College Toegepaste Quantumchemie 2017

KS-DFT – Chemische Binding – Reactiviteit

F. Matthias Bickelhaupt

IMM Institute for Molecules and Materials

Radboud University

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 1

Wed 4 Oct

1 - QM Models
KS-MO and Activ. Strain model

Theoretical Chemistry

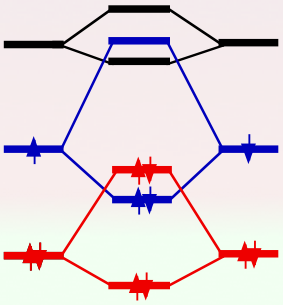
$$H\,\Psi = E\,\Psi$$

Numerical description!

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

Why does it happen?

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

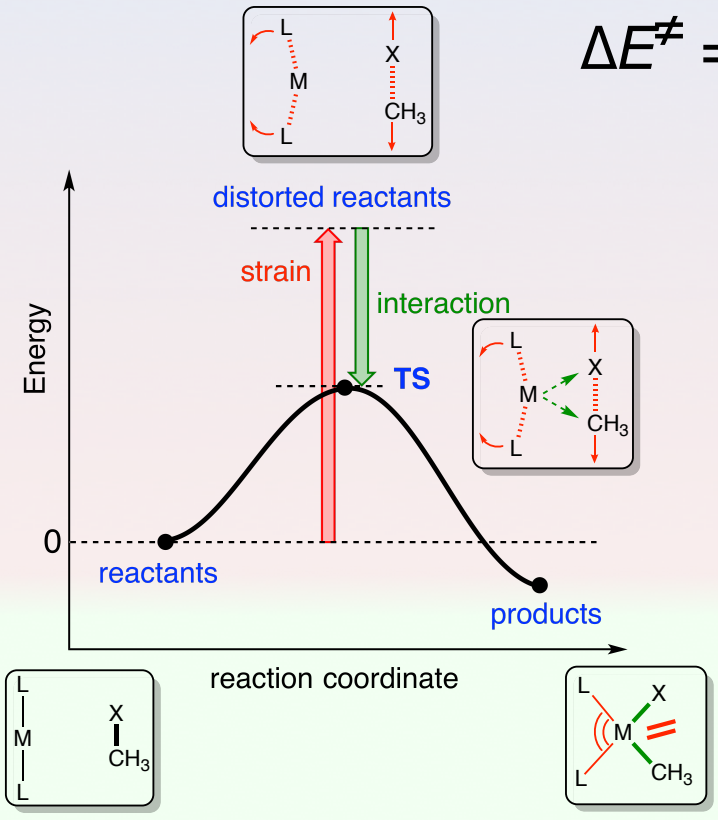


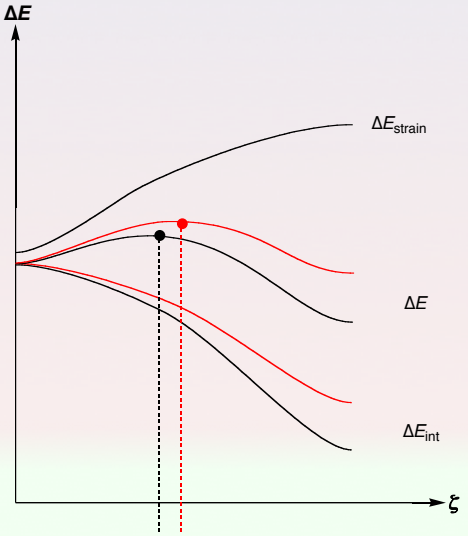
physical mechanism

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

Activation Strain model

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





$$d\Delta E_{int}(\zeta)/dt = -d\Delta E_{strain}(\zeta)/dt$$

Angew. Chem. IE **2017**, *56*, 10070

HF-MO *vs.* KS-MO

1. QM: $\hat{H}\Psi_i = E_i\Psi_i$ en $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$ *exact*

Born-Oppenheimer ($\Psi^n\Psi^e$) + 1-el.model + required antisymm.

2. HF: $\Psi_{HF} = |\varphi_1(1).....\varphi_N(N)|$ *best 1-det. approximation*

$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle \geq E_0$ *variation theorem*

$\hat{F}_i(1)\varphi_i(1) = \varepsilon_i\varphi_i(1)$ *orbitals, bonding, spectra*

$\hat{F}_i(1) = \hat{T}(1) + \hat{V}_{Ne}(1) + V_C(1) + V_{X,i}(1)$

- average rep. $\rho^{HF}(2)$
- correction self-interaction
- exchange (antisym. Ψ_{HF}) or Fermi correlation
- Coulomb correlation missing

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

HF-MO *vs.* KS-MO

3. KS-DFT:

$\hat{F}^{KS}(1)\varphi_j^{KS}(1) = \varepsilon_j^{KS}\varphi_j^{KS}(1)$

$\hat{F}^{KS}(1) = \hat{T}(1) + \hat{V}_{ne}(1) + \hat{V}_C(1) + \hat{V}_{XC}^{KS}(1)$

- exchange correlation
- **and Coulomb** correlation

$\rho^{KS}(1) = \sum_{i=1}^{N} |\varphi_i^{KS}(1)|^2$

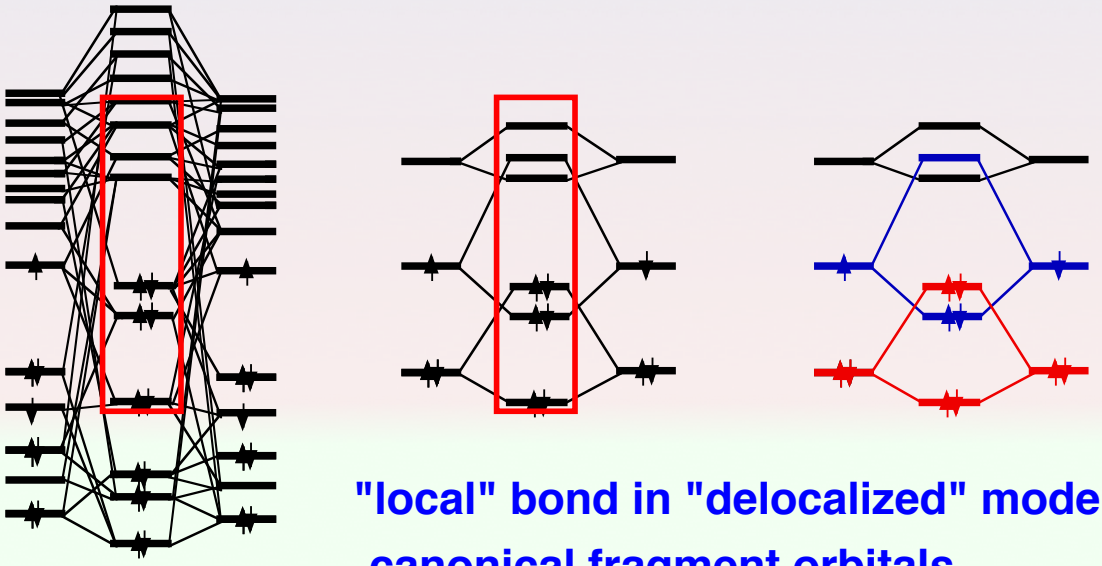
$E = E^{HK}[\rho^{KS}(1)]$

***Exact* MO model**

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

Fragment MO Approach

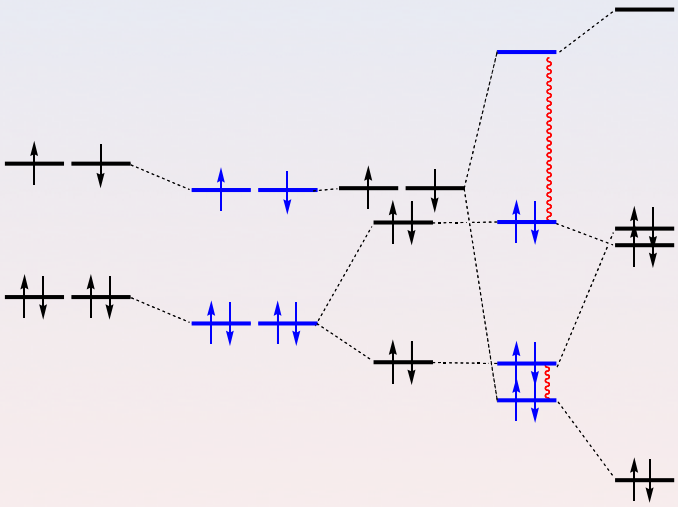
AB + CD → AB–CD



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

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

Bond Energy Decomposition



A + B → AB

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

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

$A + B \longrightarrow [A + B] \longrightarrow AB^0 \longrightarrow AB^0_{pb} \longrightarrow AB \Rightarrow \Psi_{SCF}$

Ψ_A, Ψ_B

$\rho_{[A+B]} = \rho_A + \rho_B$

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

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

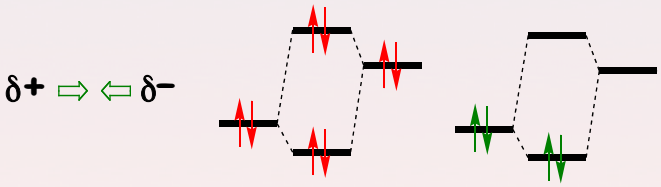
$\Psi^0_{pb} = N\,|(\text{closed-sh})_A\,(\text{closed-sh})_B\,(SOMO_A + SOMO_B)^2|$

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

Canonical MO model: *cause & effect*

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

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



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

– Causal relationship

– Quantitative

– Qualitative...

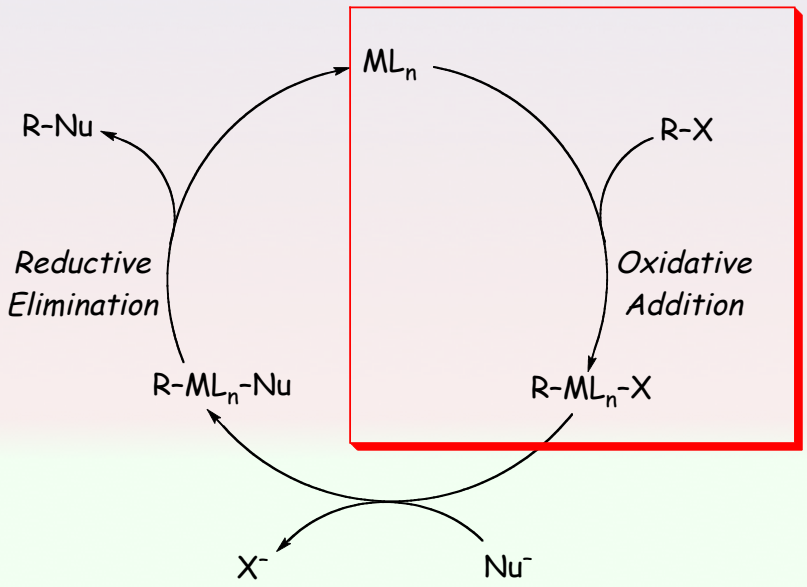
Rev. Comput. Chem. **2000**, *15*, 1.

Physical Understanding

ASM in action:
Bond Activation

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

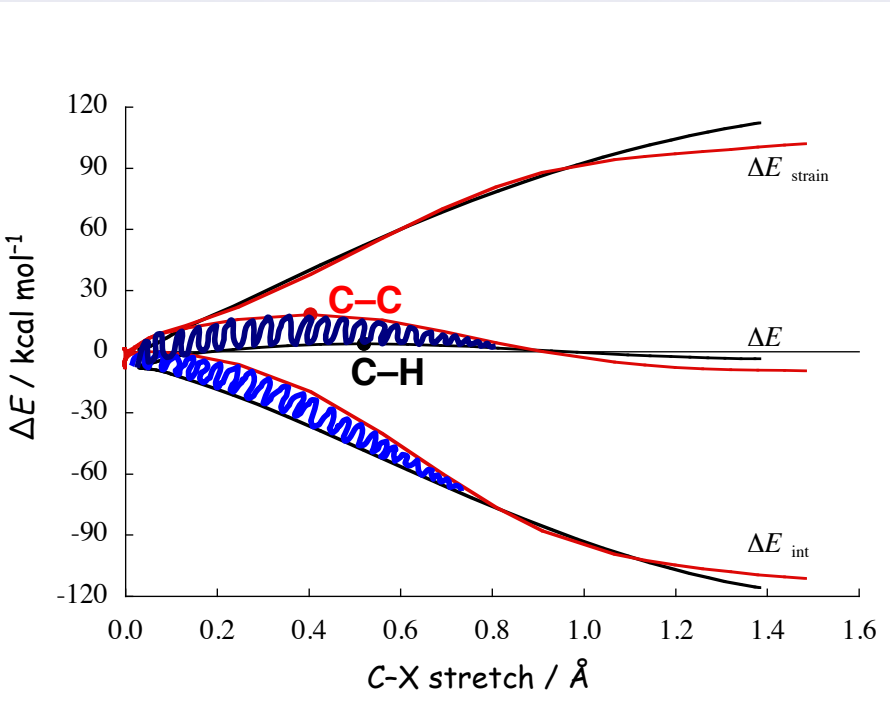
C–H vs C–C Activation

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

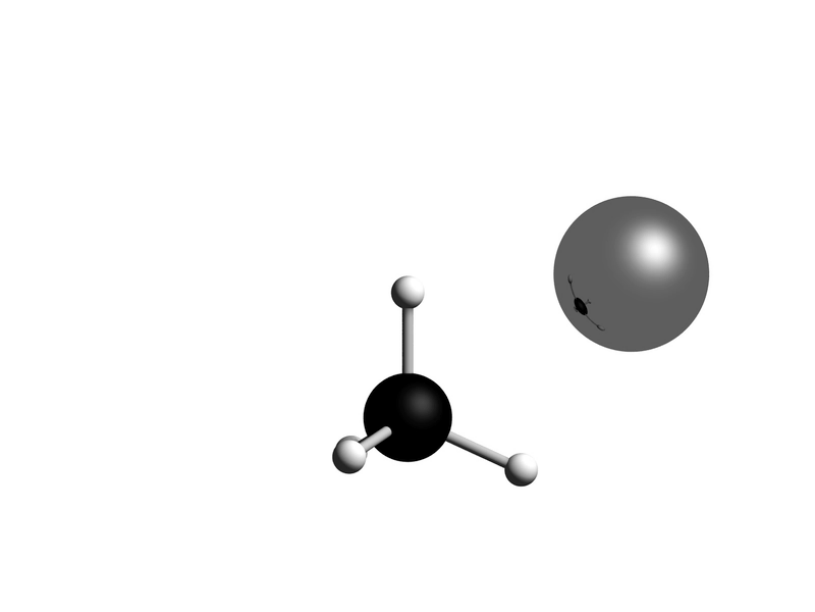
bond	BDE	$\Delta E^{\ddagger}$ bond activ
C-H	109	4
C-C	90	19

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

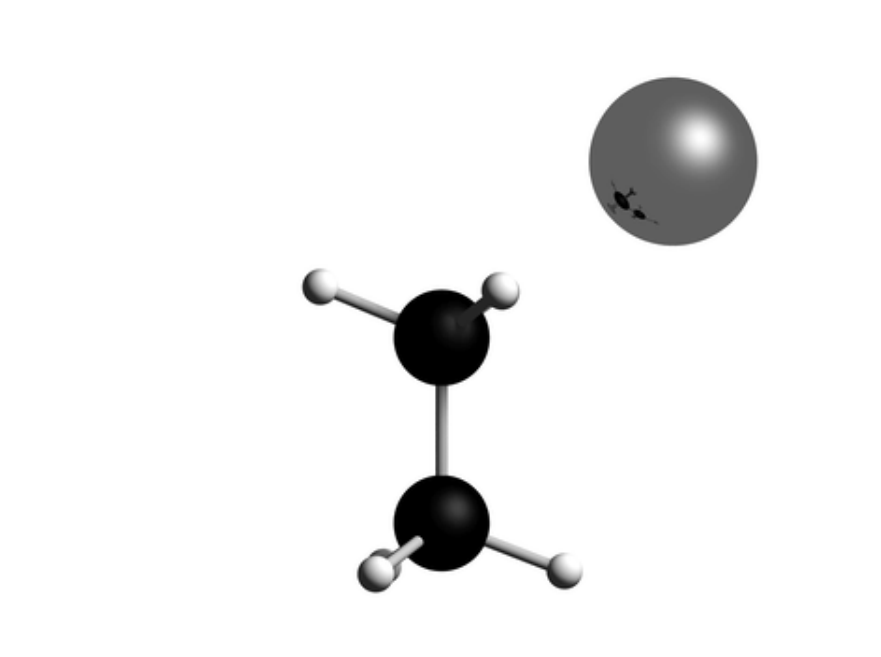
C–H vs C–C Activation



C–H vs C–C Activation

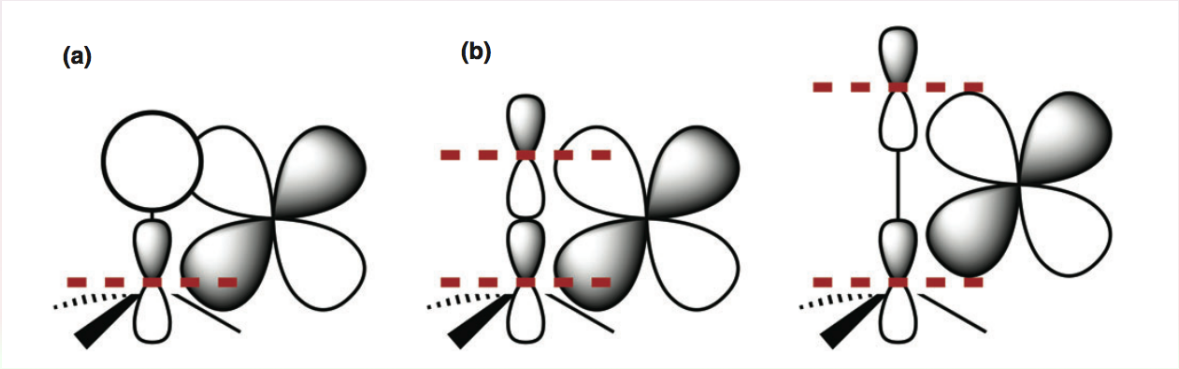


C–H vs C–C Activation

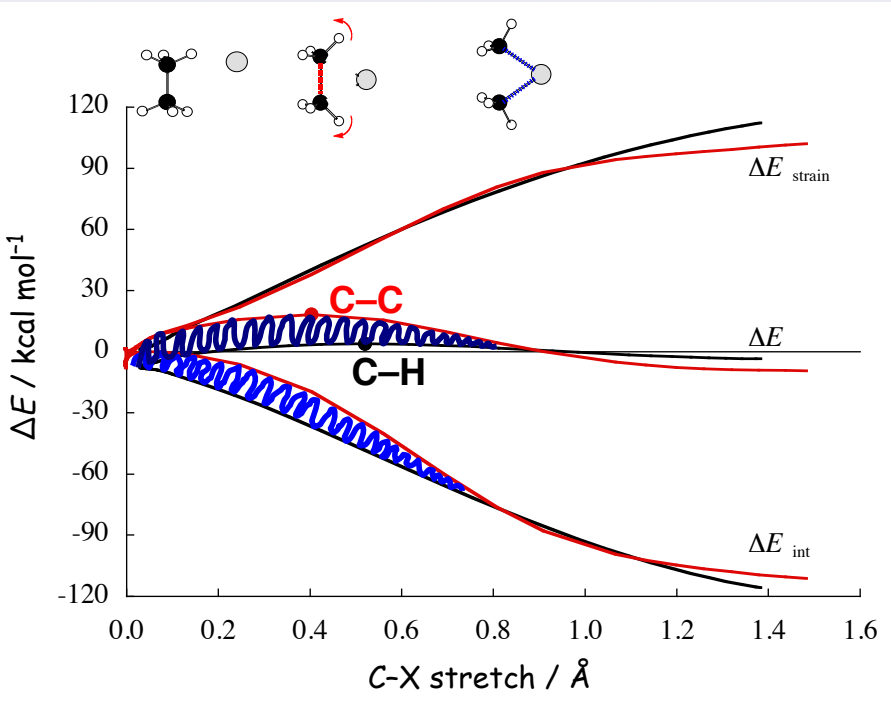


extra slide

C–H vs C–C Activation

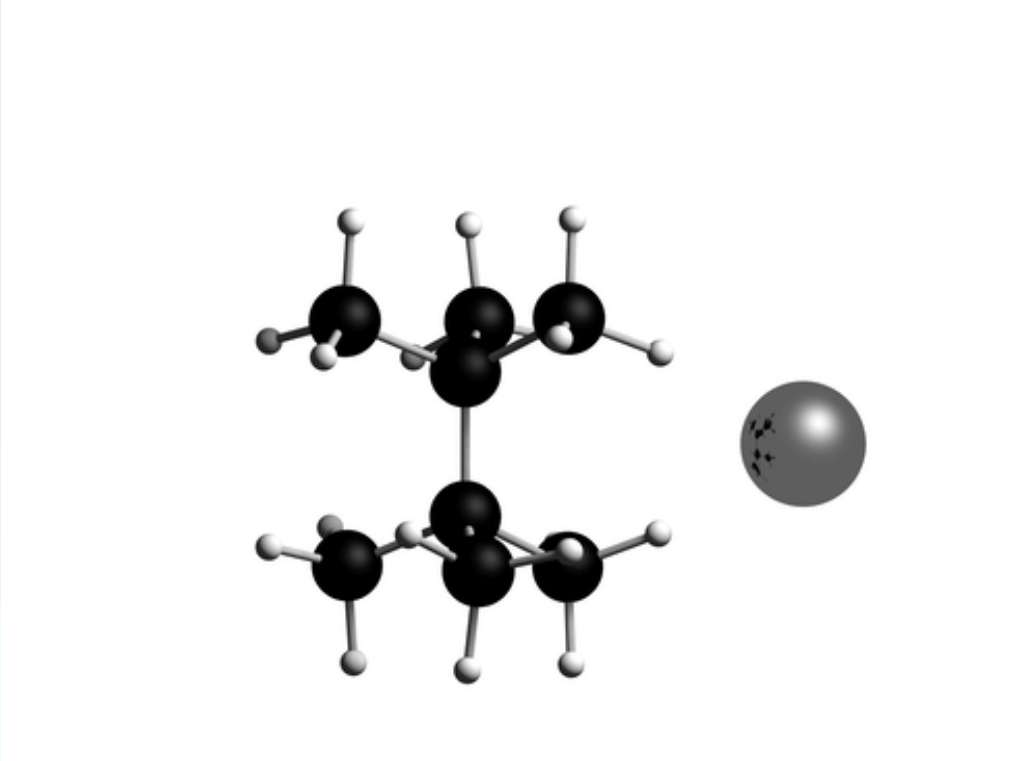


C–H vs C–C Activation



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

Bulky Substrates

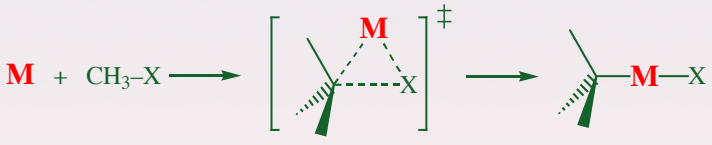


ChemPhysChem **2007**, *8*, 1170

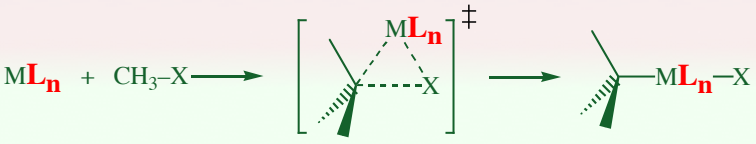
Fragment-oriented Design

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

Summary

- Steric shielding raises barrier C–C bond activ.
- First: understand intrinsic reactivity of metal
- Then: enhance/attenuate good/bad properties

Take-Home Message

- **KS-MO: causal** model of bonding mechanism
- Quantitative **EDA** **incomplete without bond. mech. !**
- Activation Strain Model generalization to reactions

Physically sound QM design principles

Further Reading

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