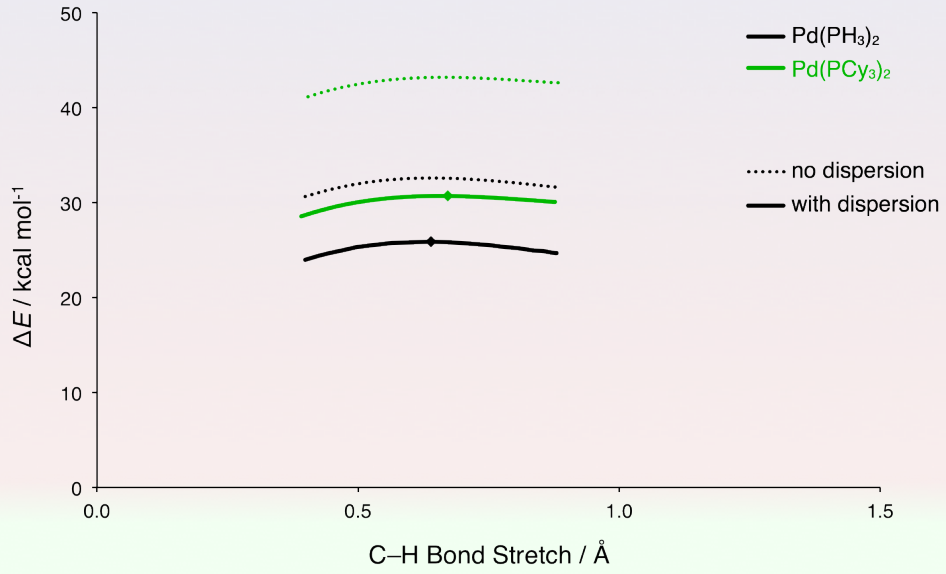
- Energy profiles for bending $Pd(PR_3)_2$



Dispersion pulls minimum to **148°** ...

... **132°** for $Pd(PPh_3)_2$!

Application to H_3C–H Activation

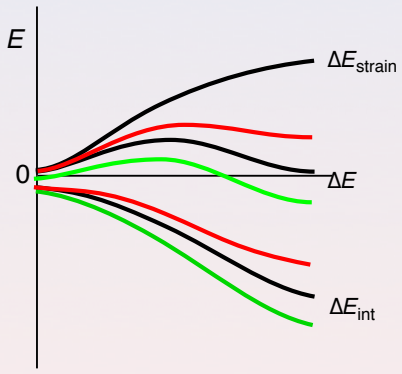


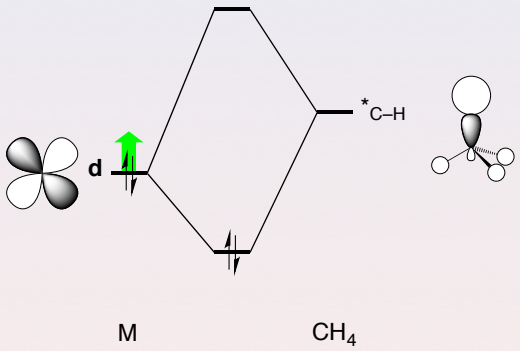
More flexible bite angle → less activation strain

The "right bulk" provides steric protection + low barrier

3 - Electronic Regimes of Catalysts

Electronic Regimes





	$RhCO^- \rightarrow RhPH_3^-$
$\Delta\varepsilon_{HOMO}$	**+0.6** eV
$E^{\neq}$	**–3.4** kcal/mol

	$AgCO^+ \rightarrow AgPH_3^+$
$\Delta\varepsilon_{HOMO}$	**+1.7** eV
$E^{\neq}$	**+9** kcal/mol

ASM and MO work perfectly

➔ rational design, but...

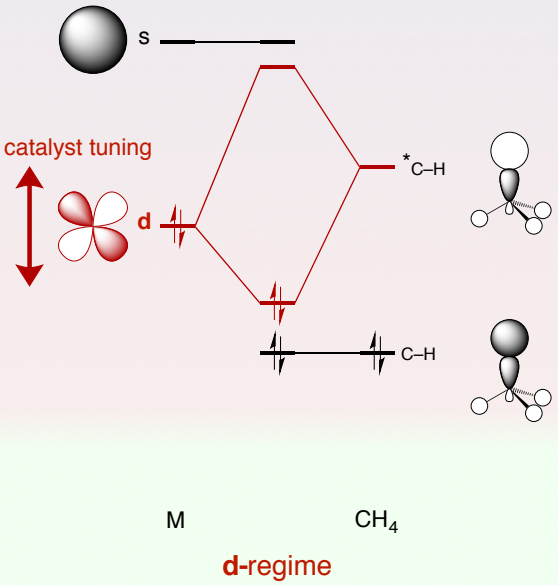
What causes the opposite trend?

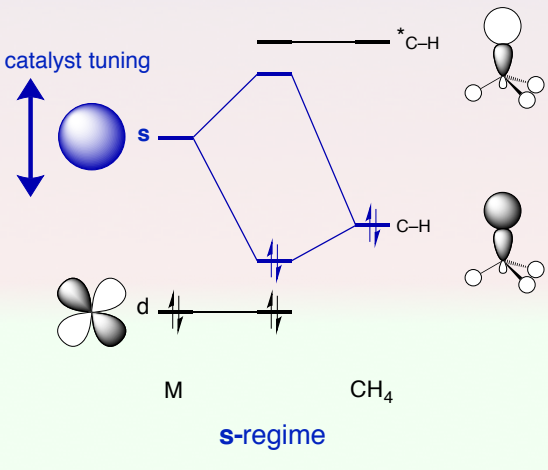
Chem. Asian J. **2015**, *10*, 2272; *WIRES Comput. Mol. Sci.* **2015**, *5*, 324

Electronic Regimes

Same electronic configuration, yet opposite effect on barrier:

Change of electronic REGIME from d-regime to s-regime





Chem. Asian J. **2015**, *10*, 2272; *WIRES Comput. Mol. Sci.* **2015**, *5*, 324

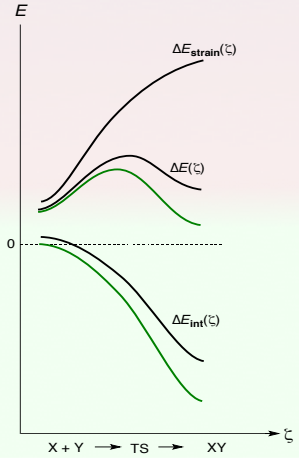
Summary

- Bite-angle effect on reactivity has steric origin...
- What matters is: bending strain (or flexibility).
- Opposite tuning behavior: d-regime or s-regime.

Take-Home Message

- KS-MO & EDA : causal model of bonding mechanism
- Activation Strain Model generalization to reactions
- Physical Understanding and Rational Design

$$\Delta E(\zeta) = \Delta E_{strain}(\zeta) + \Delta E_{int}(\zeta)$$



Further Reading

- *Reviews in Computational Chemistry*; K. B. Lipkowitz, D. B. Boyd, Eds.; Wiley-VCH: New York, **2000**, Vol. 15, pp. 1-86
- *Nature Chem.* **2010**, *2*, 417
- *Chem. Soc. Rev.* **2014**, *43*, 4953
- *WIRES Comput. Mol. Sci.* **2015**, *5*, 324
- *Angew. Chem. Int. Ed.* **2017**, *56*, 10070 (**!**)