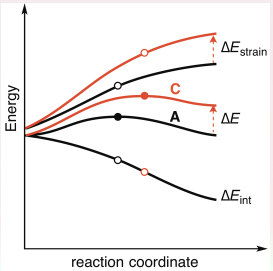
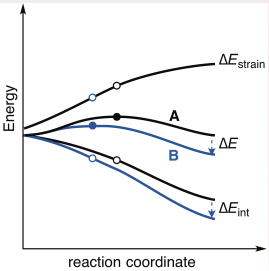
Theory of Chemical Bonding and Reactivity

Quantitative

Orbital and Activation Strain Models





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Radboud University Nijmegen

Outline

1. Activation Strain model and KS MO theory

   ASM in action: **bond activation**

2. Bite Angle and Bite-Angle Flexibility

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

ADF: ZORA BLYP-(D3)/TZ2P

kcal/mol – Å – deg

1 - Activation Strain model & KS-MO

Theoretical Chemistry

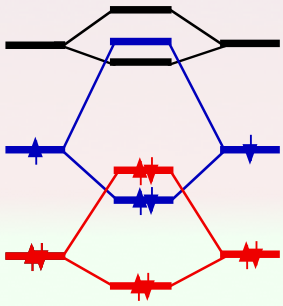
$$H \Psi = E \Psi$$

Numerical description

$$[T + V_{Ne} + V_{ee,C} + V_{ee,XC}] \psi = E \psi$$

Understanding and design!

$$[T + V_{Ne} + V_{ee,C} + V_{ee,XC}] \psi = E \psi$$

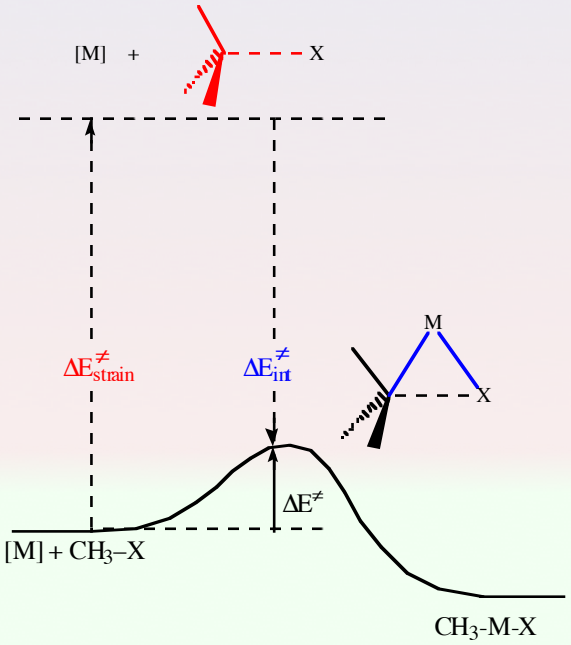


physical mechanism

Rev. Comput. Chem. **2000**, *15*, 1.

Activation Strain Model

- Decompose barrier:

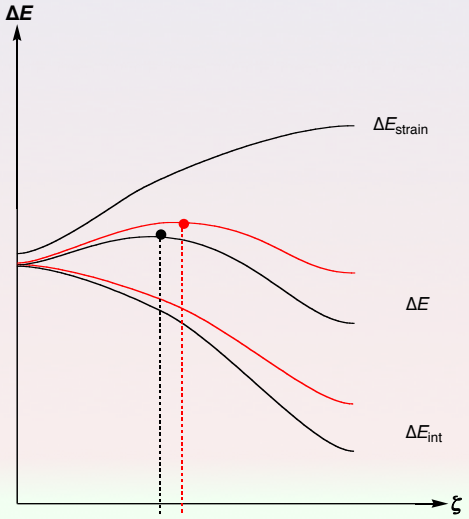


$$\Delta E^{\neq} = \Delta E^{\neq}_{strain} + \Delta E^{\neq}_{int}$$

J. Comput. Chem. **1999**, *20*, 114; *Chem. Soc. Rev.* **2014**, *43*, 4953

Activation Strain Model

- Analysis along reaction coordinate ζ

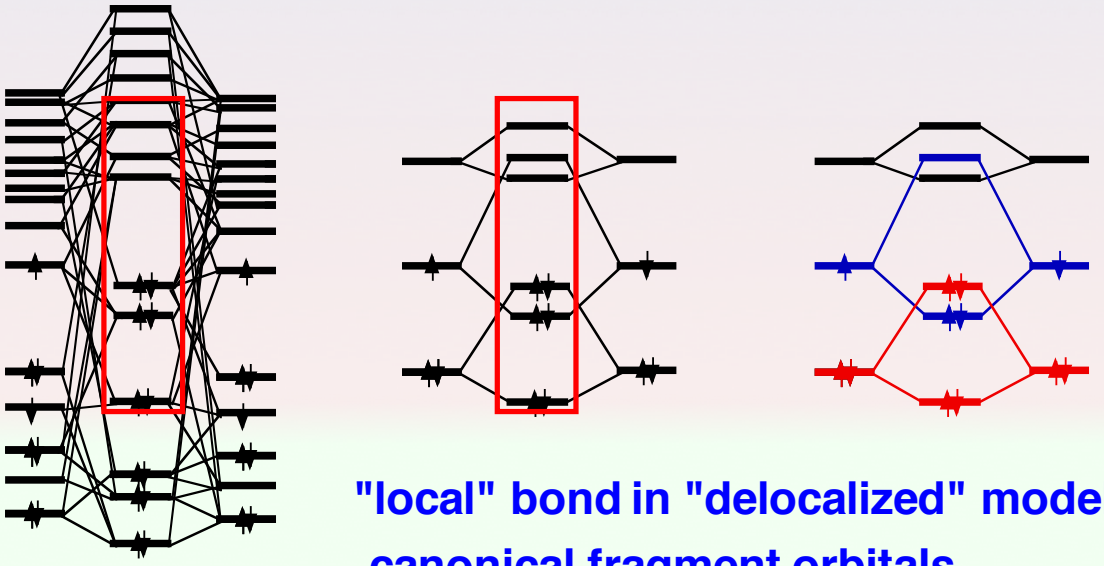


- Interplay $\Delta E_{strain}(\zeta) + \Delta E_{int}(\zeta)$ determines TS

J. Comput. Chem. **1999**, *20*, 114; *Chem. Soc. Rev.* **2014**, *43*, 4953

Fragment MO Approach

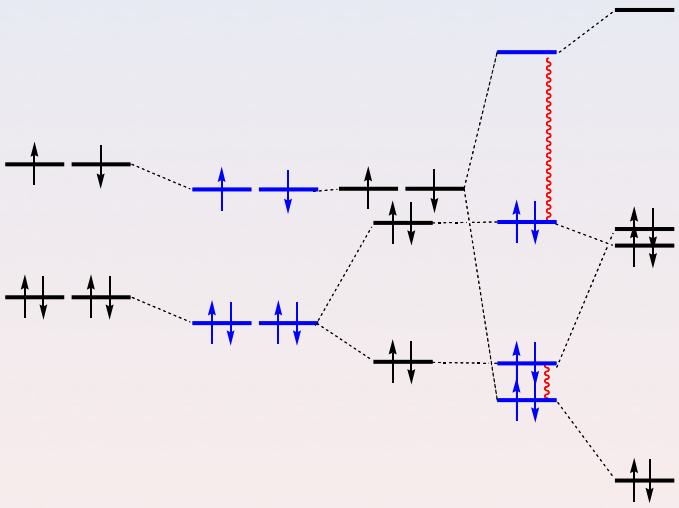
A + B → A–B



"local" bond in "delocalized" model
canonical fragment orbitals

Rev. Comput. Chem. **2000**, *15*, 1.

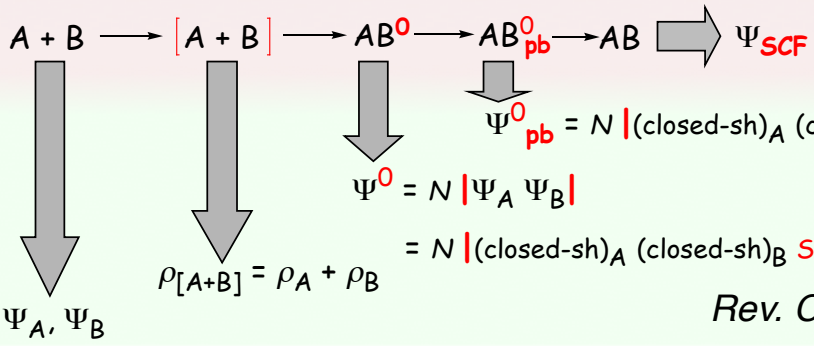
Bond Energy Decomposition



A + B → AB

$\Delta E_{bond} = \Delta E_{strain} + \Delta E_{int}$

$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi,pb} + \Delta E_{oi,relax}$



$\Psi^0_{pb} = N\,|(\text{closed-sh})_A\,(\text{closed-sh})_B\,(SOMO_A + SOMO_B)^2|$

$\Psi^0 = N\,|\Psi_A\,\Psi_B|$

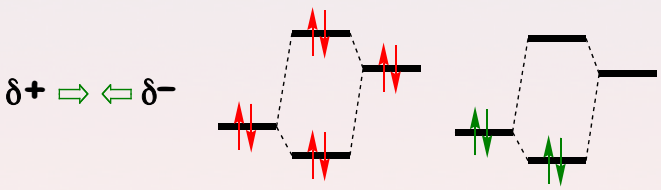
$= N\,|(\text{closed-sh})_A\,(\text{closed-sh})_B\,SOMO_A(1)\alpha(1)\,SOMO_B(2)\beta(2)|$

Rev. Comput. Chem. **2000**, *15*, 1.

MO model: *cause and effect*

$$\Delta E = \Delta E_{strain} + \Delta E_{int}$$

$$\Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} + \Delta E_{disp}$$



$$\Delta E_{oi} = \frac{|\langle \psi_A | h_{KS} | \psi_B \rangle|^2}{\varepsilon_A - \varepsilon_B}$$

$$\Delta E_{oi} \sim \frac{S^2}{\Delta\varepsilon}$$

– Causal relationship

– Quantitative

– Qualitative...

Rev. Comput. Chem. **2000**, *15*, 1.

Physical Understanding

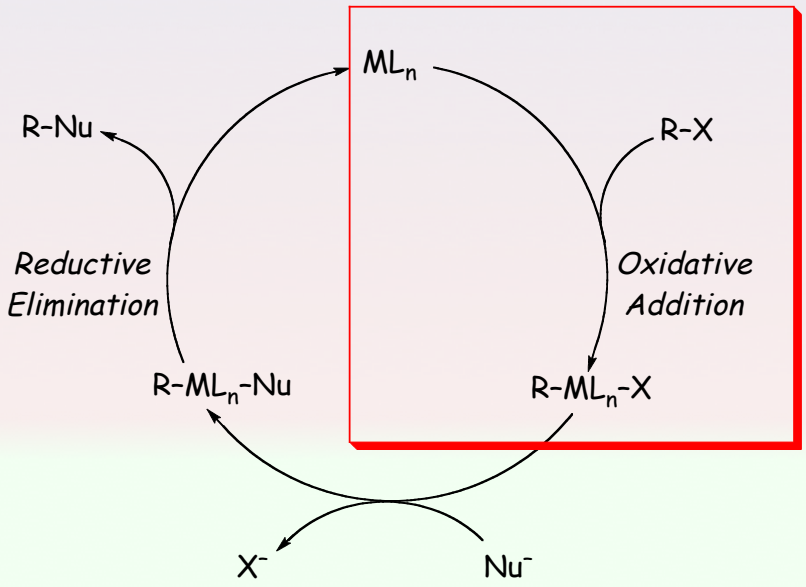
ASM in action:
Bond Activation

ADF: ZORA BLYP-(D3)/TZ2P

kcal/mol – Å – deg

Catalysis

- Model: Catalytic C–X Bond Activation



C–H vs C–C Activation

- Computational and experimental facts (in kcal/mol):

bond	BDE
C-H	109
C-C	90

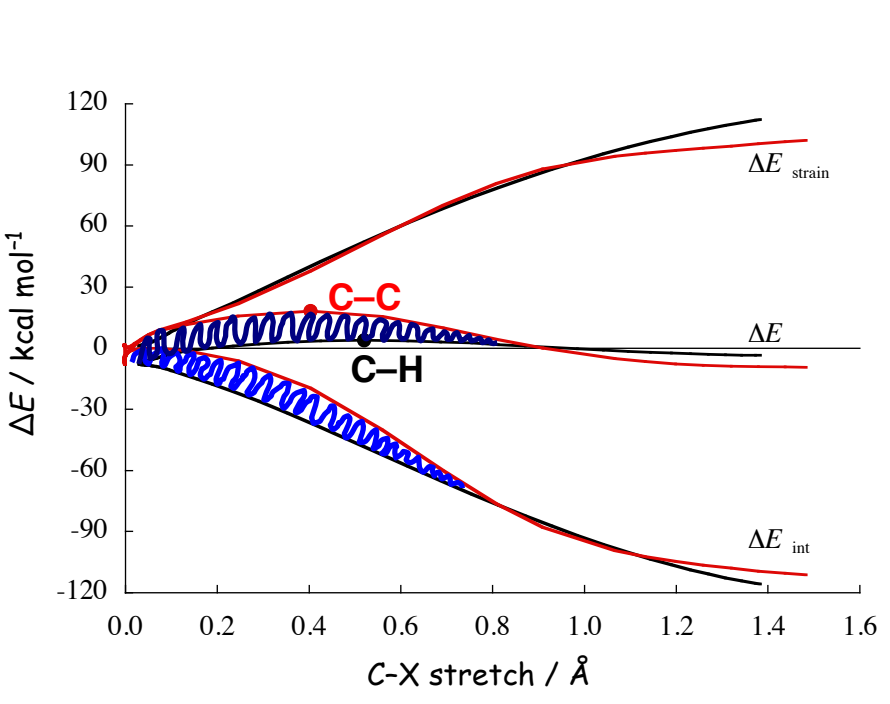
C–H vs C–C Activation

- Computational and experimental facts (in kcal/mol):

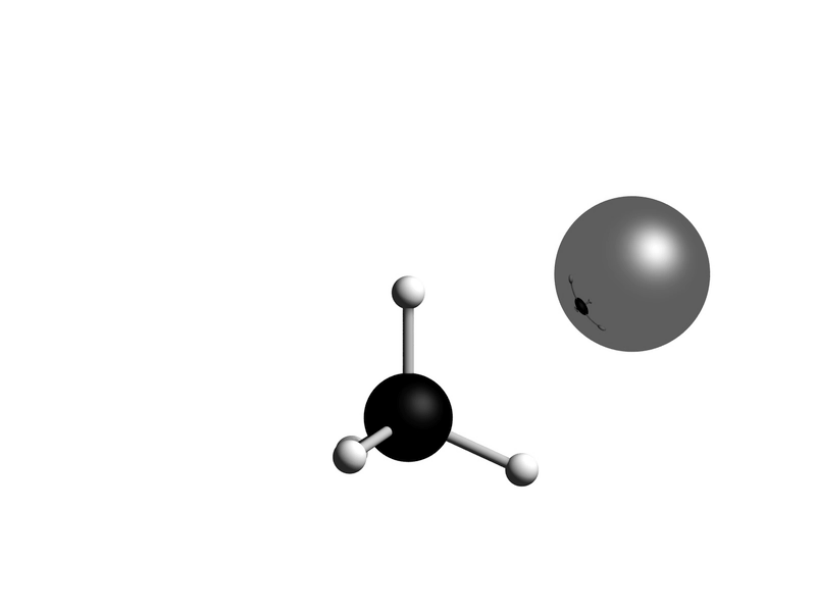
bond	BDE	$\Delta E^{\neq}$ bond activ
C-H	109	4
C-C	90	19

***Why* is C–C activ. more difficult than C–H activ. ?**

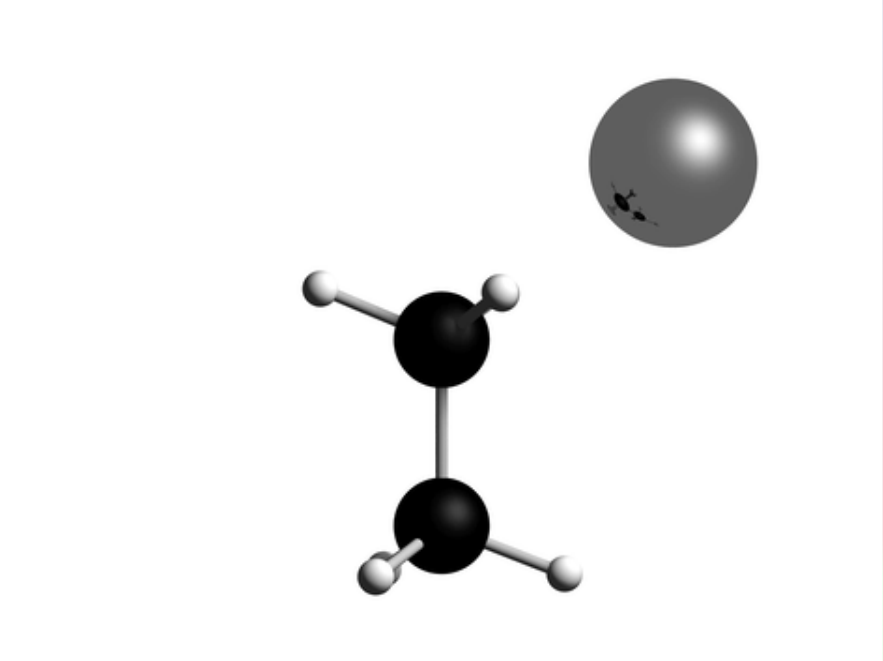
C–H vs C–C Activation



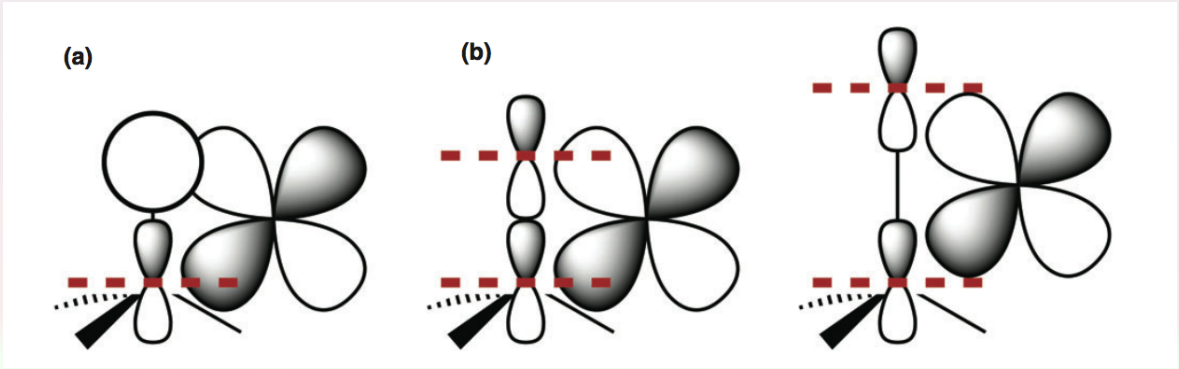
C–H vs C–C Activation



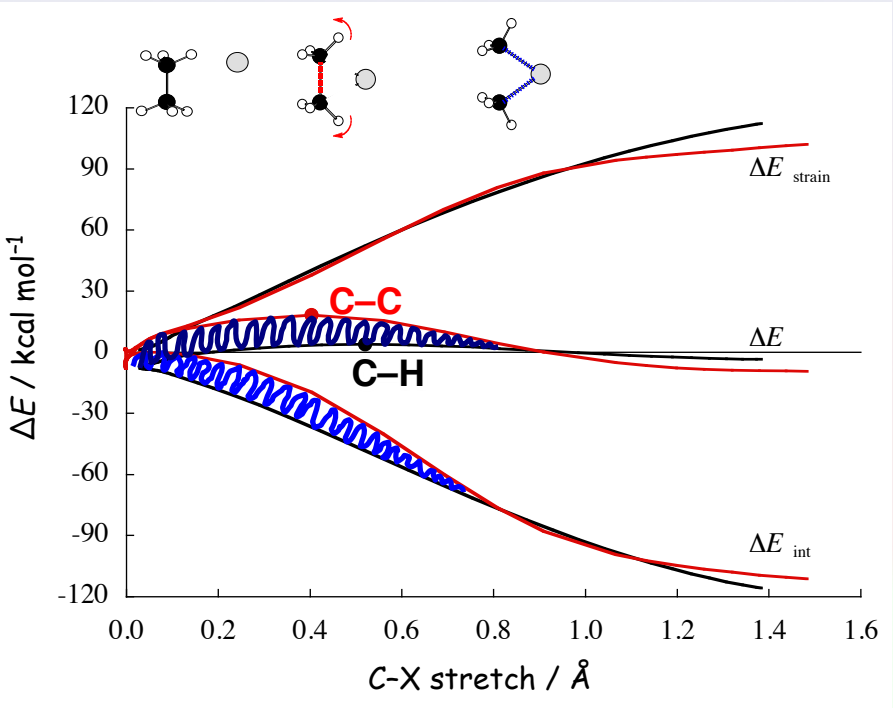
C–H vs C–C Activation



C–H vs C–C Activation

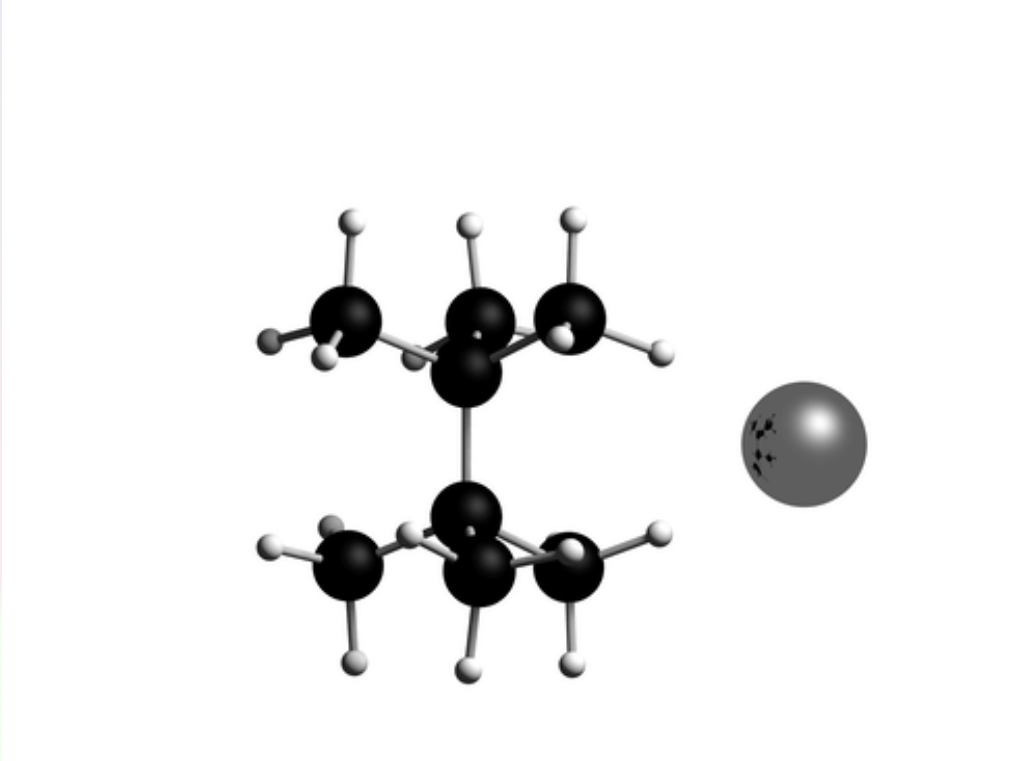


C–H vs C–C Activation



C–H bonds shield C–C bond → delayed [M]–[C–C] interaction

Bulky Substrates

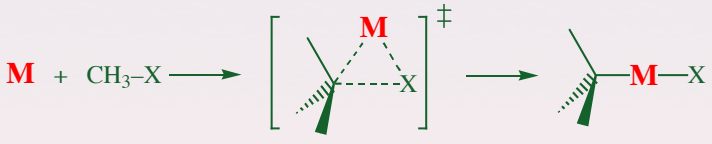


ChemPhysChem **2007**, *8*, 1170

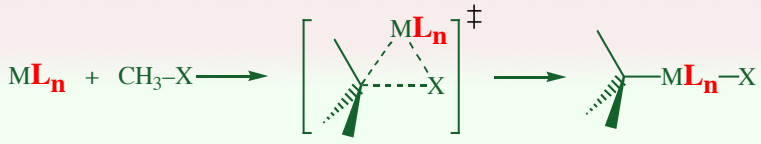
Fragment-oriented Design

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

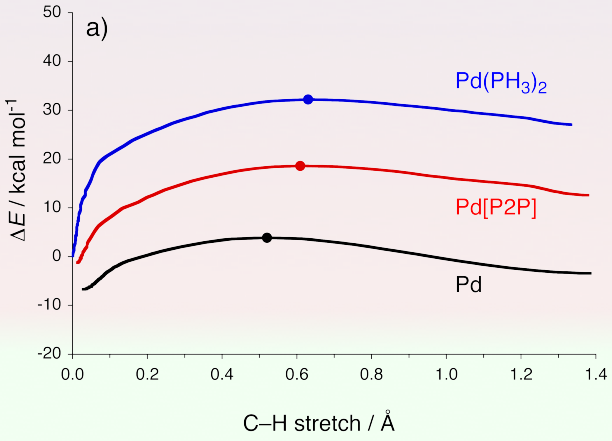
2 - Bite Angle & Bite-Angle Flexibility

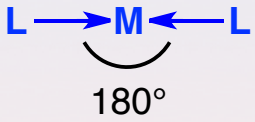
Bite Angle:
steric nature

Bidentate Ligands

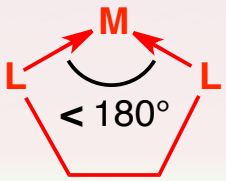
and the Steric Nature of the Bite Angle

Methane C–H activation:





- ligands raise barriers



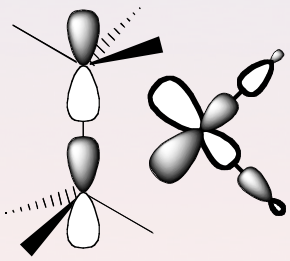
- smaller bite angle
  ➔ lower barrier

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

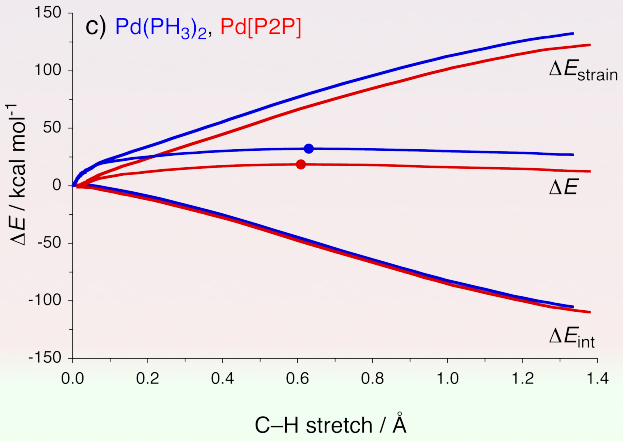
- this view is **not entirely exact**

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

Bidentate Ligands

and the Steric Nature of the Bite Angle

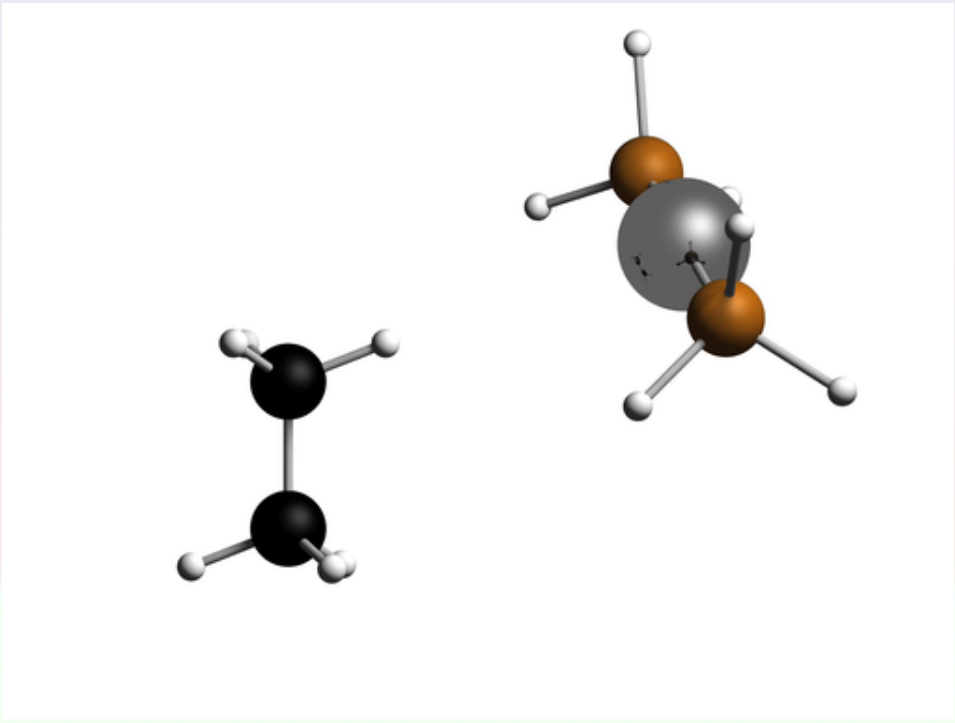
Bite-Angle Effect: **Activation Strain analyses**:



- HOMO–LUMO interaction only marginally improved

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

Ligands

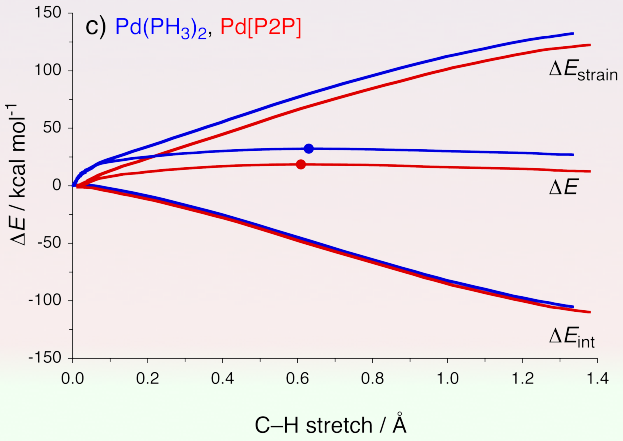


J. Organomet. Chem. **2005**, *690*, 2191

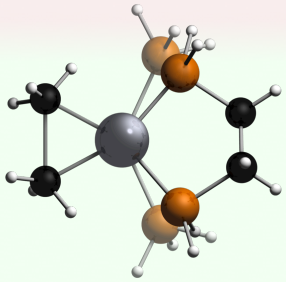
Bidentate Ligands

and the Steric Nature of the Bite Angle

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



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



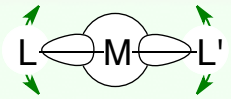
Chem. Eur. J. (communication) **2009**, *15*, 6112
Org. Biomol. Chem. **2010**, *8*, 3118
Nature Chem. **2010**, *2*, 417

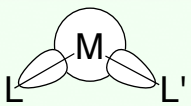
Variation M and L

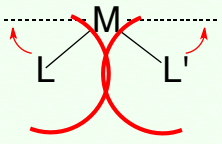
- Oxidative addition with **non-chelating** d^{10}-ML_2 complexes
- **Metal variation**: metals around Pd in the periodic table:
- **Ligand variation**: NH_3, PH_3 or CO

Co⁻	Ni	Cu⁺
Rh⁻	Pd	Ag⁺
Ir⁻	Pt	Au⁺

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







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
$Ir(PH_3)_2^-$	144	2	$Pt(PH_3)_2$	180	0	$Au(PH_3)_2^+$	180	0
$Ir(CO)_2^-$	134	13	$Pt(CO)_2$	159	1	$Au(CO)_2^+$	180	0

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$Co(CO)_2^-$	**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
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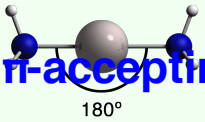

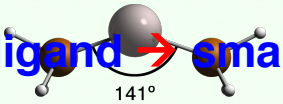

better π-accepting ligand → smaller bite angle

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
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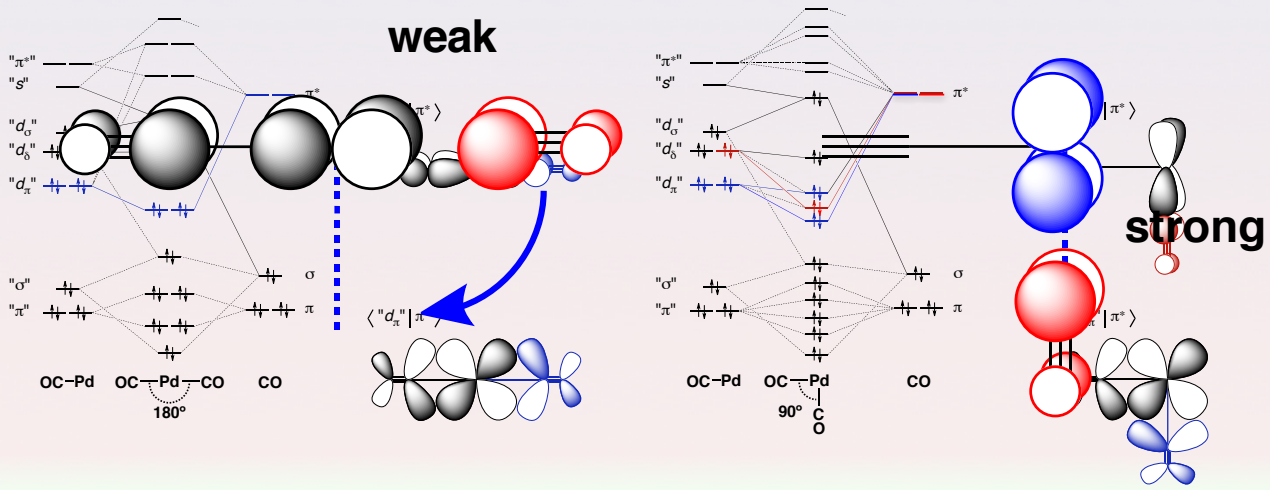
$Ir(CO)_2^-$	134	13	$Pt(CO)_2$	159	1	$Au(CO)_2^+$	180	0

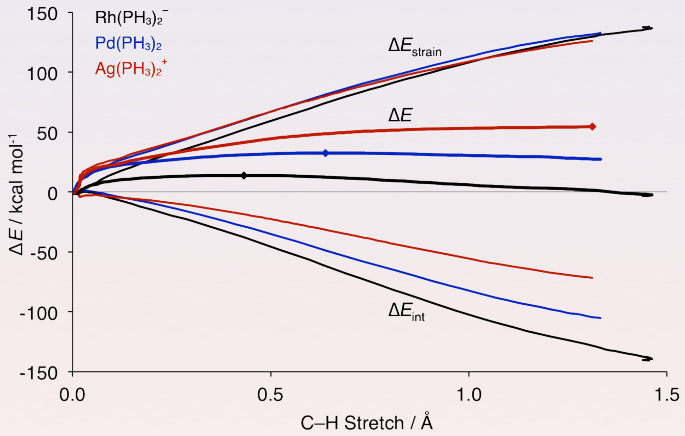
better π-backdonating metal → smaller bite angle

ML–L Bonding Analysis



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

Application to H_3C–H Activation



smaller bite → less cat. strain

higher d → more stab. int.

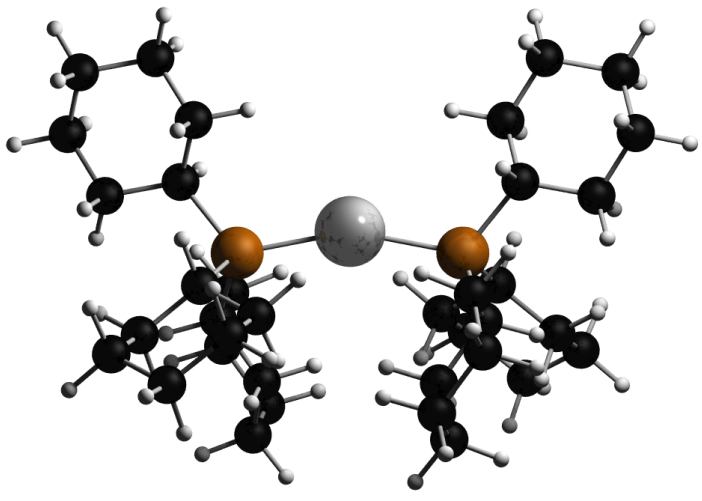
design principles

Bite-Angle Flexibility:

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

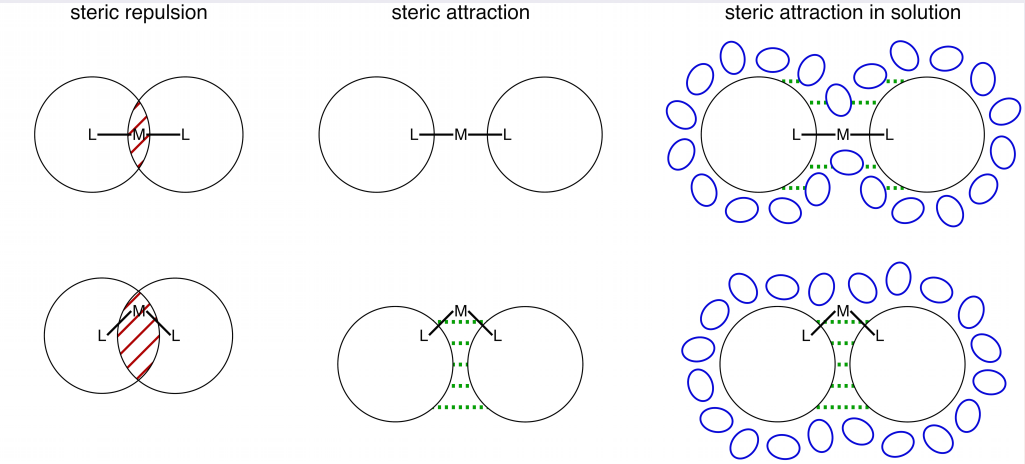
Steric Attraction !

- 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**

Steric Attraction !

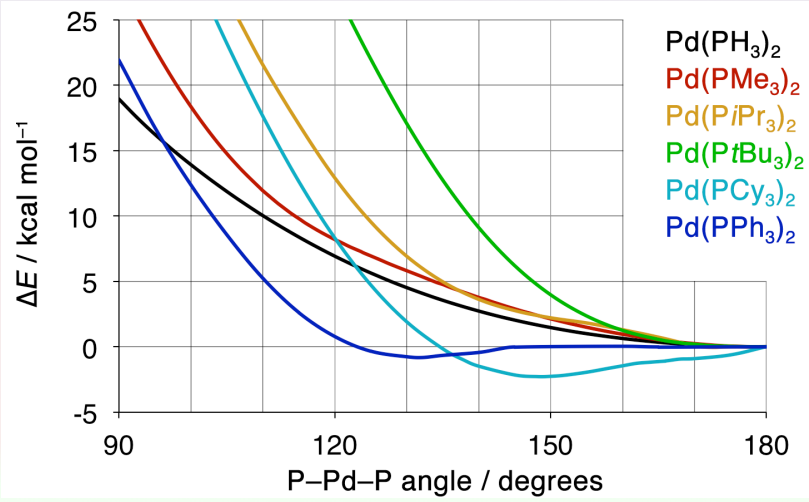


big <u>surfaces</u> stick together through Van der Waals forces

"Anisotropic Bulk" + Room = Steric Attraction

Bite-Angle Flexibility

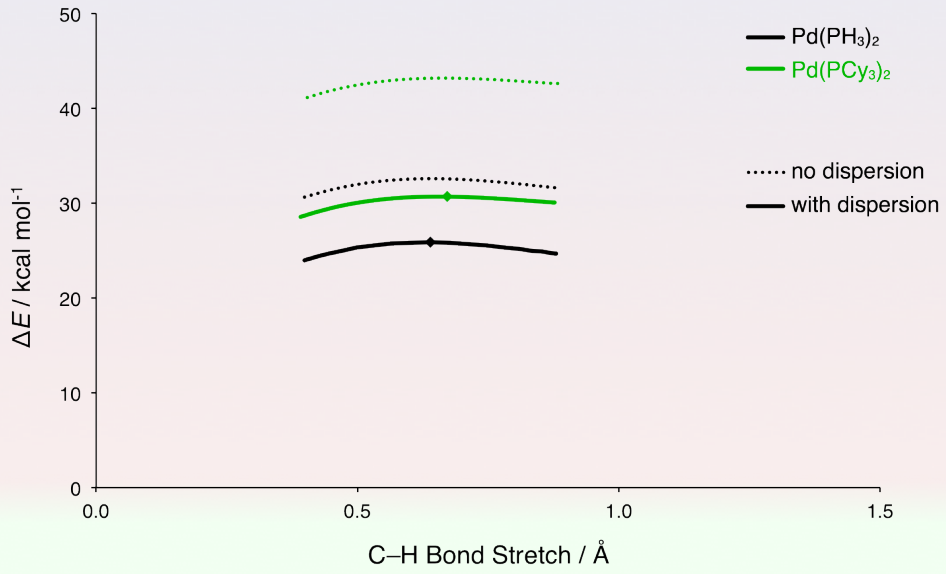
- Energy profiles for bending $Pd(PR_3)_2$



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

... **132°** for $Pd(PPh_3)_2$!

Application to H_3C–H Activation

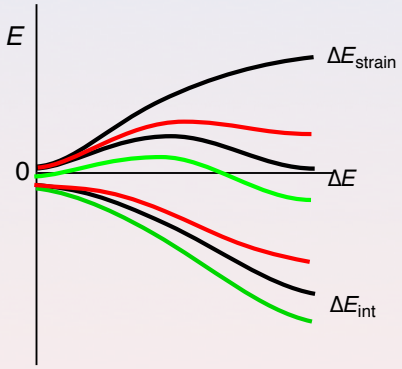


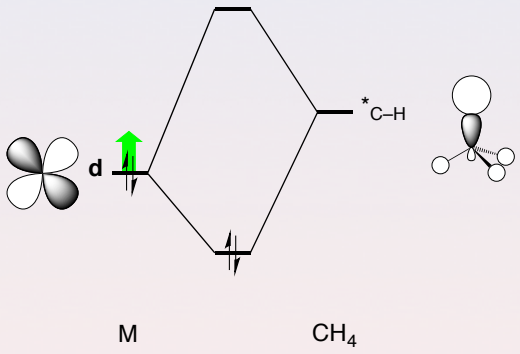
More flexible bite angle → less activation strain

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

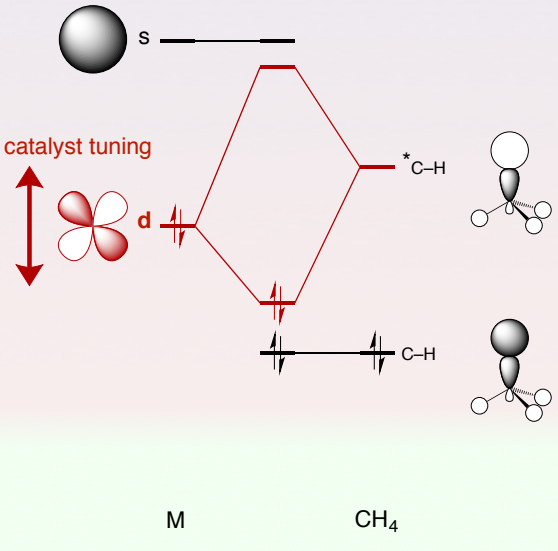
➔ rational design, but...

Break-down of model ?

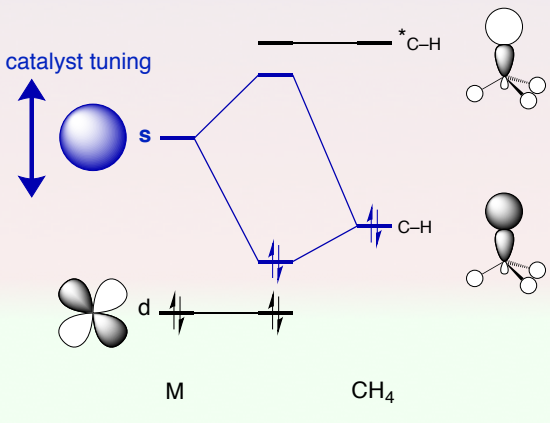
electronic regimes

Break-down of model ?

NO, we just went from **d-regime** to **s-regime**



d-regime



s-regime

Conclusions

- Bite-angle effect on reaction has steric origin...
- actually, what matters is bite-angle **flexibility**
- d-regime or s-regime, that is the question

Take-Home Message

- **KS-MO** is physically sound **causal** model
- **EDA without** bonding mechanism is **incomplete**
- Activation Strain model (**ASM**) is a powerful generalization to reactions...

Further reading

1. *Reviews in Computational Chemistry*; Wiley-VCH: New York, **2000**, Vol. 15, pp. 1-86
2. *Chem. Soc. Rev.* **2014**, *43*, 4953
3. *WIRES Comput. Mol. Sci.* **2015**, *5*, 324