Reaction path analysis of benzene hydrogenation on Pt based on ab initio calculations

M. Saeys, G.B. Marin

Laboratory for Petrochemical Engineering, Ghent University

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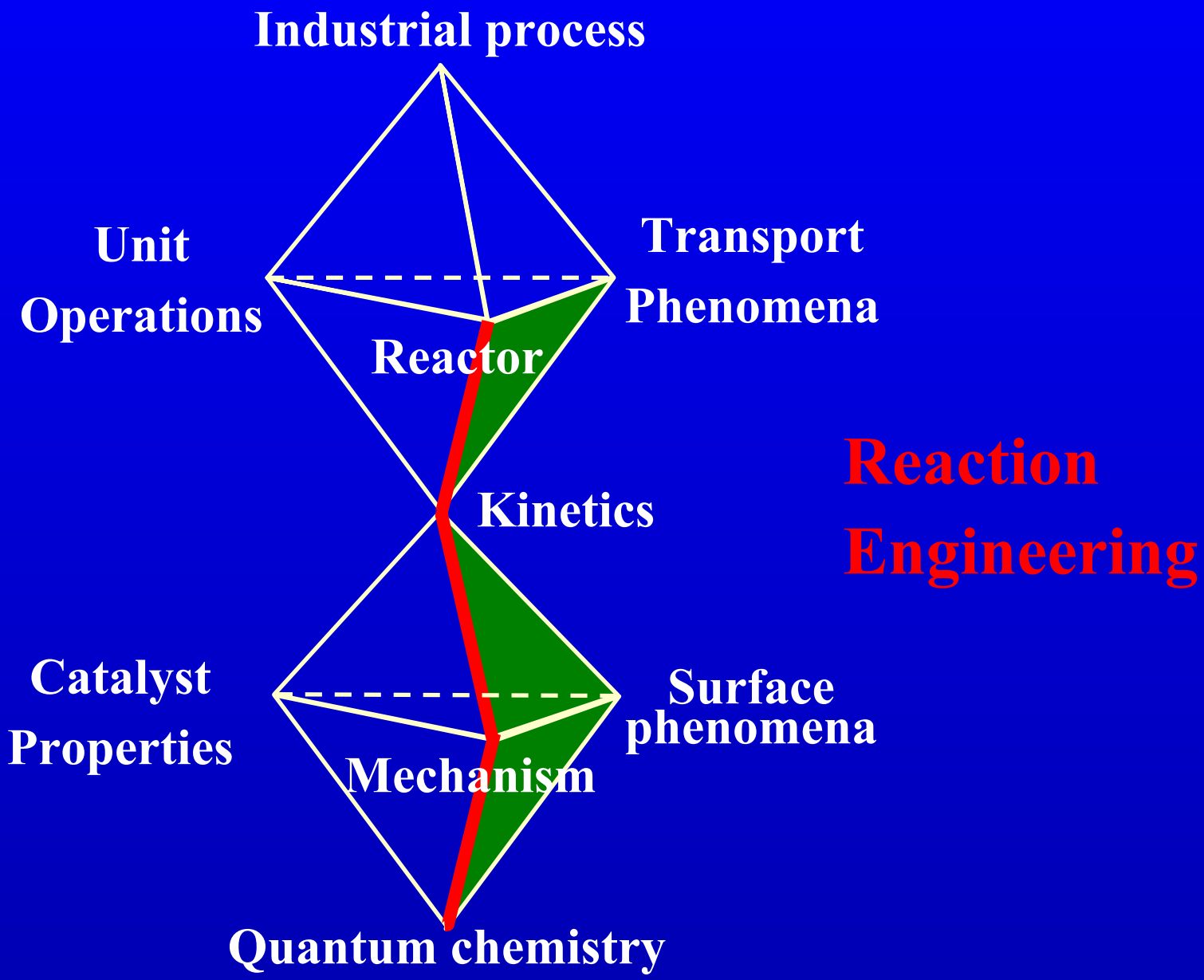
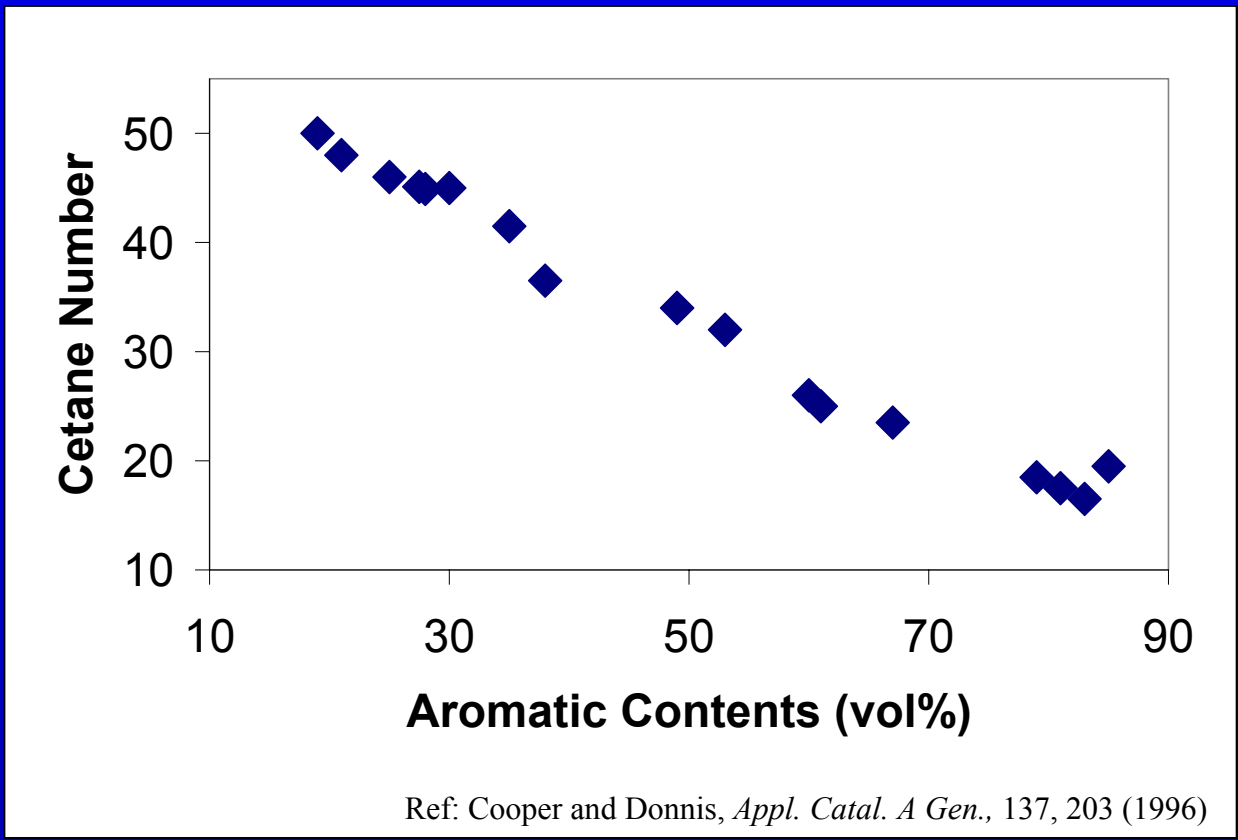

Industrial process
Unit Operations
Transport Phenomena
Reactor
Kinetics
Reaction Engineering
Catalyst Properties
Surface phenomena
Mechanism
Quantum chemistry

- Motivation of study
  - Hydrogenation/dehydrogenation cyclic C_6
  - Industrially important
    - naphtha reforming/petroleum refining
    - hydrocracking
  - Pt: very effective (de)hydrogenation catalyst
  - Model reaction
  - Experimental studies
    - kinetic and spectroscopic
  - Goals
    - kinetic model (qualitative)
    - kinetic parameters (quantitative)

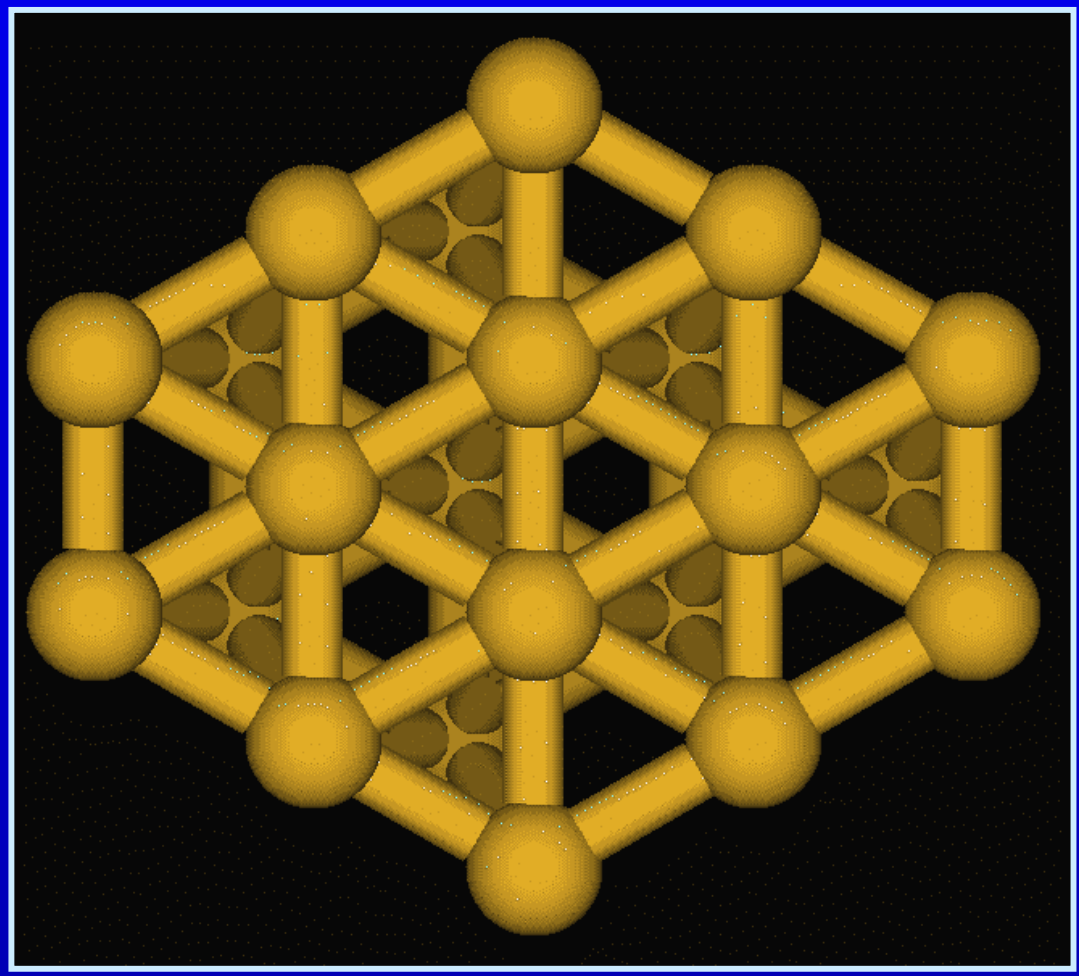
- Aromatics Removal in Hydrocracking
  - Environmental reasons: some carcinogenic
  - Quality reasons: cetane index



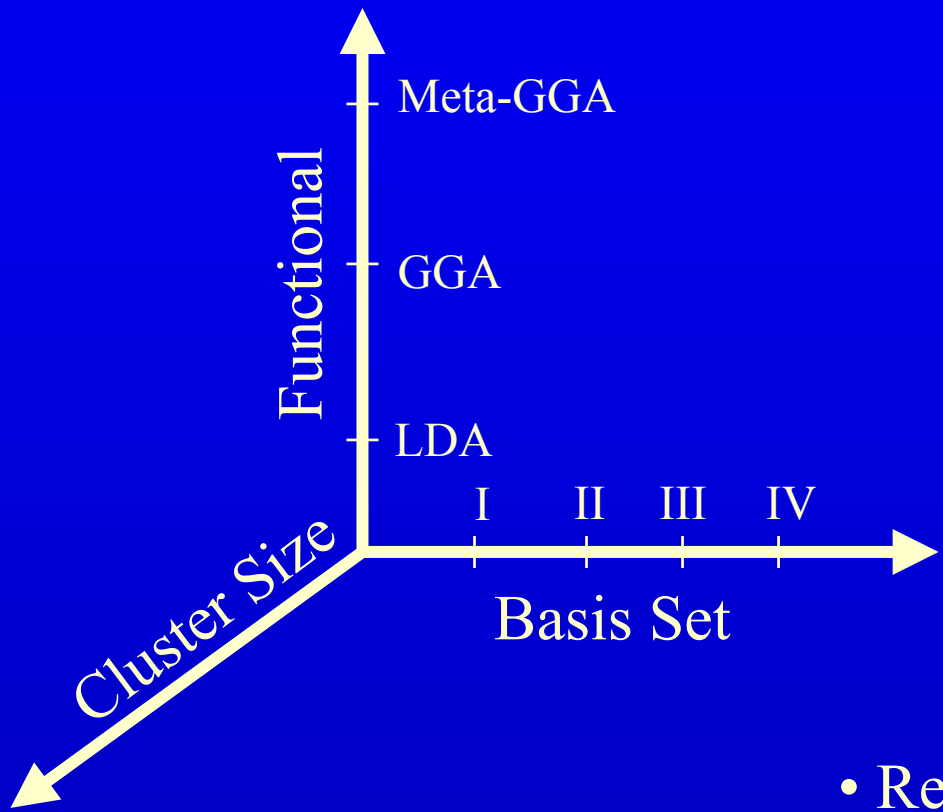
Ref: Cooper and Donnis, *Appl. Catal. A Gen.,* 137, 203 (1996)

- Density Functional Theory
  - Schrödinger Equation
  - Hohenberg-Kohn: $E=f[\rho(r),V(r)]$
  - Central variable: 3D electron-density
  - Kohn-Sham: basis set
  - Form of functional:
    - LDA, GGA, meta-GGA, hybrid

- Cluster method



Method



- Relativistic
- Cluster optimization
- Spin polarization

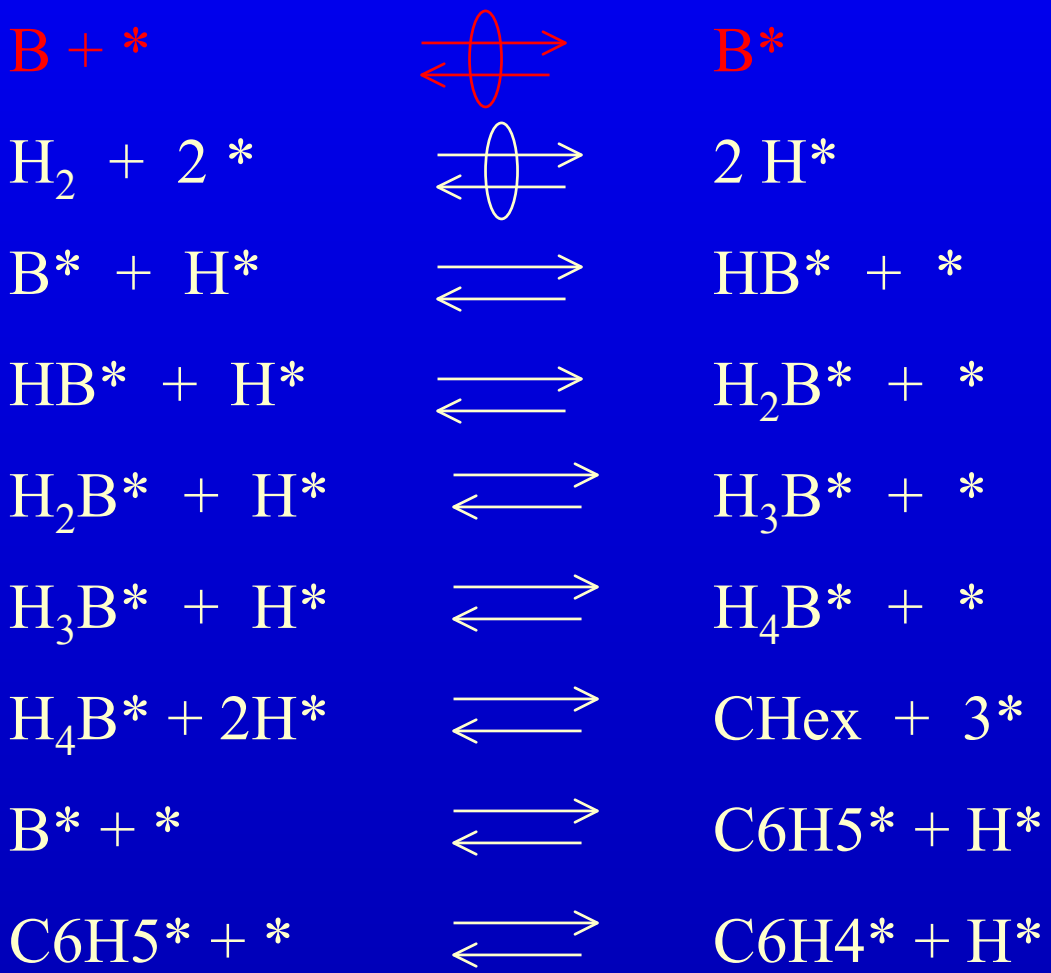
- Computational Methodology:
  - DFT with Becke Perdew86 functional (GGA)
  - Double zeta basis set with relativistic frozen core potentials for Pt (4f) and C (1s)
    - tests with larger basis set, smaller frozen core
  - Relativistic approximation: ZORA
  - Unrestricted, spin optimized
  - Amsterdam Density Functional program package
  - Fixed Pt (14,8) cluster
    - tests with larger clusters, periodic calculations
    - tests with partially optimized clusters

Benchmarking of method

- Calculation vs. Experiment
  - Adsorption of stable molecules
    - Benzene, hydrogen, cyclohexadiene, cyclohexene and cyclohexane
  - Gas phase thermochemistry

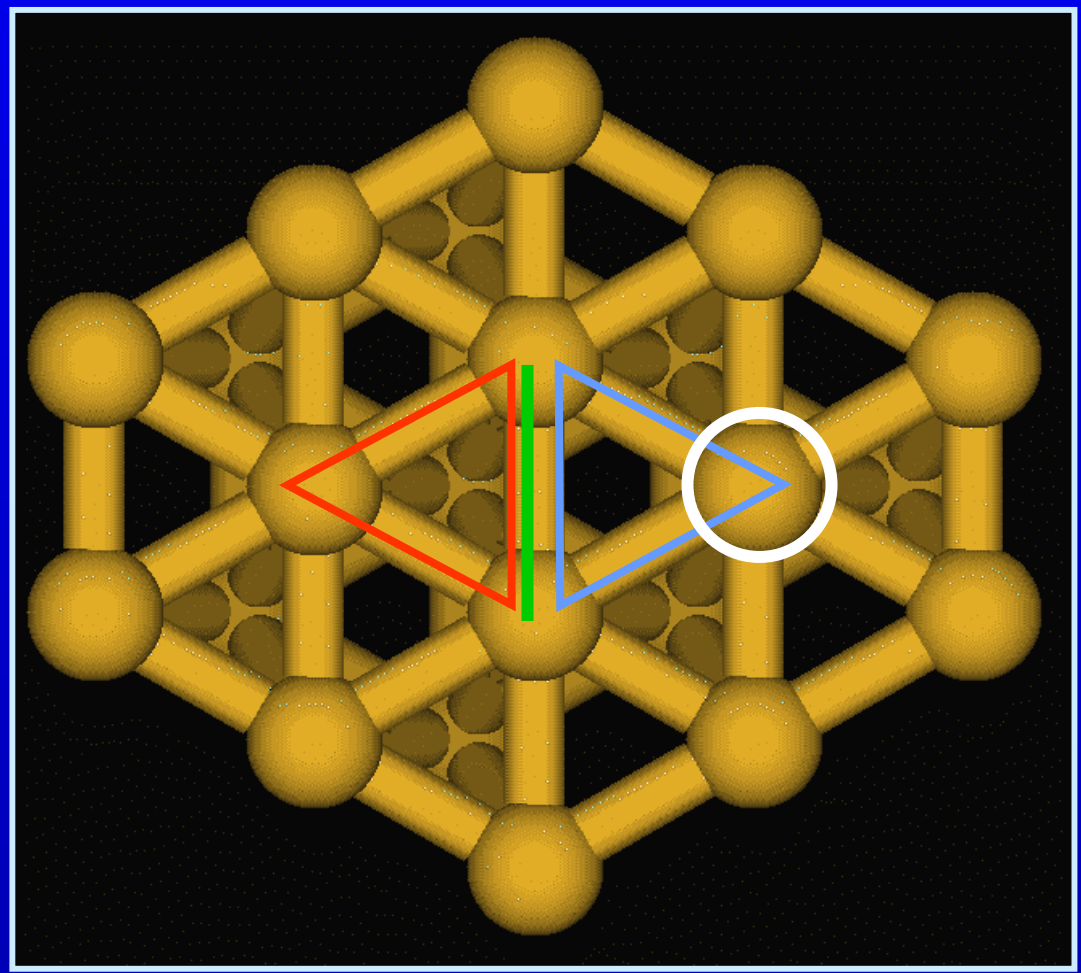
Benzene Adsorption

- Reaction mechanism:



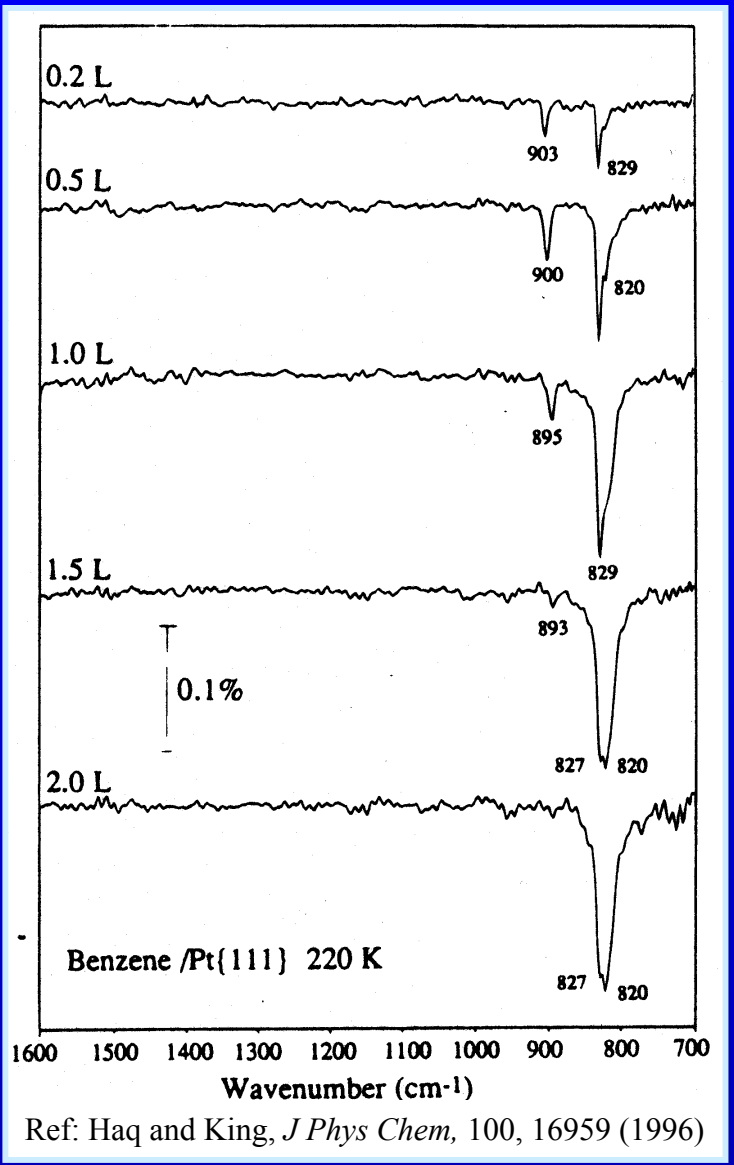
Benzene Adsorption

- Pt(111)-adsorption sites:



- Bridge —
- Hollow hcp —
- Hollow fcc —
- Atop —

Benzene Adsorption



Ref: Haq and King, *J Phys Chem,* 100, 16959 (1996)

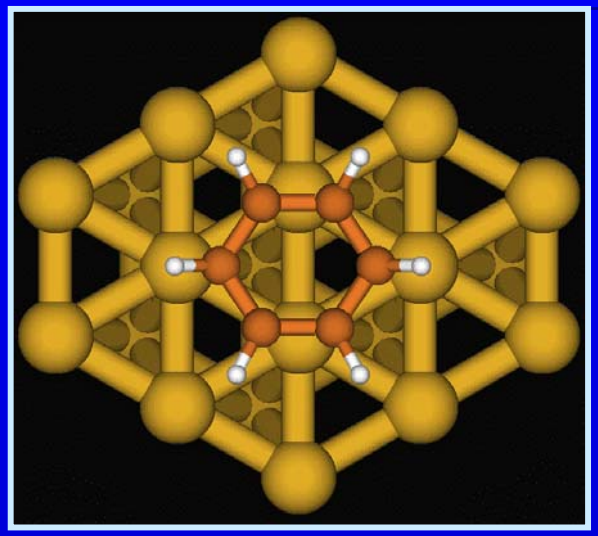
- Experimental data

– STM: - at 298K: Hollow/bridge=2/3
  - at 4K: bridge

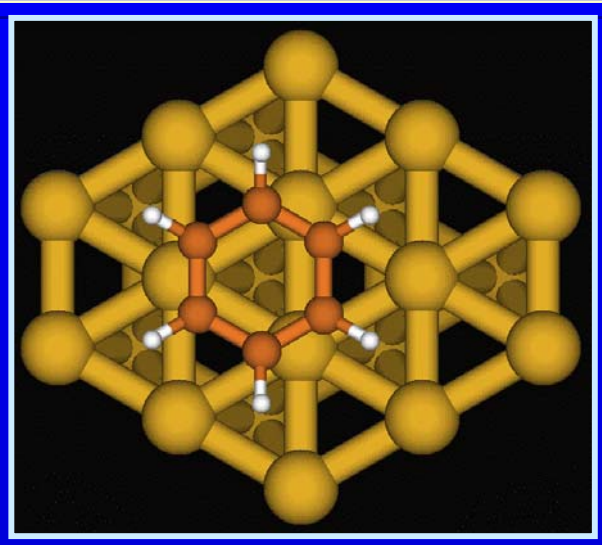
– TPD: Adsorption enthalpy: 117 kJ/mol and 82 kJ/mol

– HREELS, RAIRS:
  – 3 peaks: 820, 830 and 900 cm^{-1}
  – Coverage dependence

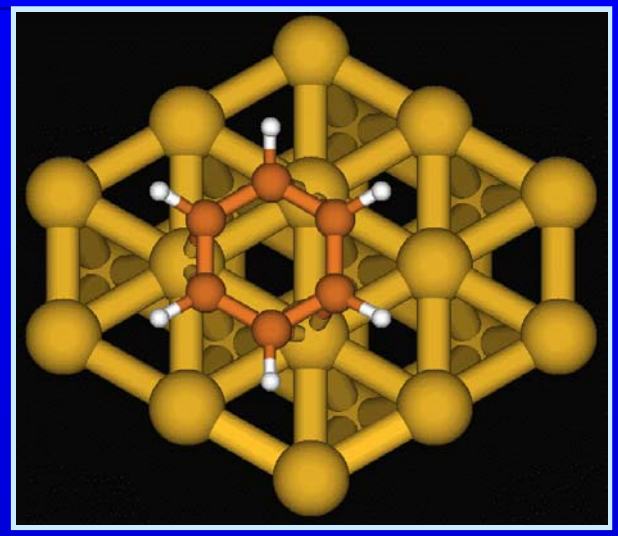
Benzene Adsorption



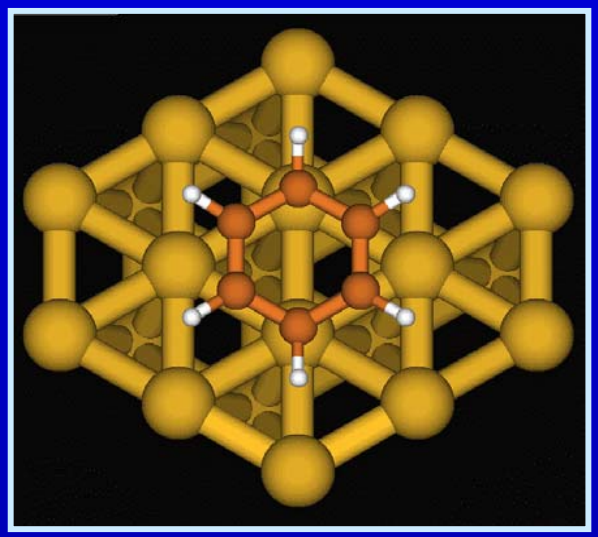
Bridge site: 102 kJ/mol



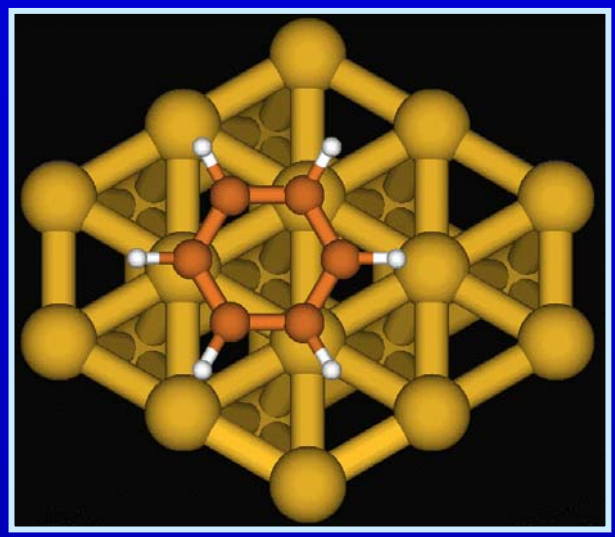
Hollow hcp: 71 kJ/mol



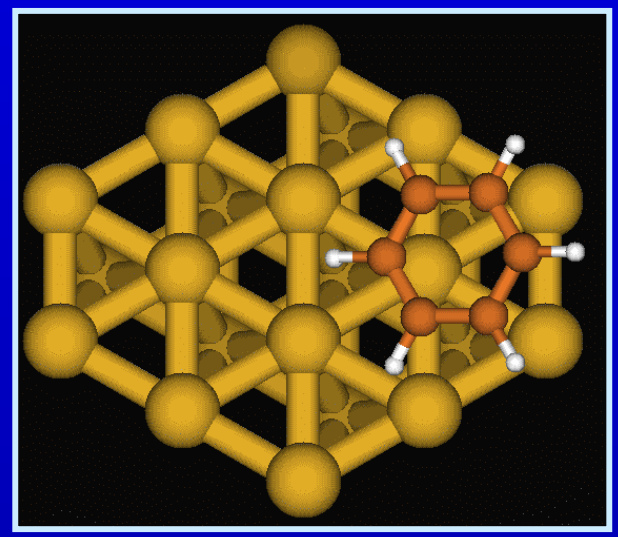
Hollow fcc: 68 kJ/mol



Bridge site II: 66 kJ/mol



Hollow hcp II: 51 kJ/mol



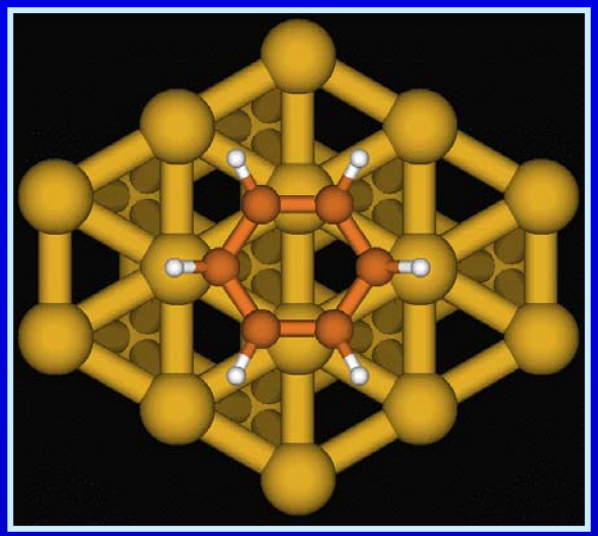
Atop: 0 kJ/mol

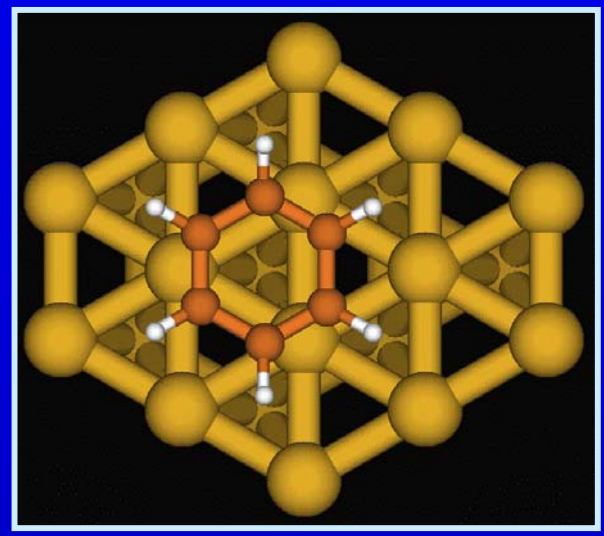
Benzene Adsorption

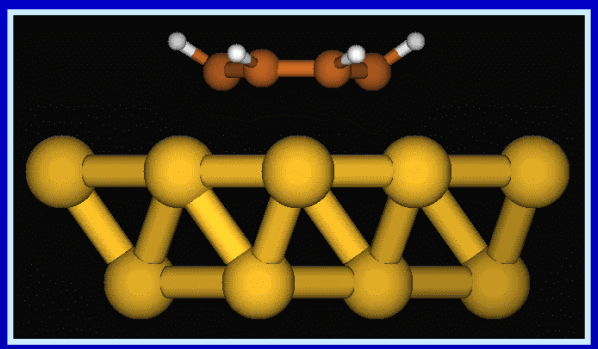
Bridge: 102 kJ/mol

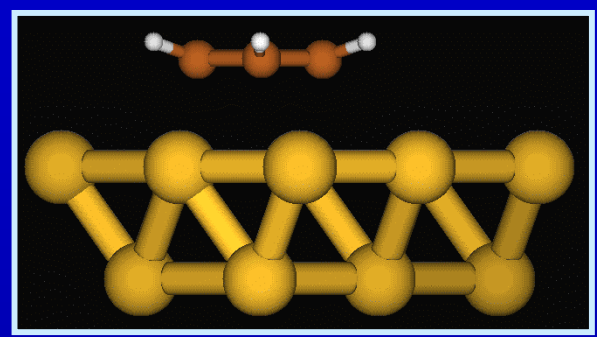
Hollow: 71 kJ/mol

Expt: 117 kJ/mol and 82 kJ/mol





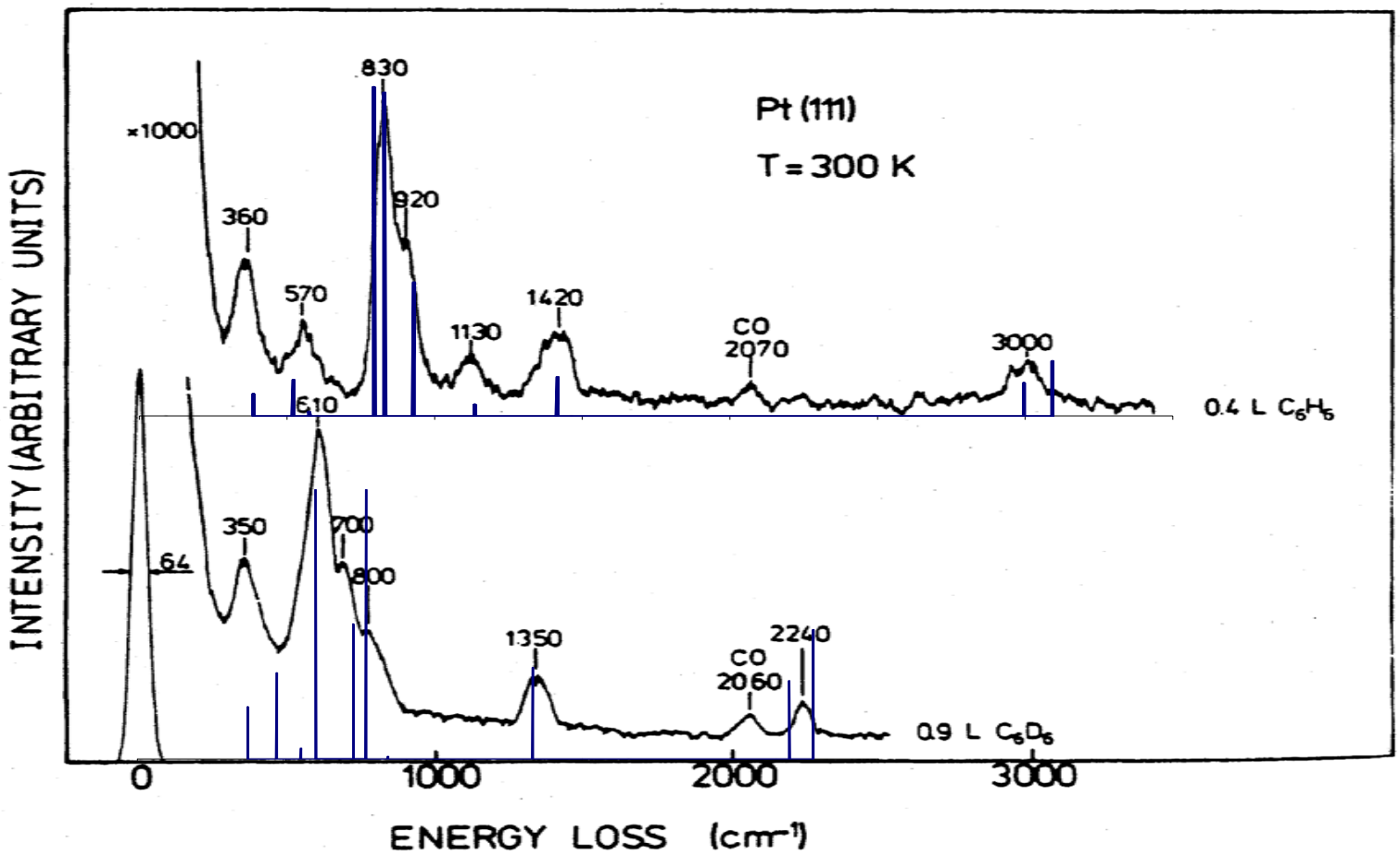




Benzene Adsorption

- Calculated/experimental vibrational spectrum

  Bridge adsorbed C_6H_6 and C_6D_6

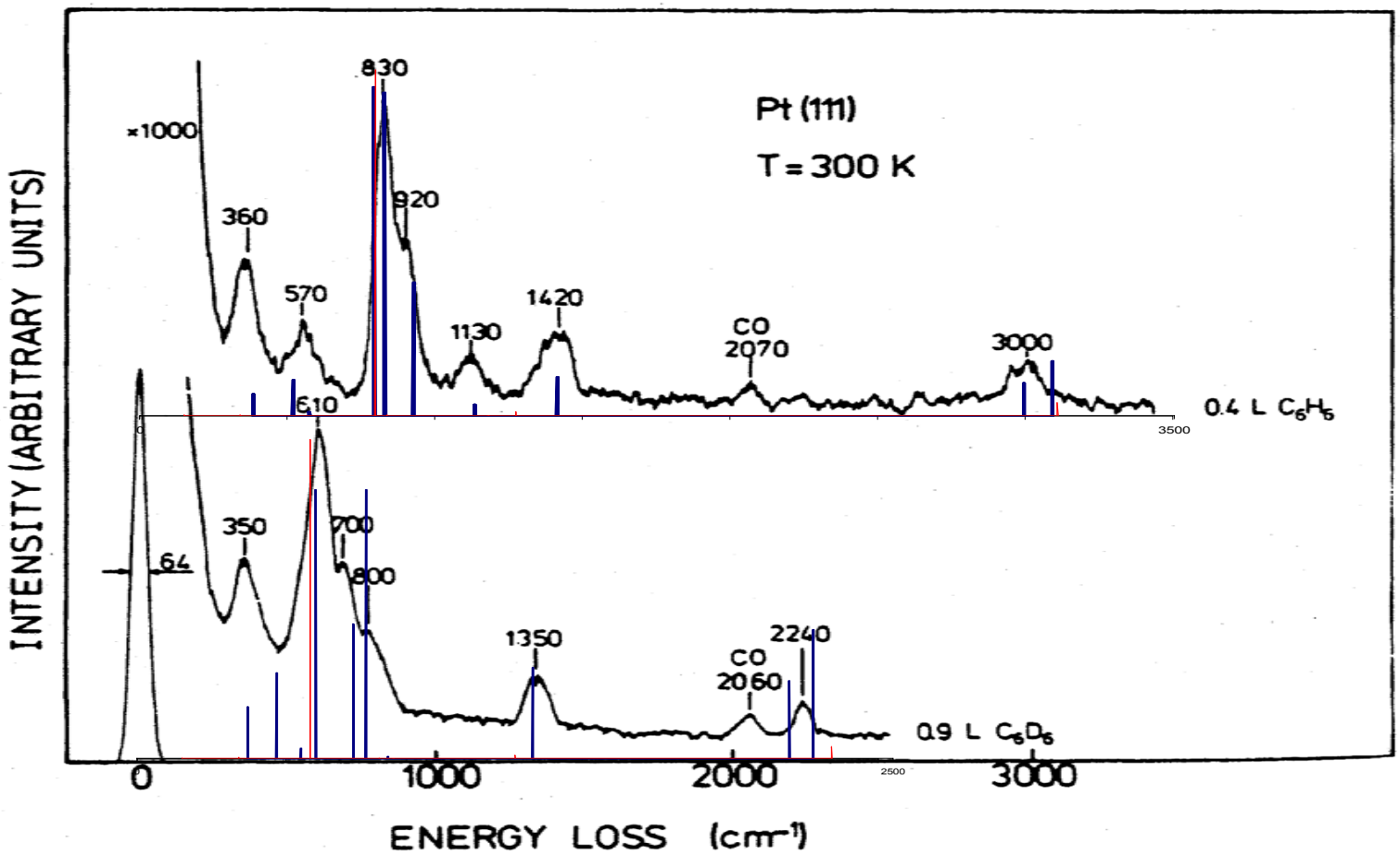


Ref: Lehwald et al, *Surf Sci*, 78(3), 577, 1978

Benzene Adsorption

- Calculated/experimental vibrational spectrum

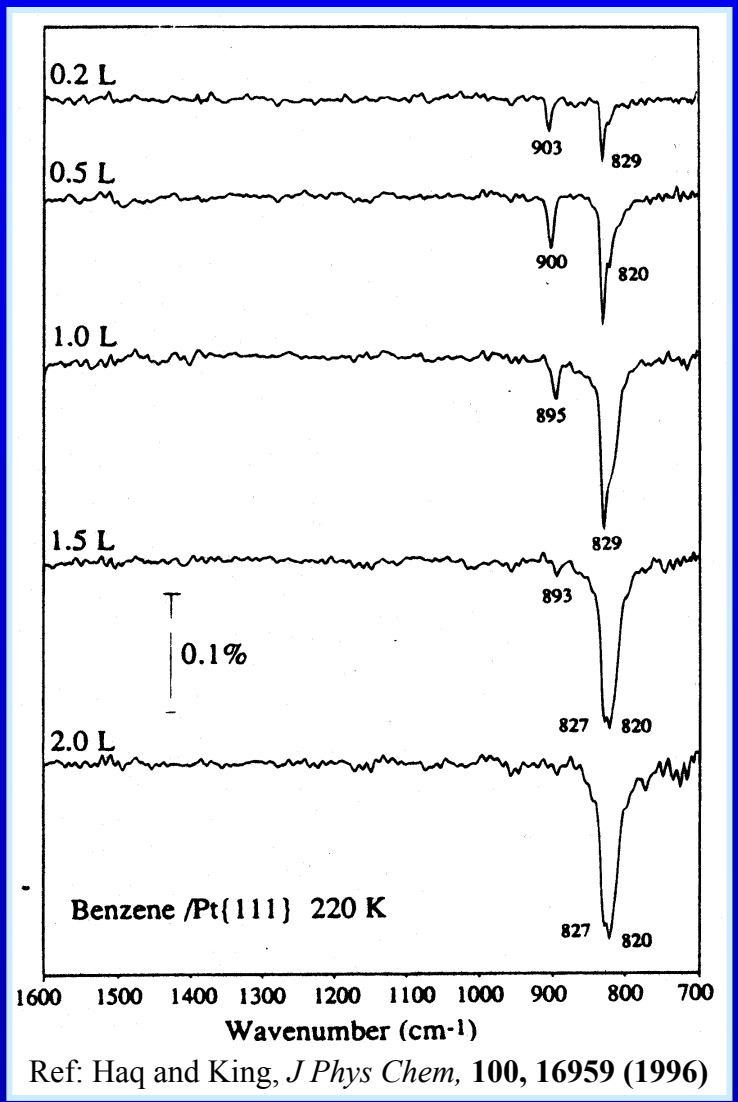
  Hollow adsorbed C_6H_6 and C_6D_6



Ref: Lehwald et al, *Surf Sci*, 78(3), 577, 1978

Benzene Adsorption

- Coverage dependence of vibrational spectrum



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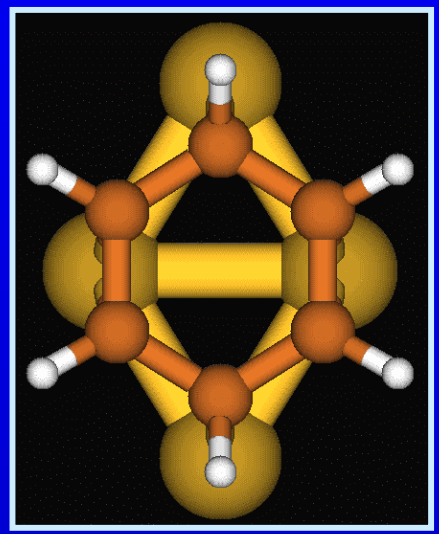
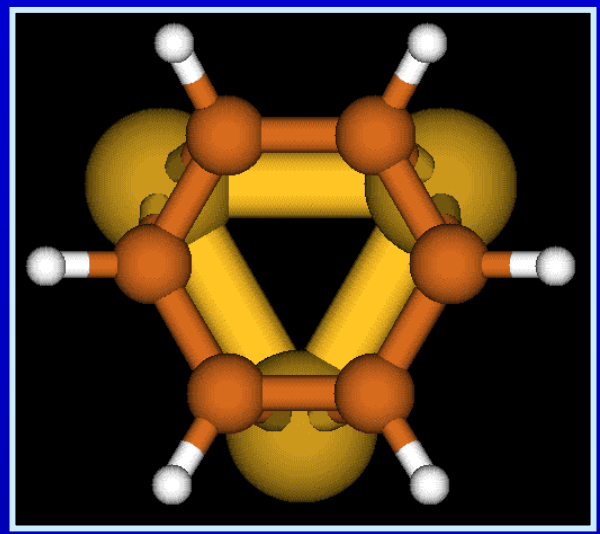


Bridge

796 cm^{-1}

831 cm^{-1}/928 cm^{-1}

1415 cm^{-1}



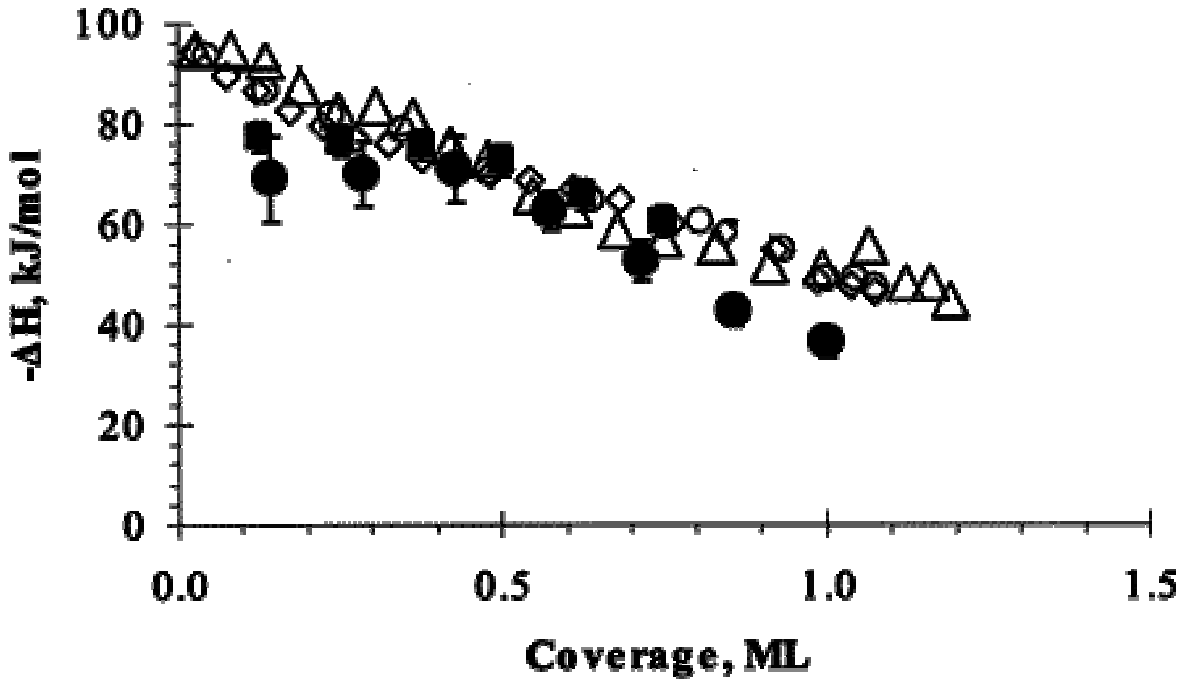
Hollow

796 cm^{-1}

- Summary
  - Two important adsorption sites: bridge and hollow
  - Bridge:
    - favoured site at low coverage
    - low mobility
  - Hollow:
    - less stable at low coverage, more important at high coverage
    - high mobility
  - Hollow hcp=Hollow fcc
  - Vibrational spectra: explained

H_2 Adsorption

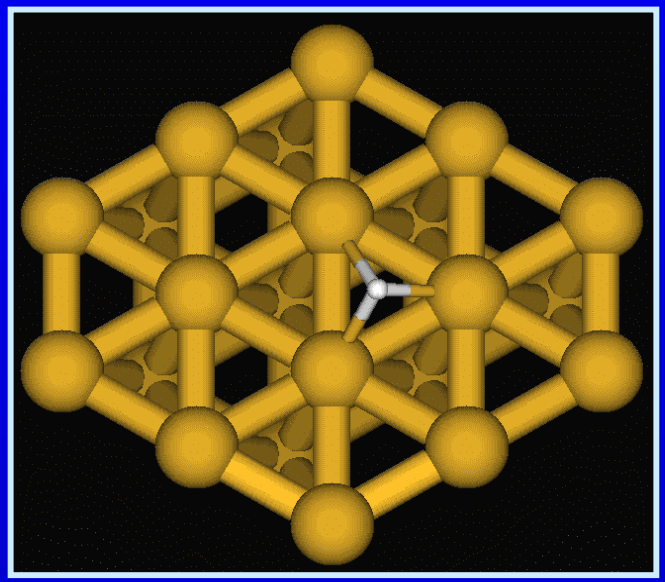
- Data
  - Many experimental and theoretical studies
  - Experimental adsorption enthalpy: coverage dependent
  - Low coverage: $\Delta H_{ads} = 90$ kJ/mol



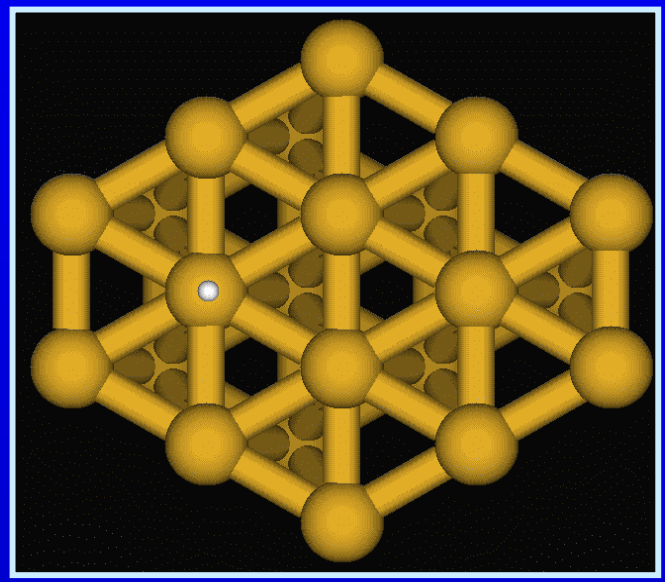
Ref: Podkolzin, Dumesic et al., *J Phys Chem B,* 105(36), 8550, 2001

H_2 Adsorption

- Calculated results



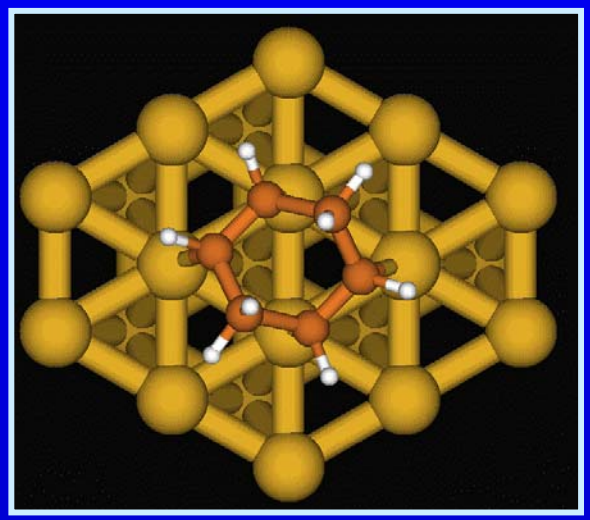
Hollow fcc: 86 kJ/mol



Top: 94 kJ/mol

- Summary
  - Good agreement with experiment
  - Top slightly more stable than hollow site
  - H is very mobile

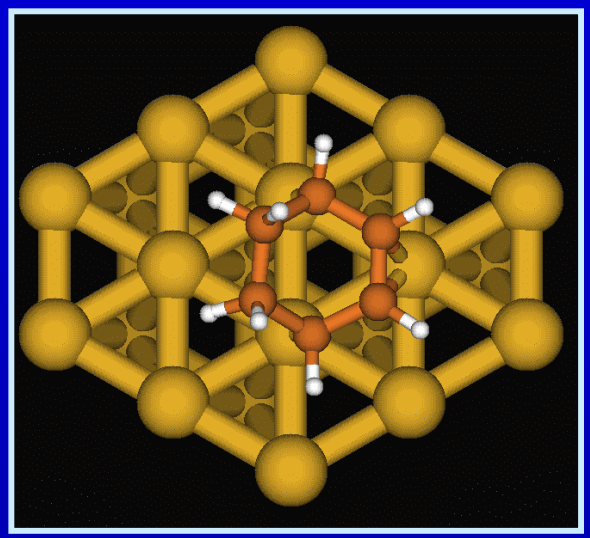
- Calculated vs. experimental results



1,4-Cyclohexadiene:

$\Delta H_{ads,calc}$: 146 kJ/mol

$\Delta H_{ads,exp} \approx$ 143 kJ/mol

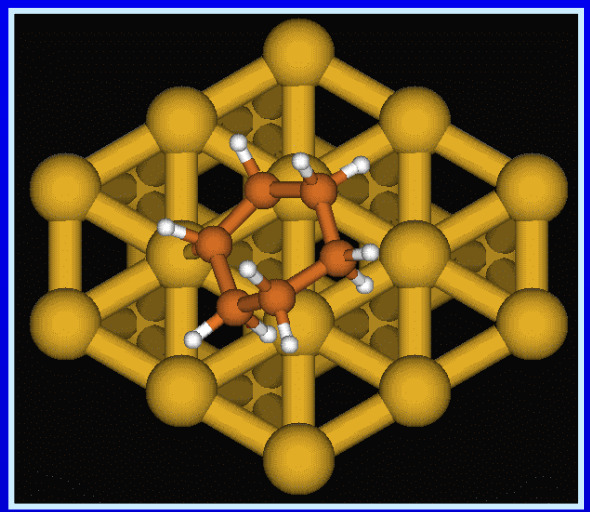


1,3-Cyclohexadiene:

$\Delta H_{ads,calc}$: 143 kJ/mol

$\Delta H_{ads,exp} \approx$ 143 kJ/mol

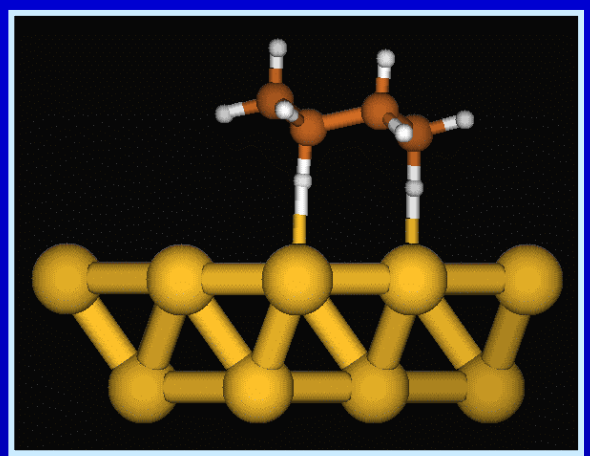
- Calculated vs. experimental results



Cyclohexene:

$\Delta H_{ads,calc}$: 68 kJ/mol

$\Delta H_{ads,exp}$ = 62-72 kJ/mol



Cyclohexane:

$\Delta H_{ads,calc}$: 28 kJ/mol

$\Delta H_{ads,exp}$ = 58 kJ/mol

Gas phase thermochemistry

- Gas phase reaction enthalpy (kJ/mol): (de)hydrogenation of benzene:

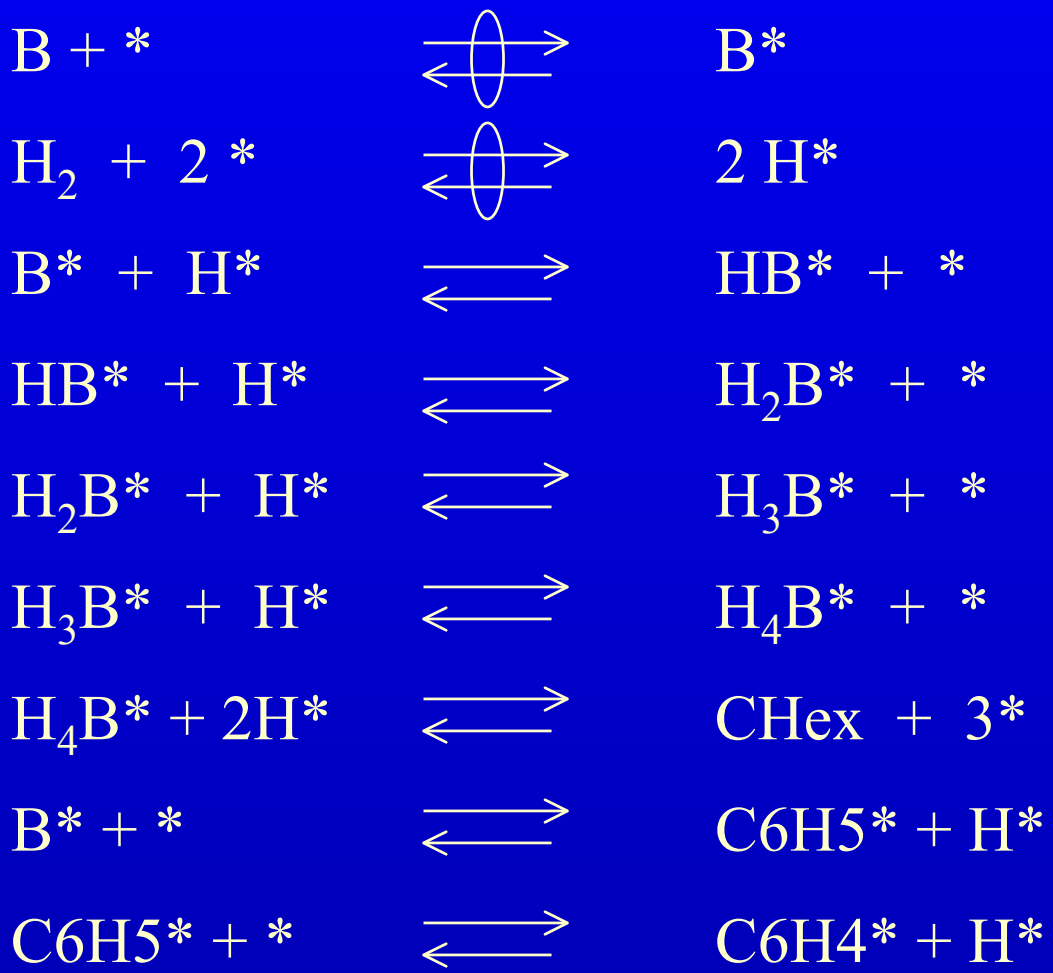
Product	$\Delta H_r°$ (298K) Calc	$\Delta H_r°$ (298K) Exp	Error
Benzyne	**+380**	**+379**	**+1**
1,4-cyclohexadiene	**+37**	**+29**	**+8**
Cyclohexene	**-71**	**-86**	**+15**
Cyclohexane	**-187**	**-207**	**+20**

- Approach:

– Start from experimental gas phase enthalpies and combine with calculated adsorption enthalpies

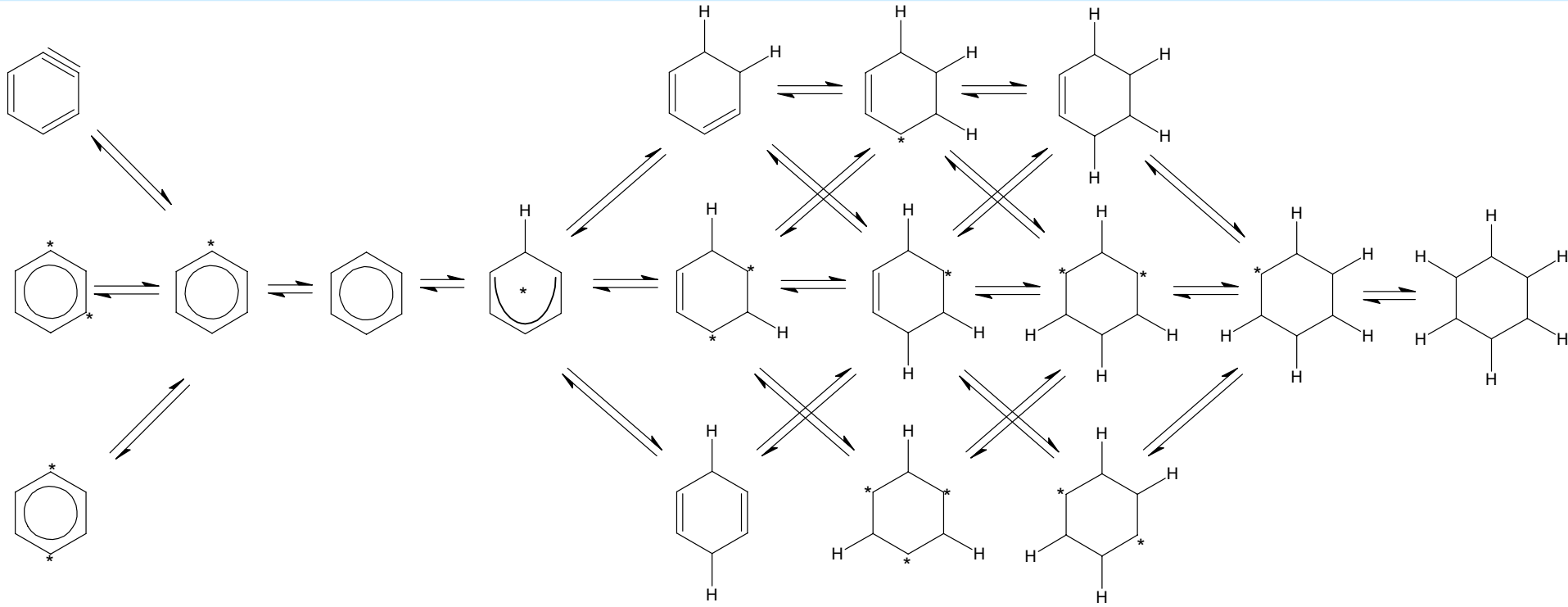
– TS: use average

- Horiuti-Polanyi:



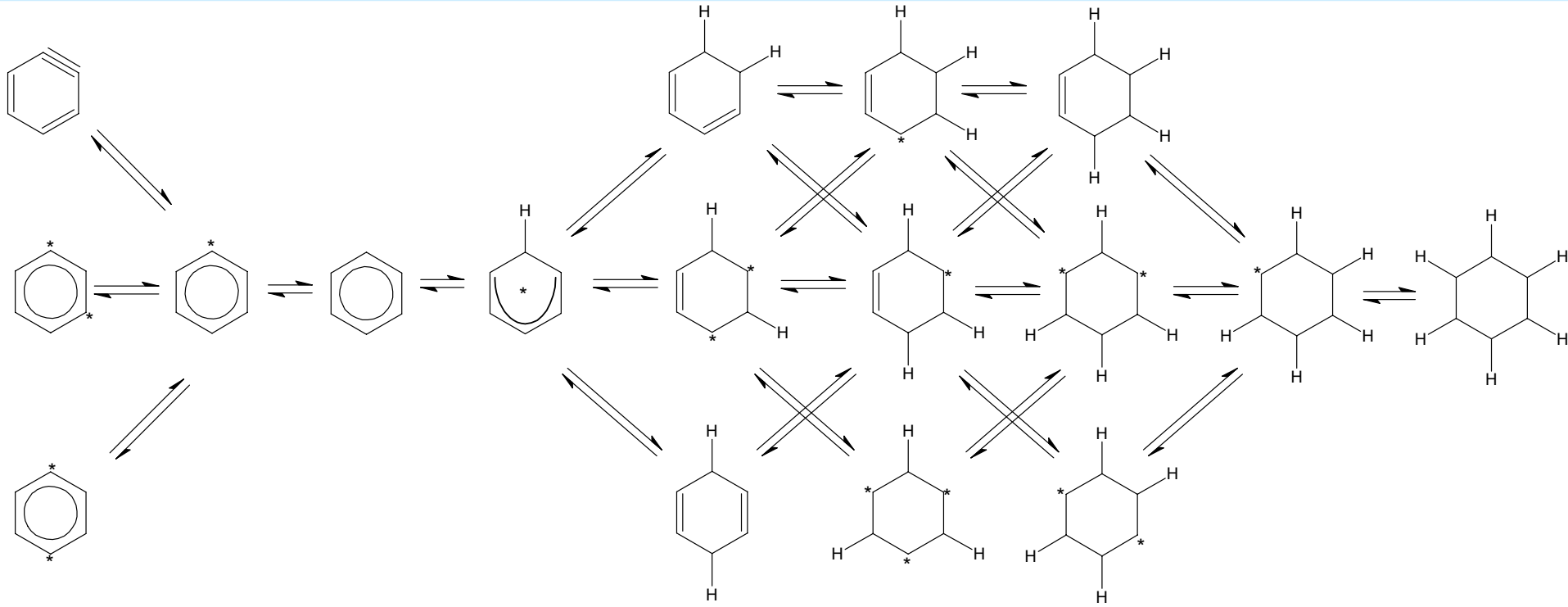
Reaction Mechanism

- More Detailed:



- Is there a dominant Reaction Path?
- Is there a RDS?
- Is dehydrogenation of benzene important?

- Reaction mechanism: Approach

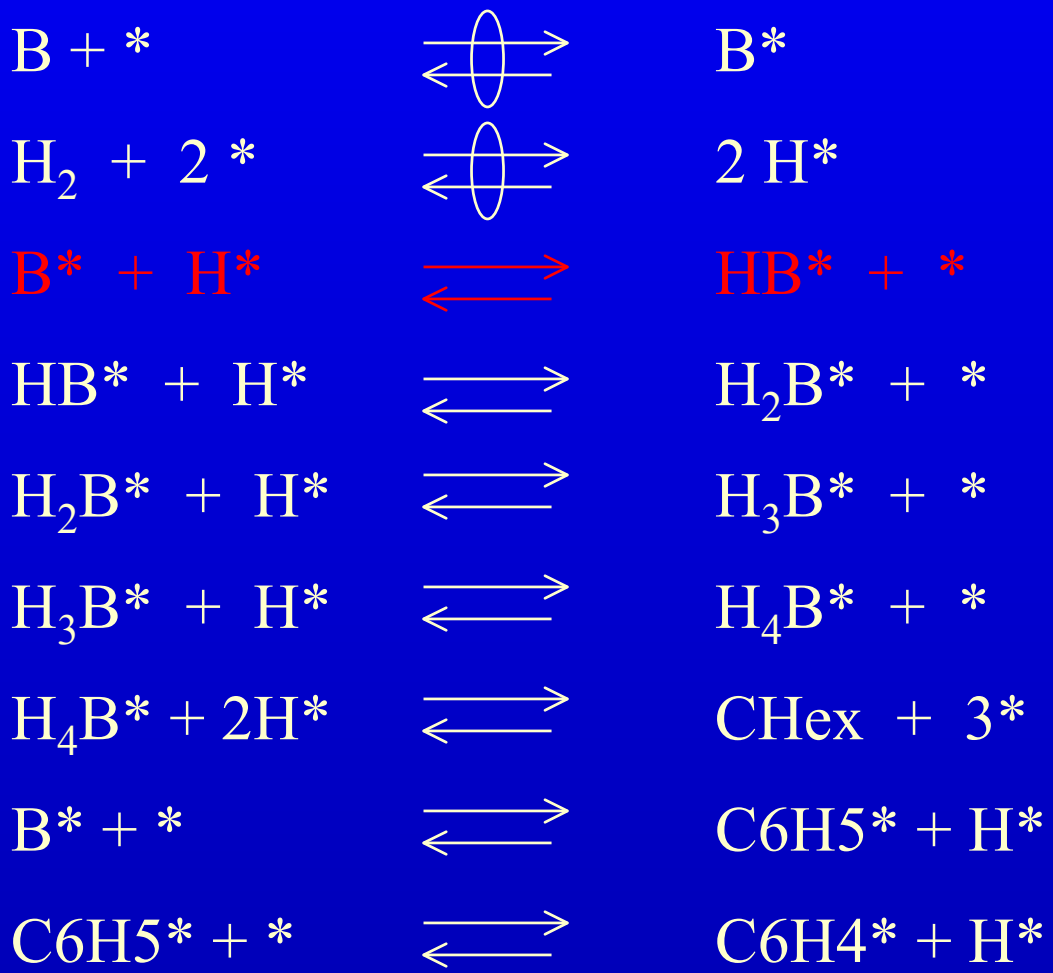


1. Start from reactant: calculate all E_a's

2. Only consider kinetically favoured route for next step

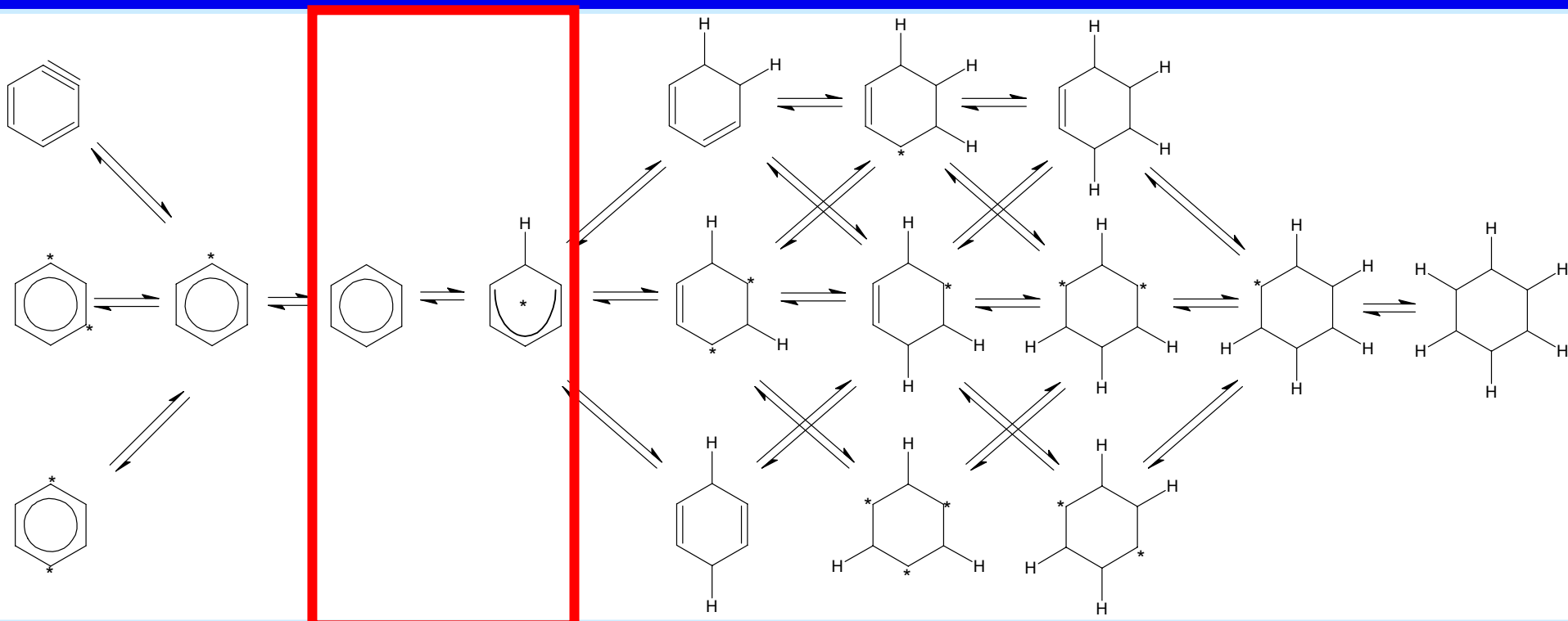
Addition of the first H

- Reaction mechanism:

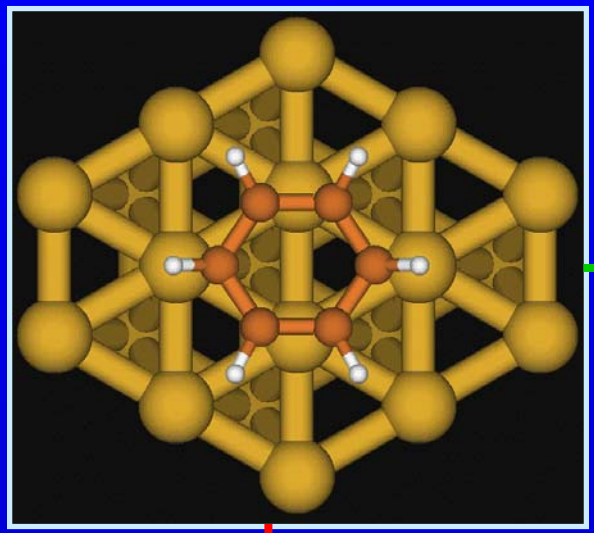


Addition of the first H

- Reaction mechanism:

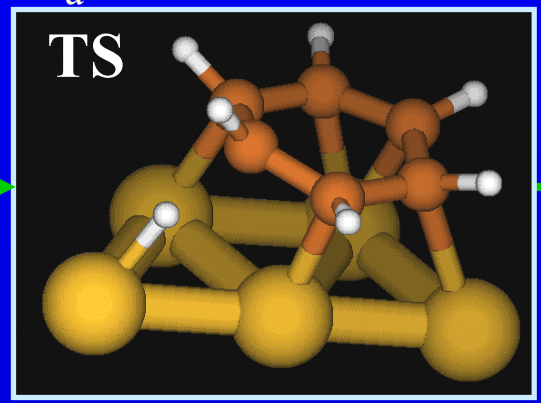


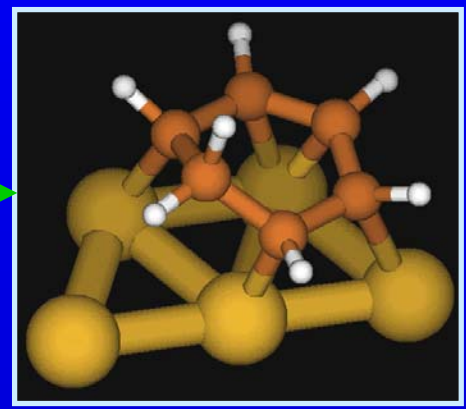
Addition of the first H

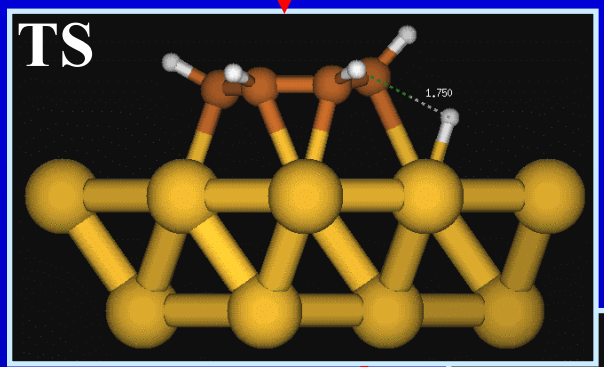


"Slip"

E_a= 120 kJ/mol; ΔH_r= +42 kJ/mol



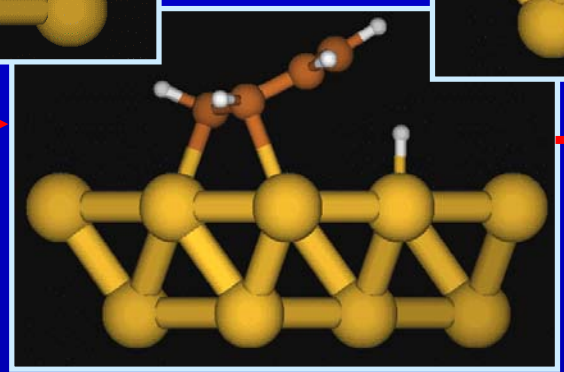


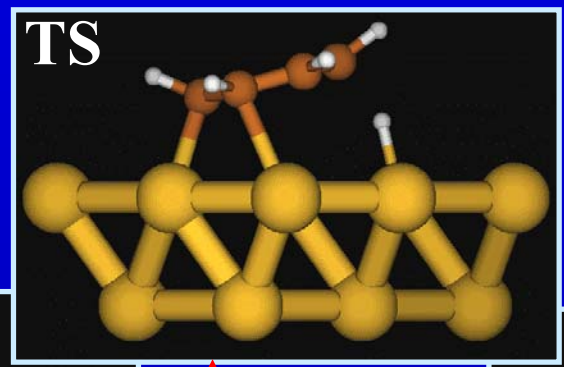


"3-Centered"

E_a=100 kJ/mol

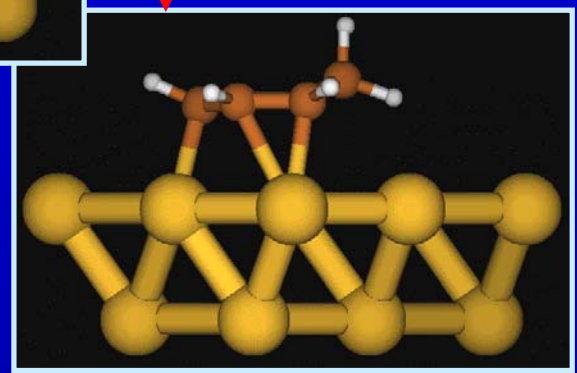
ΔH_r=+71 kJ/mol



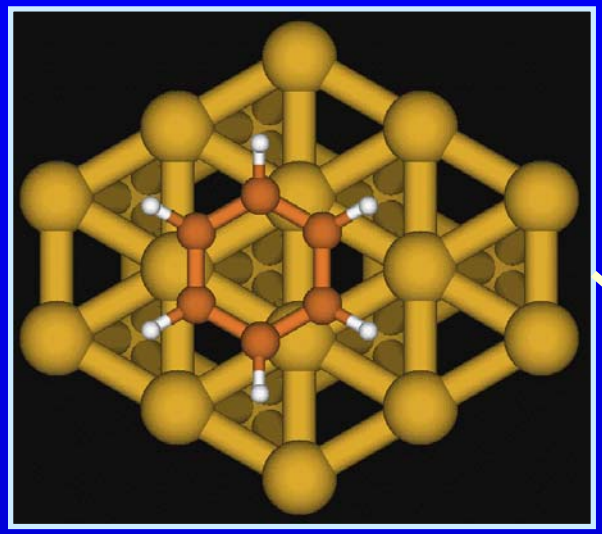


E_a= 26 kJ/mol

ΔH_r= -20 kJ/mol

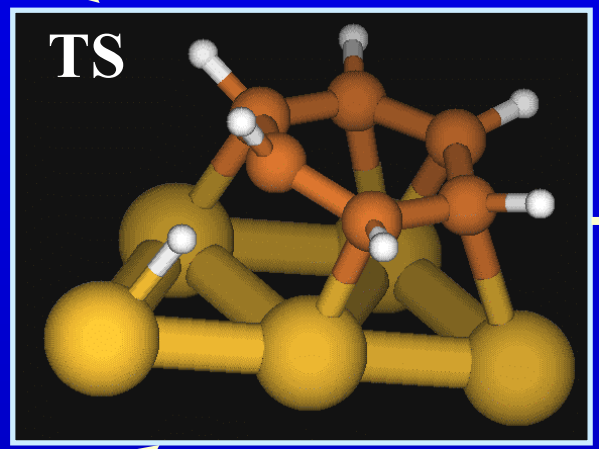


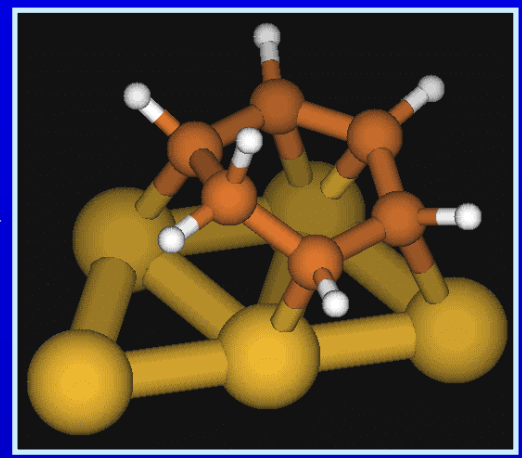
Addition of the first H

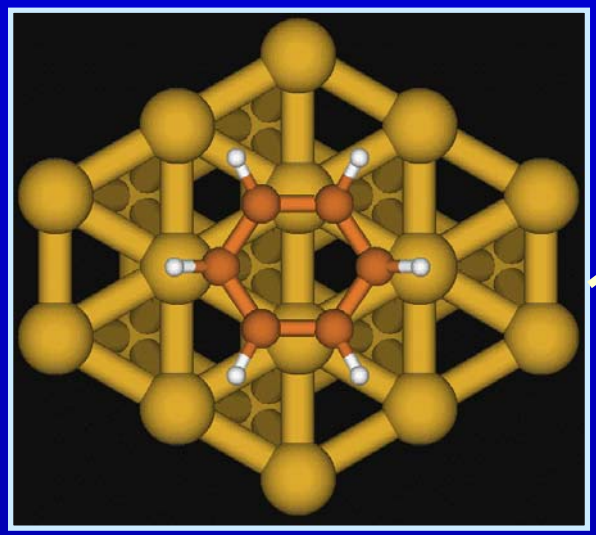


E_a = 89 kJ/mol

ΔH_r = +11 kJ/mol







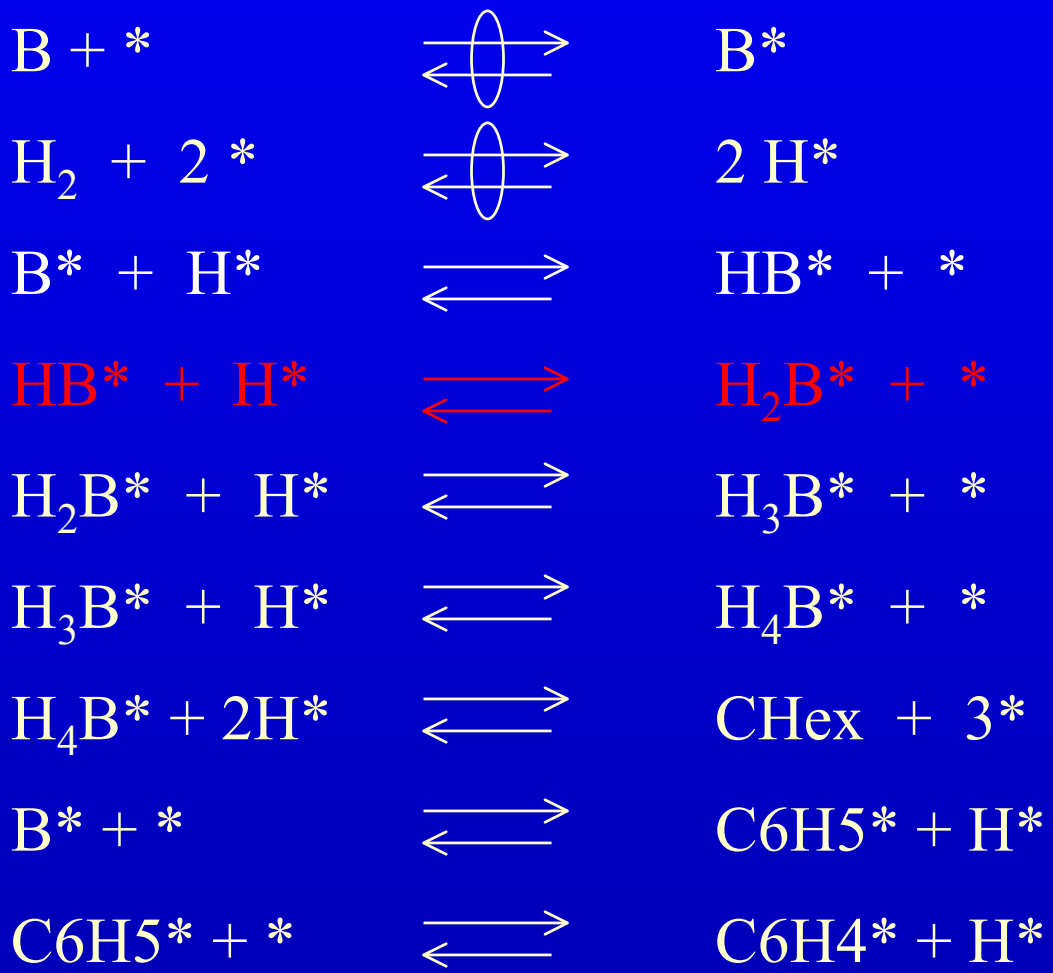
E_a = 120 kJ/mol

ΔH_r = +42 kJ/mol

- Summary
  - Three possible reaction paths
  - Two types of reaction mechanisms: Slip and 3-centered
  - Benzene adsorbed at hollow site is reactive species
  - Benzene adsorbed at bridge site is too strongly adsorbed
  - cfr. Ethylene hydrogenation

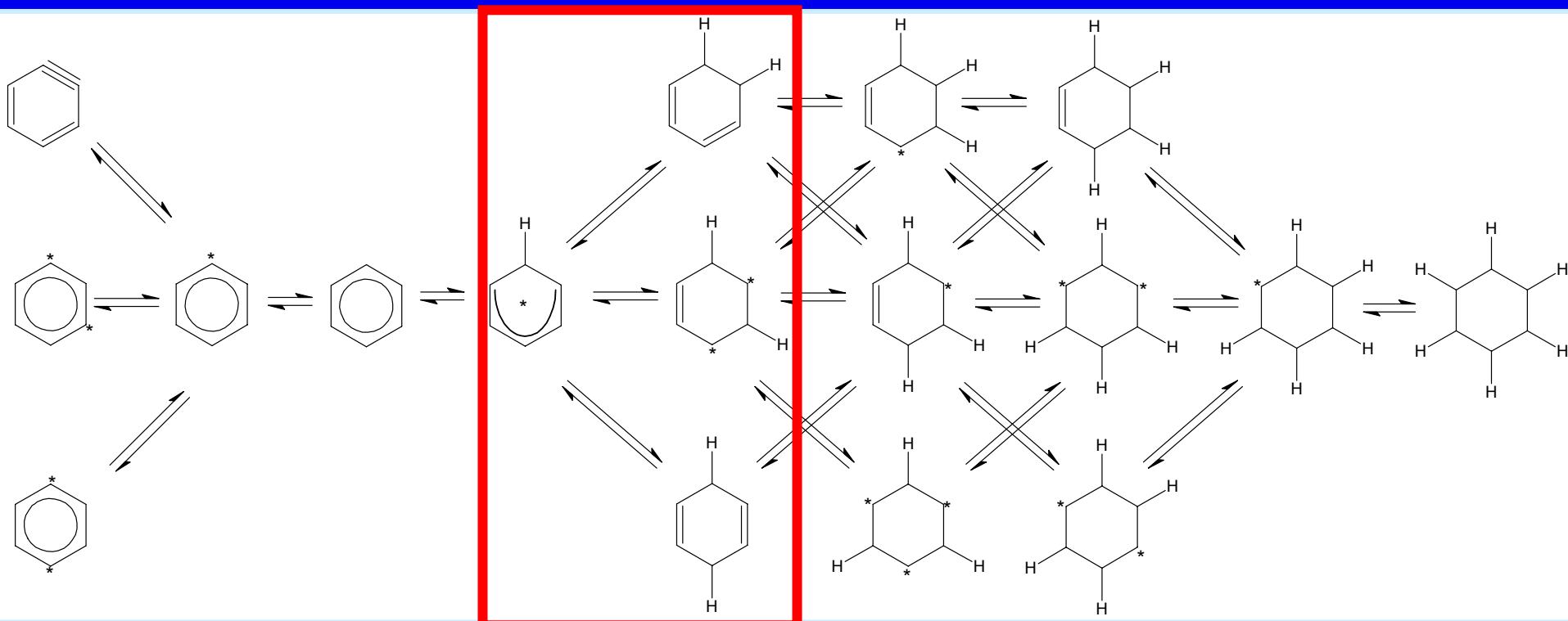
Addition of the second H

- Reaction mechanism:



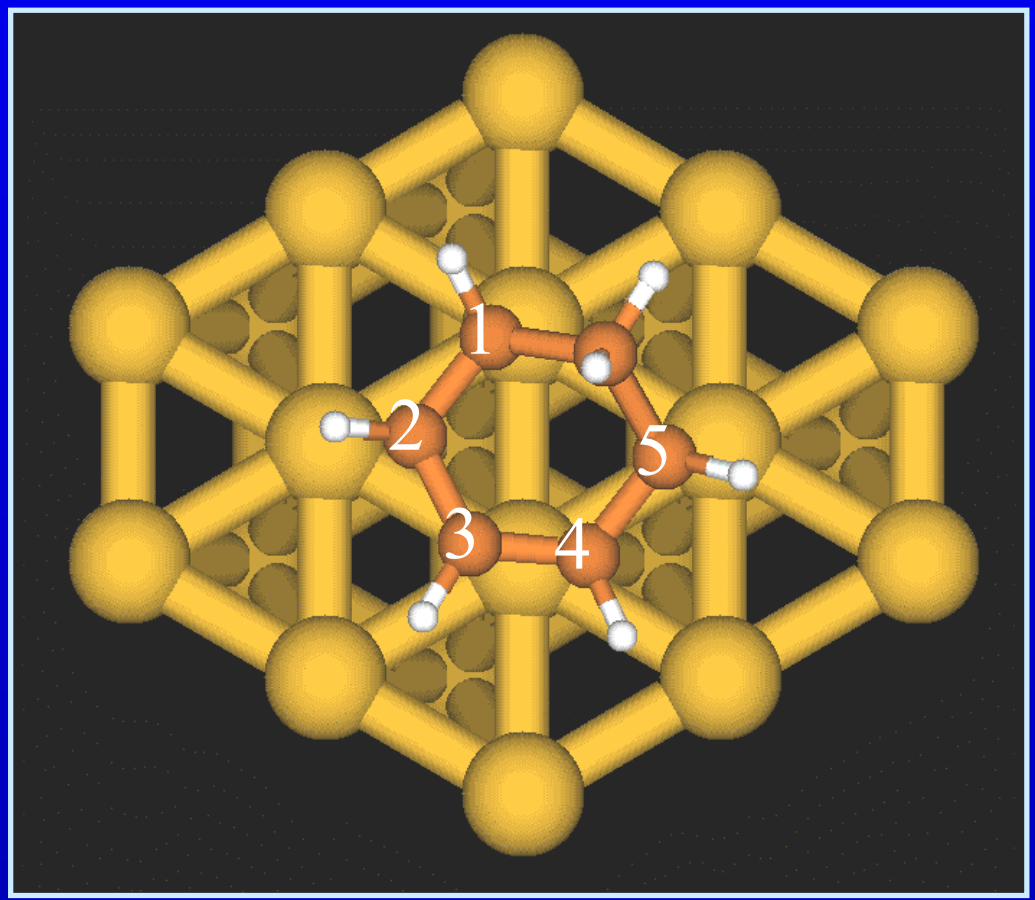
Addition of the second H

- Reaction mechanism:



Addition of the second H

- Reaction paths:



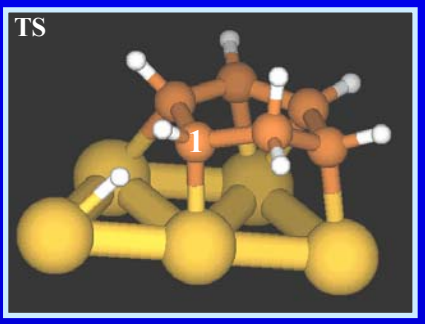
1 and 5 → 1,3-CHD

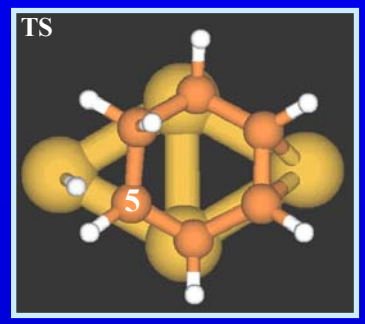
2 and 4 → 1,3-dihydroB

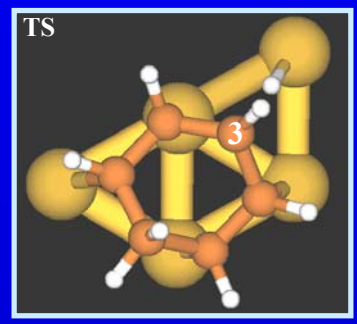
3 → 1,4-CHD

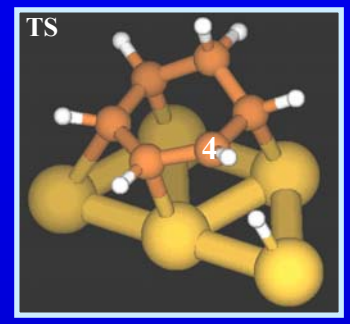
Addition of the second H

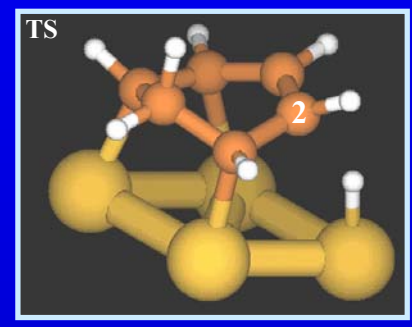
- **5 different reaction paths**

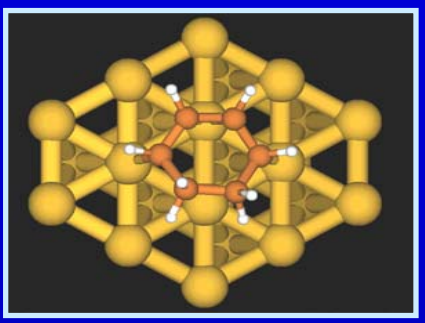


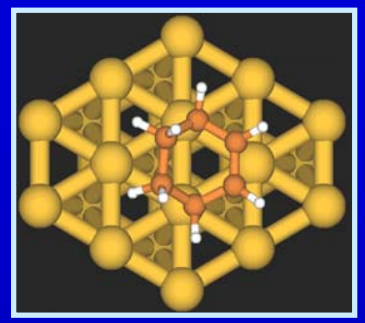


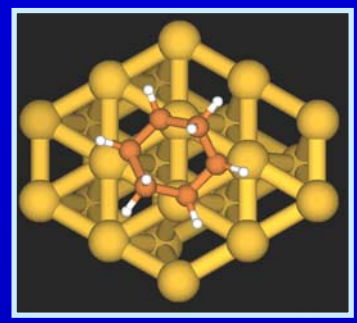


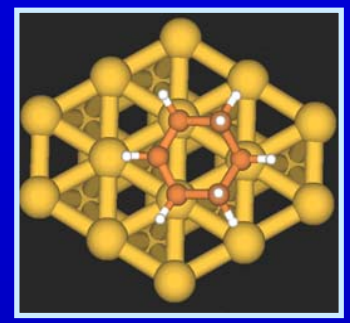


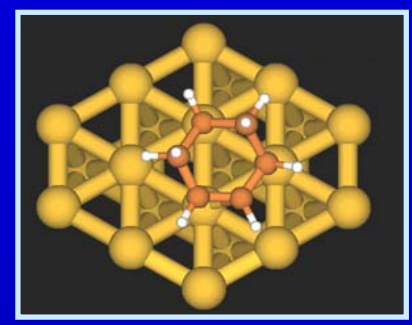












E_a= 134 kJ/mol
ΔH_r= +106 kJ/mol

1,3-CHD

E_a= 104 kJ/mol
ΔH_r= +39 kJ/mol

1,3-CHD

E_a= 126 kJ/mol
ΔH_r= +36 kJ/mol

1,4-CHD

E_a= 108 kJ/mol
ΔH_r= +26 kJ/mol

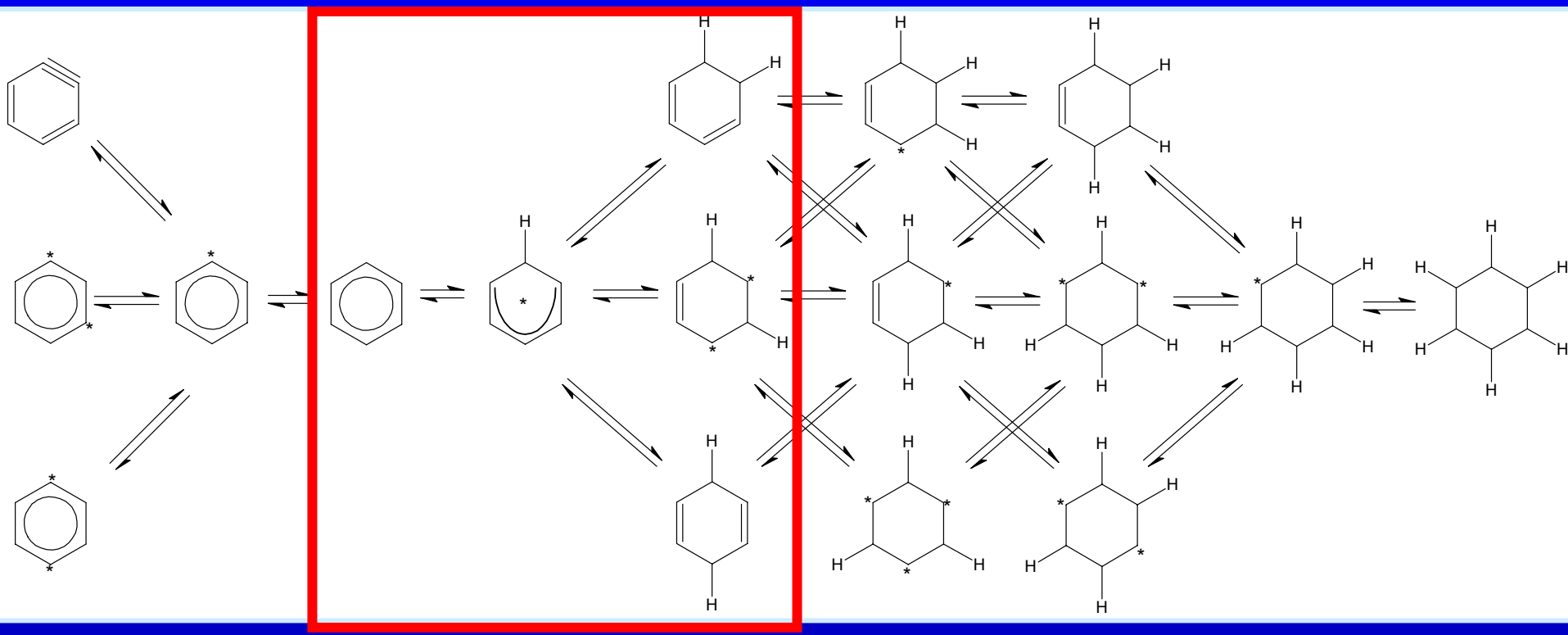
1,2-dihydroB

E_a= 89 kJ/mol
ΔH_r= +35 kJ/mol

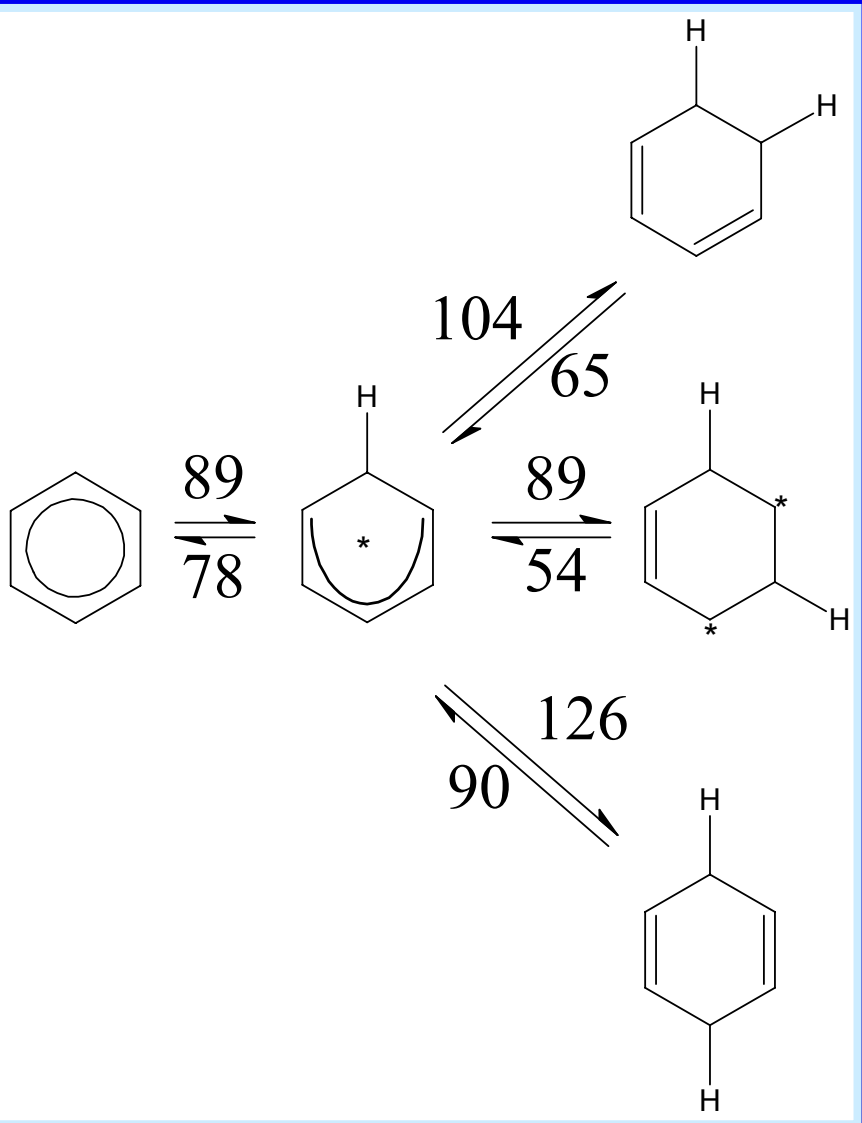
1,2-dihydroB

Summary

- Reaction mechanism:



Summary



Discussion:

– Addition of first and second H have identical E_a

– 1,3-dihydrobenzene is the intermediate

– Dehydrogenation of 1,3-CHD faster than 1,4-CHD

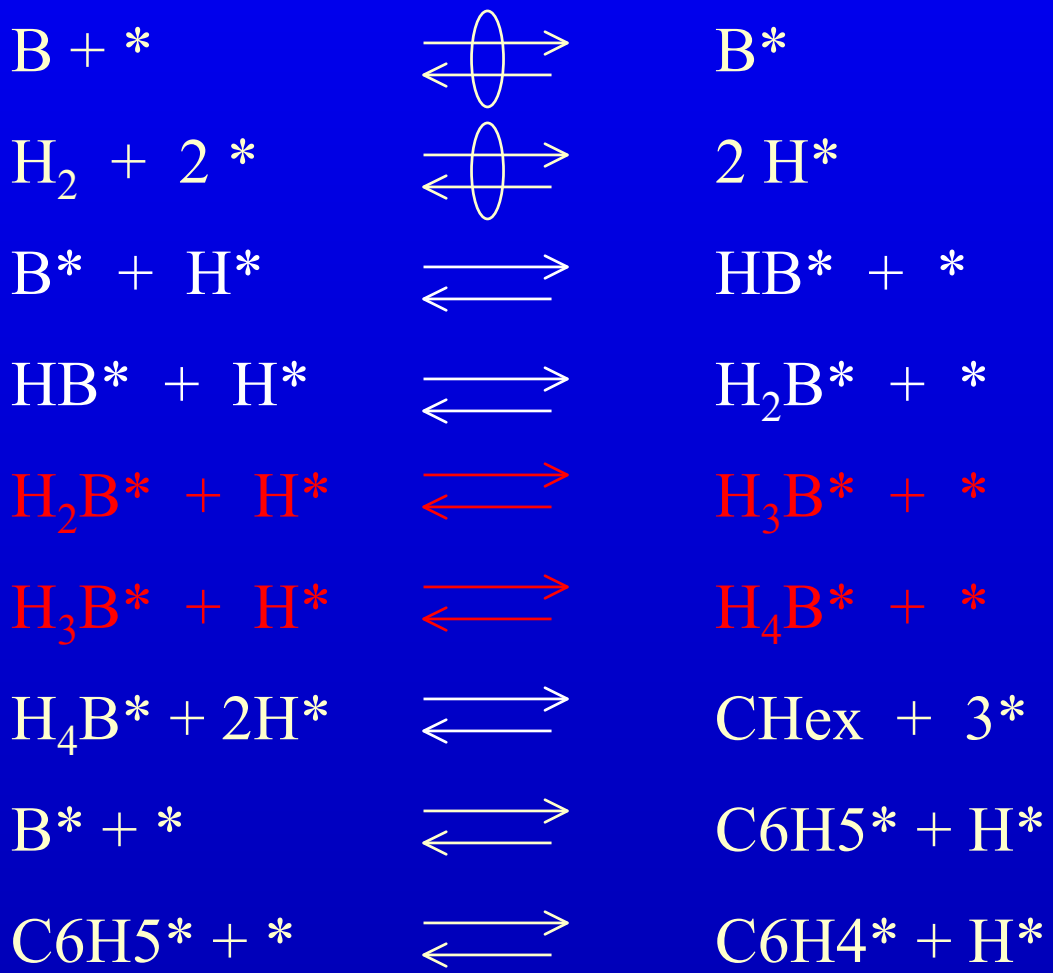
– Experimental E_a dehydro 1,3-CHD: 57-63 kJ/mol

– Intermediate in TPR 1,3-CHD

– No intermediate in TPR 1,4-CHD

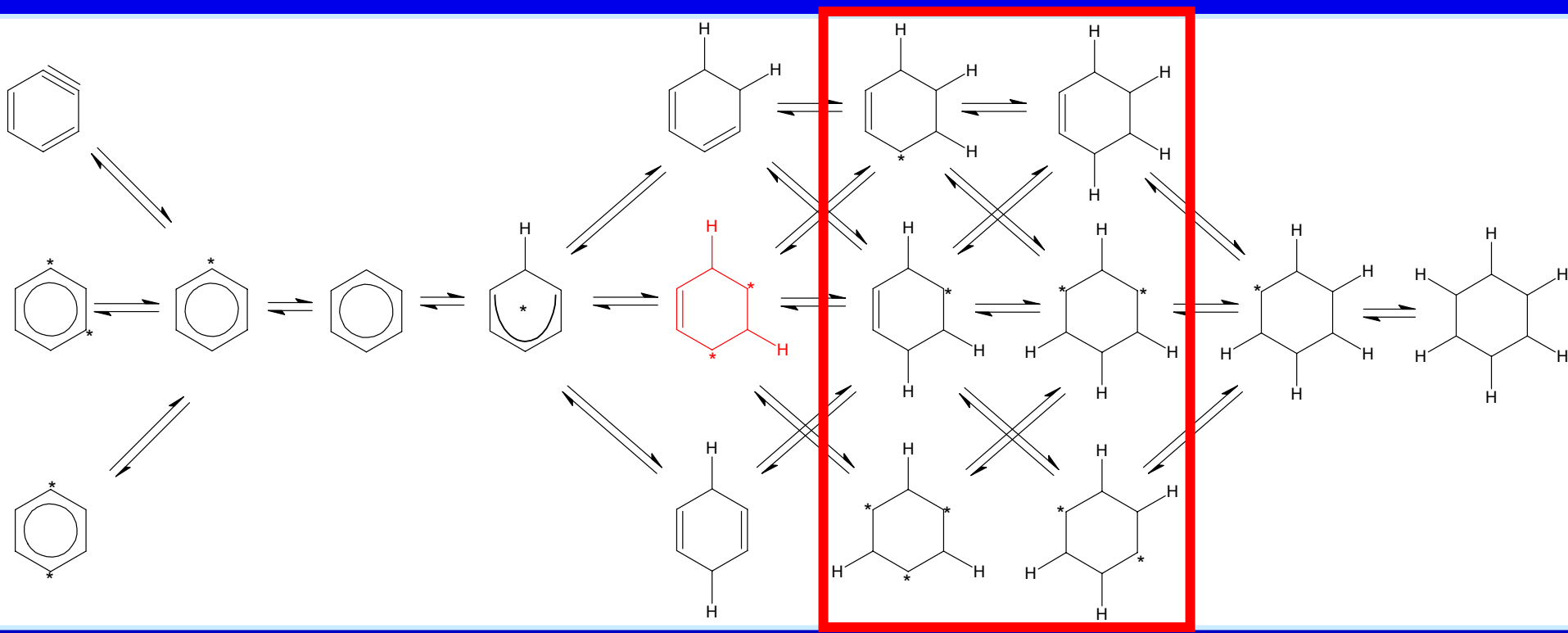
Addition of Third and Fourth H

- Reaction mechanism:



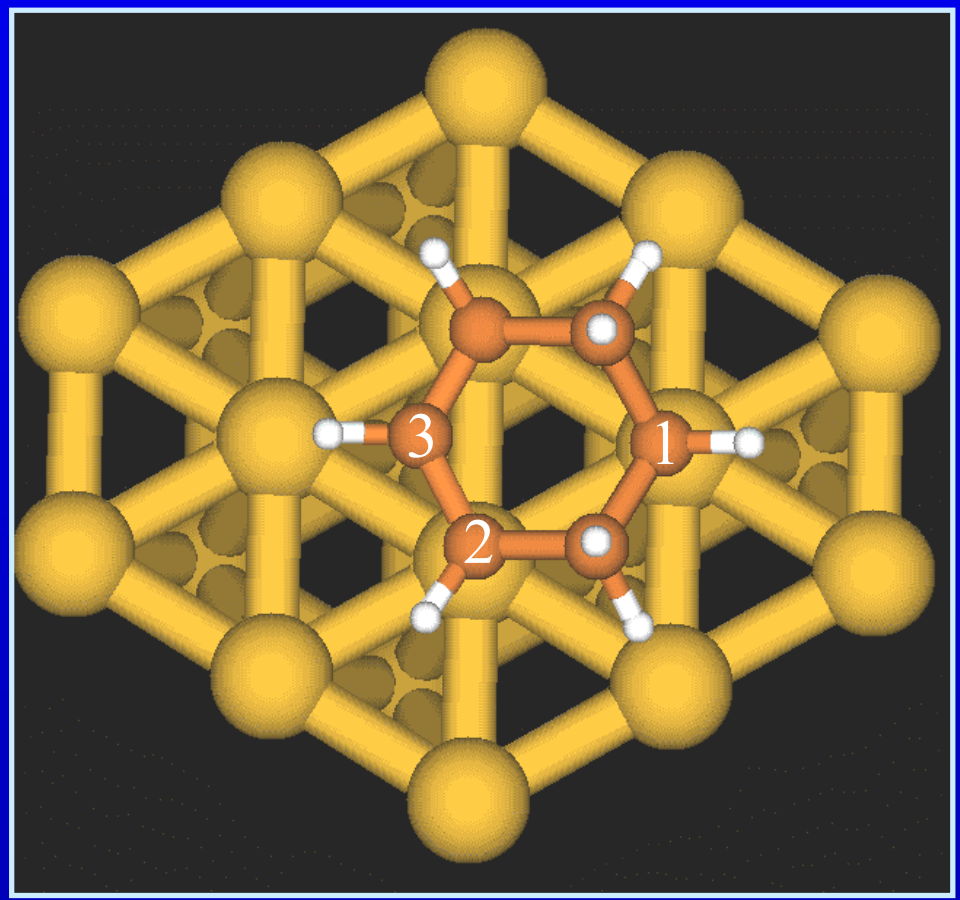
Addition of Third and Fourth H

- Reaction mechanism:



Addition of Third H

- Reaction paths:



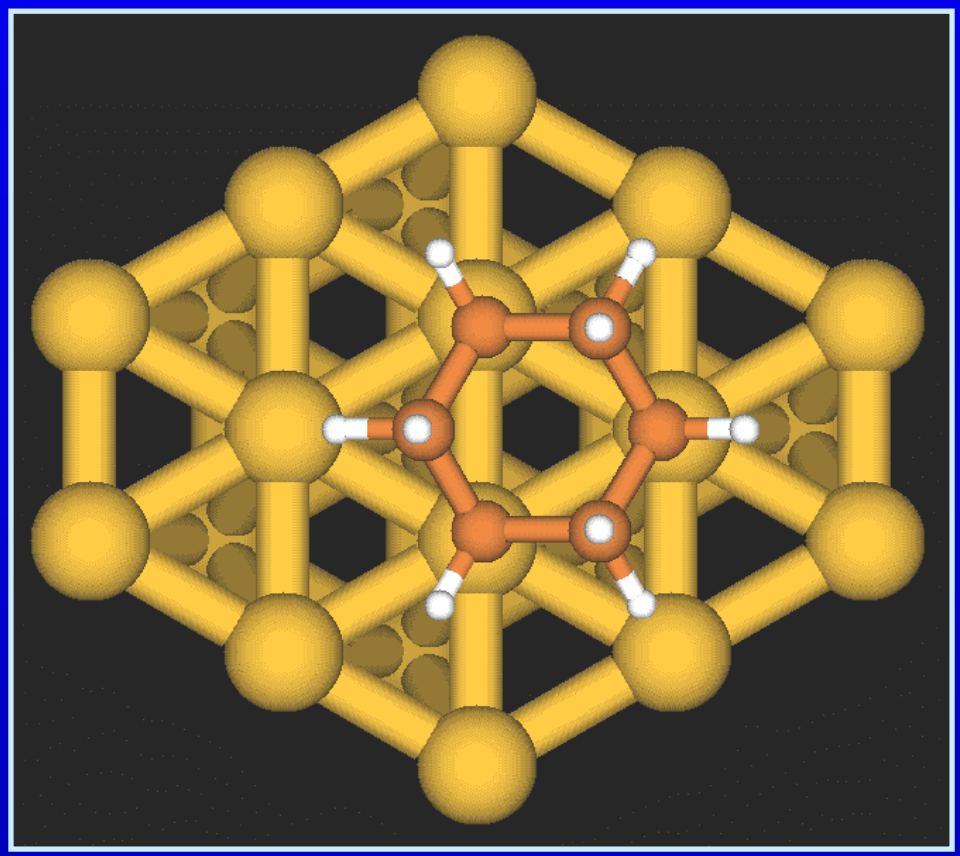
1: E_a= 158 kJ/mol,
ΔH_r= +22 kJ/mol

2: E_a = 135 kJ/mol

3: E_a = 89 kJ/mol,
ΔH_r= +33 kJ/mol

Addition of Fourth H

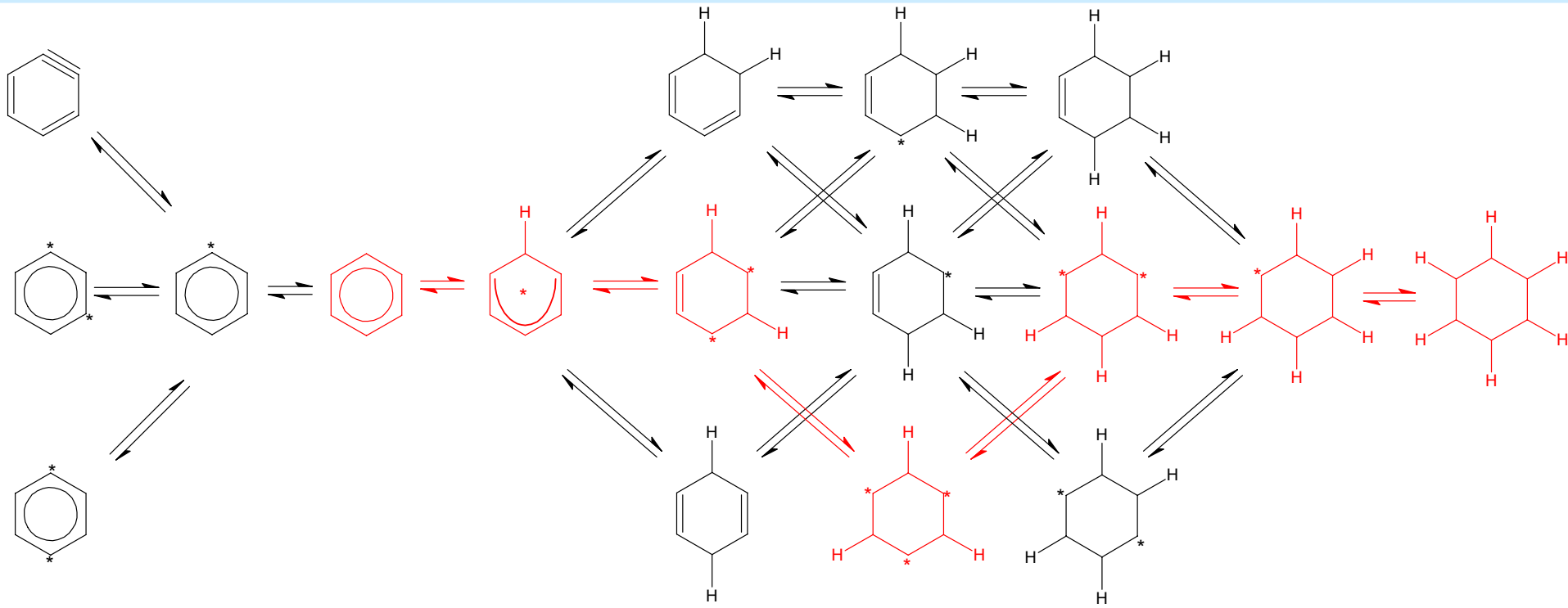
- Reaction path:



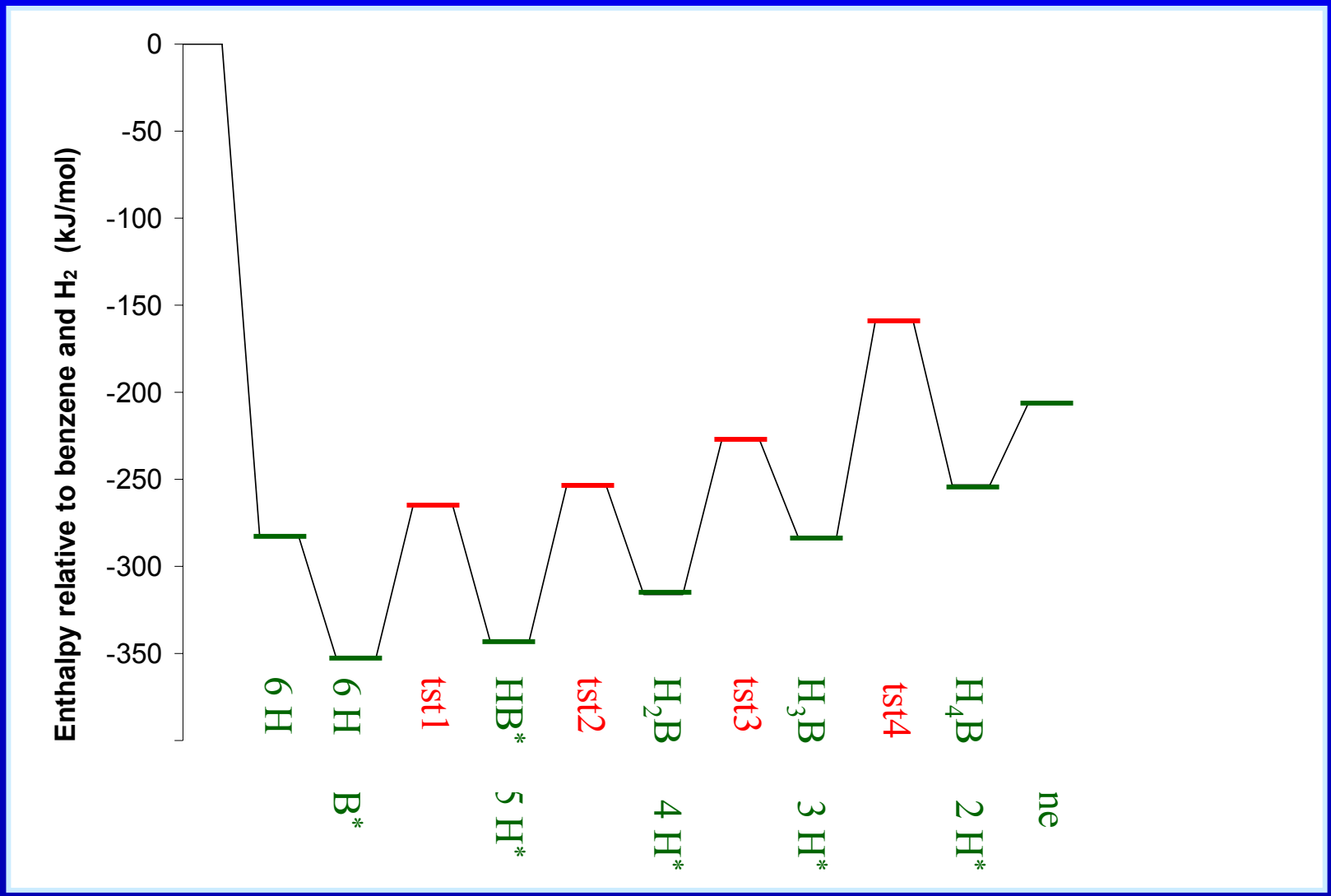
1: E_a= 118 kJ/mol,
ΔH_r=+ 30 kJ/mol

Reaction Path

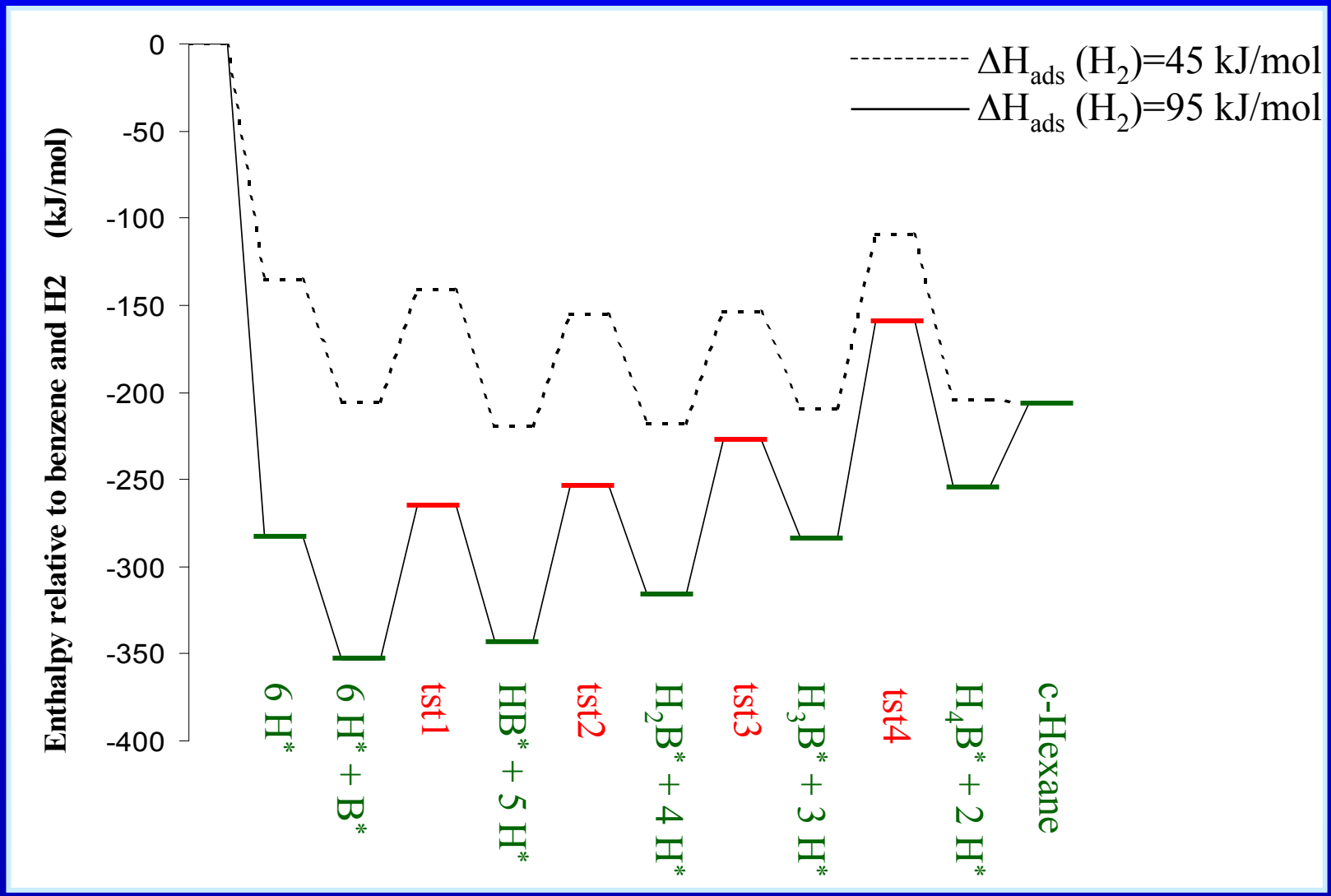
- Reaction mechanism:



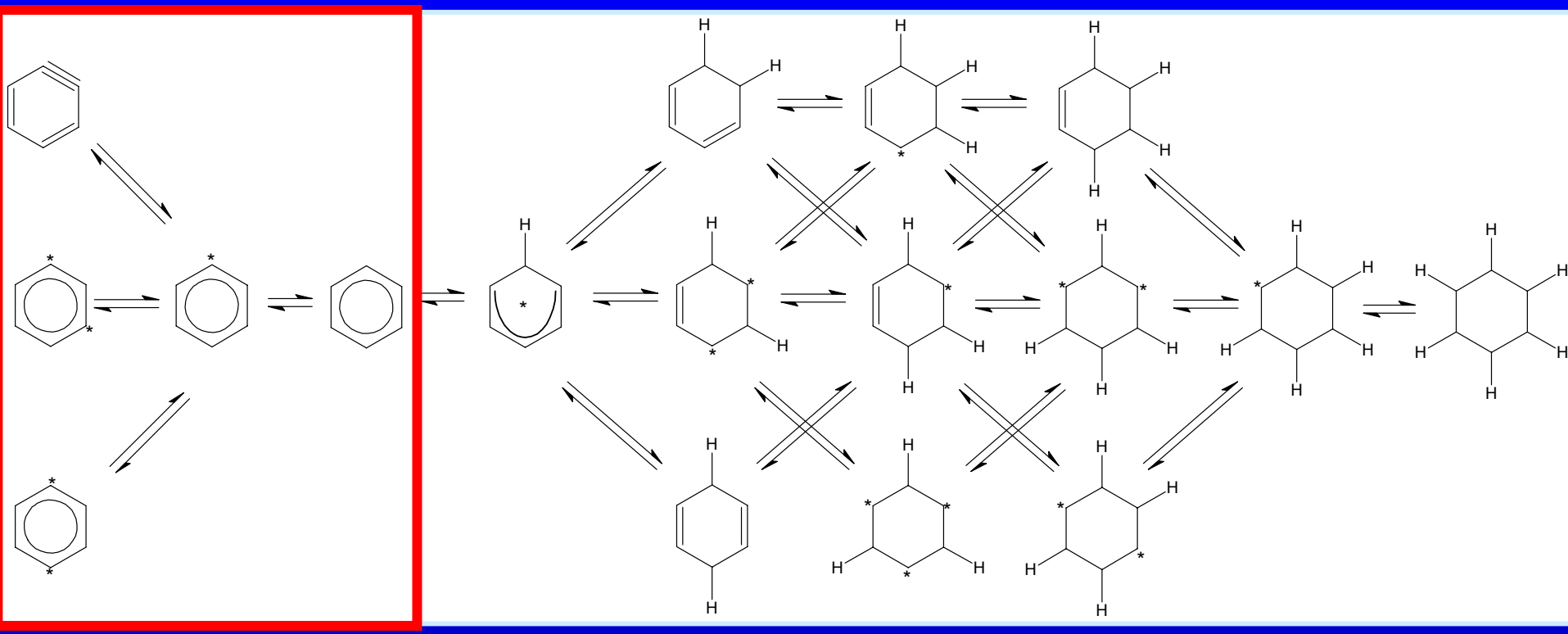
Energy Profile:



Energy Profile:

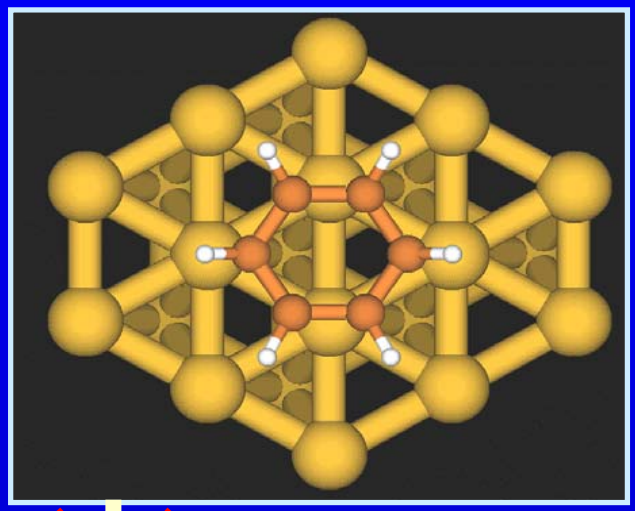


Dehydrogenation

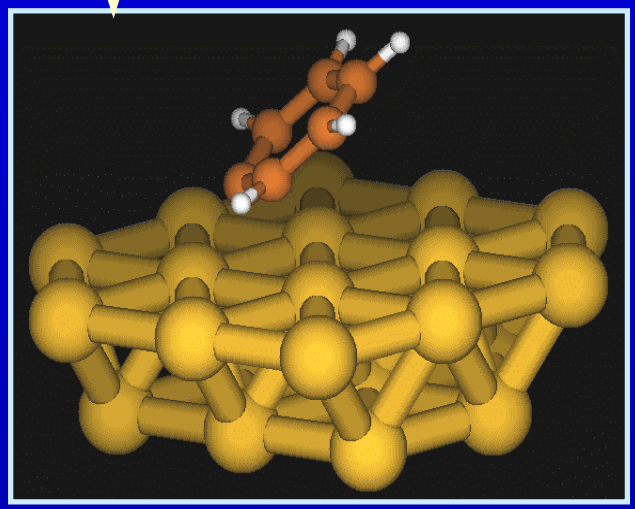


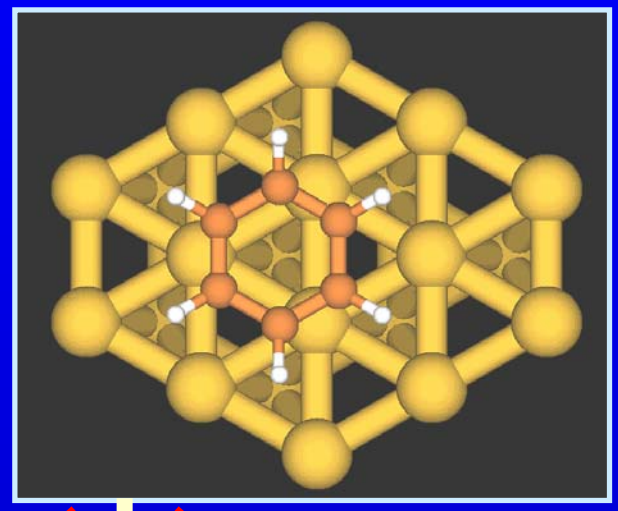
- Is there a C_6H_5- or C_6H_4-species thermodynamically favoured?
  - Some kinetic studies indicate a dehydrogenated species to be the Most Abundant Surface Intermediate (MASI)
  - Benzene dehydrogenates in TPD

Dehydrogenation

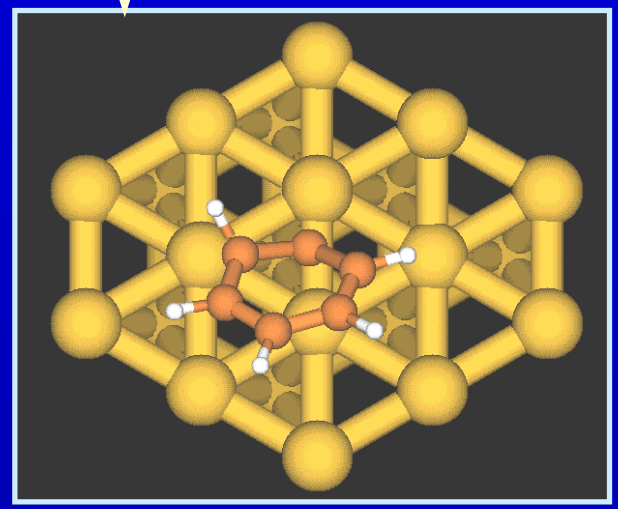


ΔH_r=+76-100 kJ/mol

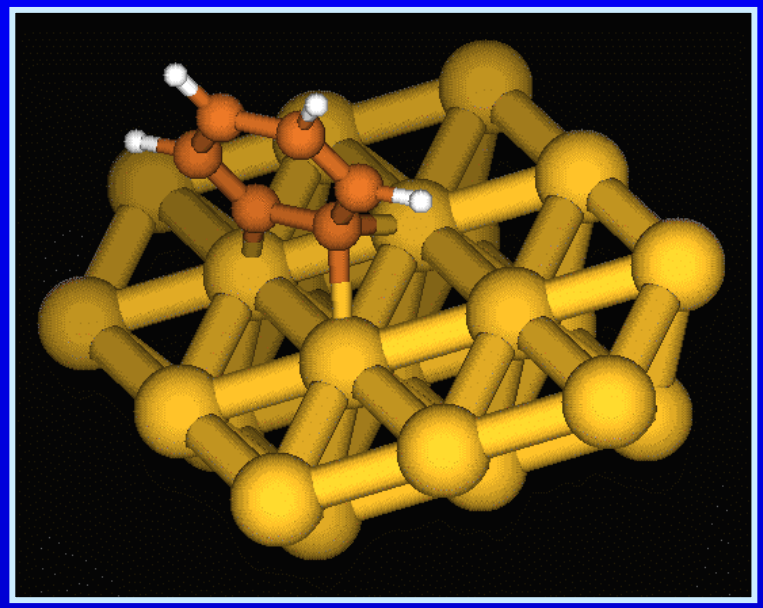




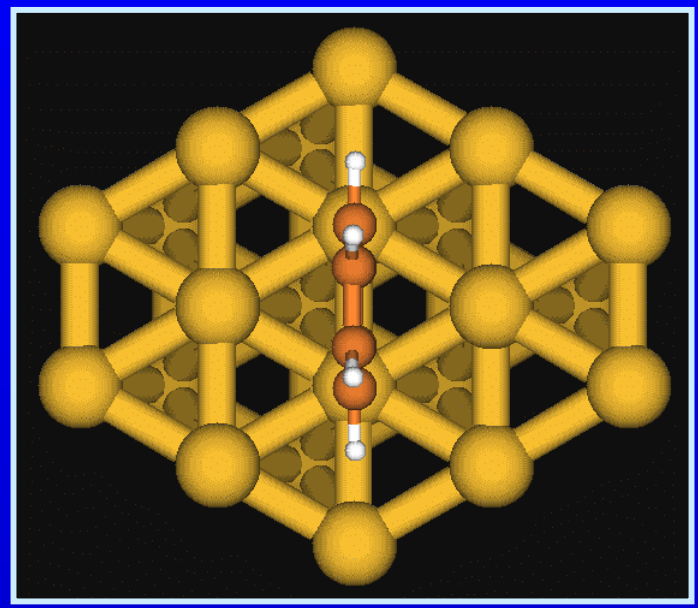
ΔH_r=+50-74 kJ/mol



Dehydrogenation



ΔH_r = +13-63 kJ/mol



ΔH_r = +20-70 kJ/mol

m- and p-benzyne were found to be >160 kJ/mol less stable than o-benzyne

- Summary
  - Due to the high endothermicity of the dehydrogenation, C_6H_5 and C_6H_4 are not expected to be formed much under hydrogenation conditions
  - MASI might be non-reactive benzene adsorbed on the bridge site

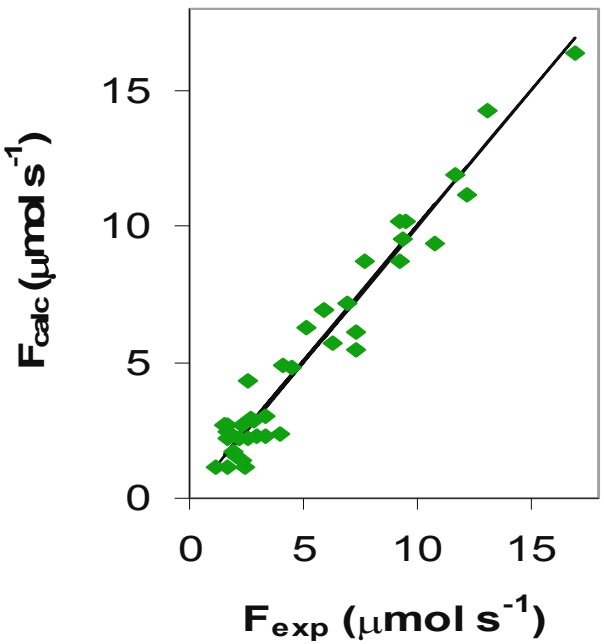
Kinetic Modelling using ab initio reaction path analysis

– Hydrogenation of Toluene on Pt/ZSM-22: experimental

– Model Assumptions:

- LHHW model
- Competitive H_2 and toluene chemisorption
- Reactant adsorption quasi-equilibrated
- 5^{th} & 6^{th} H addition are quasi-equilibrated
- Product desorption fast and irreversible
- No dehydrogenation
- 4^{th} H addition RDS

Kinetic Modelling using ab initio reaction path analysis



General results:

	4 H RDS
F-value	10^4
$E_{a,surf}^{Comp}$ (kJ/mol)	-59±7
ΔH_{ads} (H_2) (kJ/mol)	-42±12
ΔH_{ads} (Arom)(kJ/mol)	-70±2

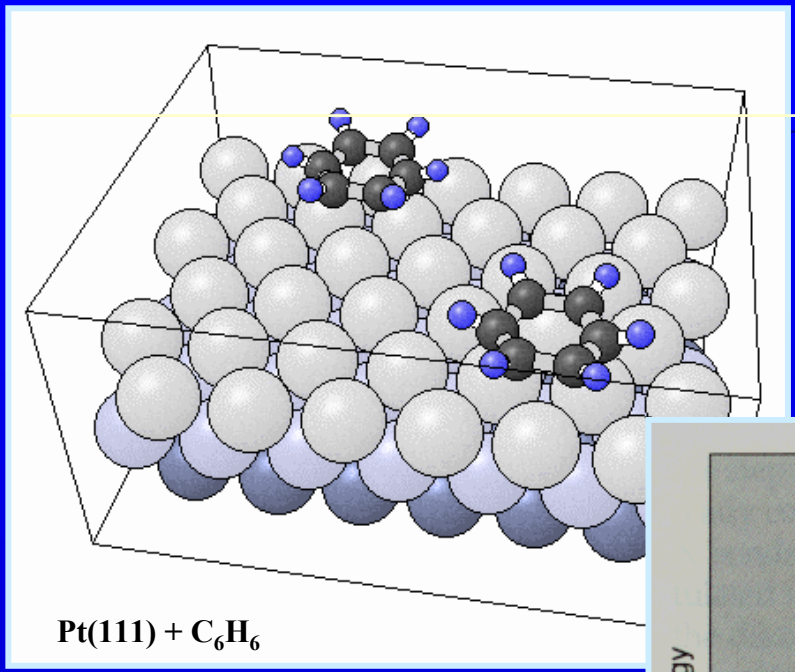
$$E_{a,surf}^{comp} = E_{a,4} + \Delta H_{arom} + 2\Delta H_{H_2} + \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$E_{a,surf}^{Comp}(calc) = 100 - 71 - 2 \times 42 - 7.5 = -62.5$$

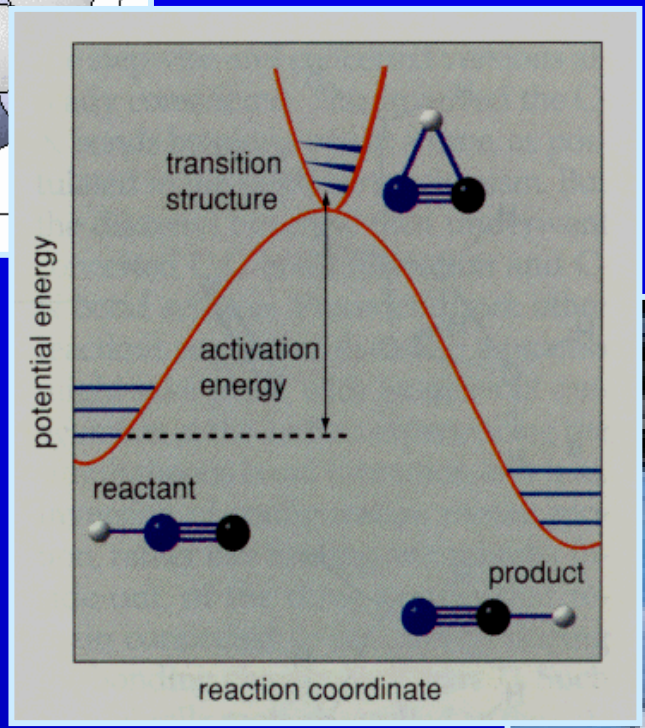
Conclusions

- Benzene adsorption
  - Bridge site: most stable, unreactive
  - Hollow site: reactive species
- H addition
  - One dominant reaction path: H addition in meta position
  - Addition of 4th H atom requires the highest activation energy
  - $E_{a,1,2,3}$= 64 kJ/mol, $E_{a,4}$=100 kJ/mol
  - Good agreement with experiment
- Dehydrogenation
  - Thermodynamically not favoured

Conclusions



$Pt(111) + C_6H_6$



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