

OVERVIEW Computational Modeling

Computational Modeling

Quantum Mechanical Approach

Molecular Mechanical Approach

Amber, UFF, MM etc.

Hybrid Approaches: QM/MM and ONIOM

Ab Initio Approach

Density Functional Approach

- Hartree-Fock (HF)
- Electron Correlation
- Basis Sets
- Effective Core Potentials

- Kohn-Sham theorem

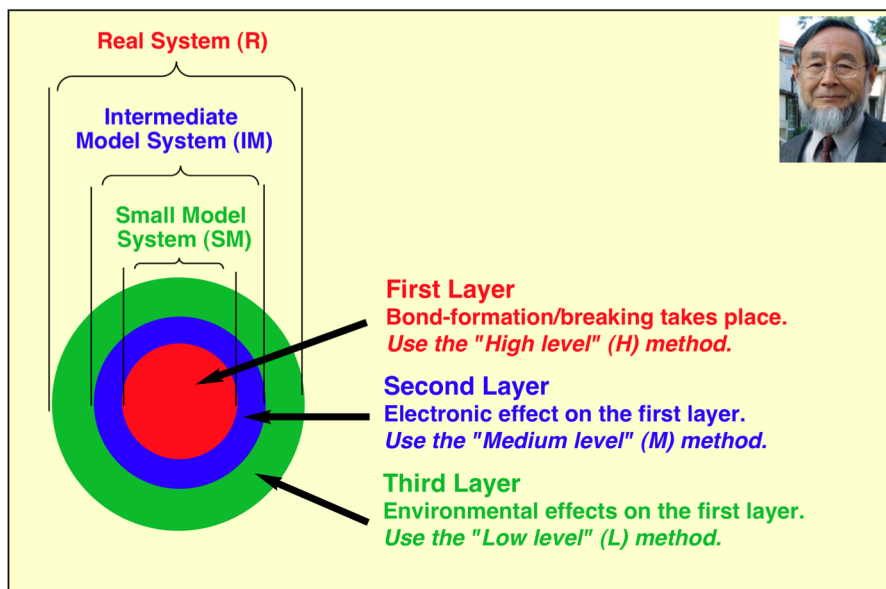


Hybrid Density Functional: B3LYP, BLYP, M06, etc.

Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM), and ONIOM Approaches

The ONIOM Method (an ONION-like method)

(Our own *N*-layered Integrated molecular Orbital and molecular Mechanics)



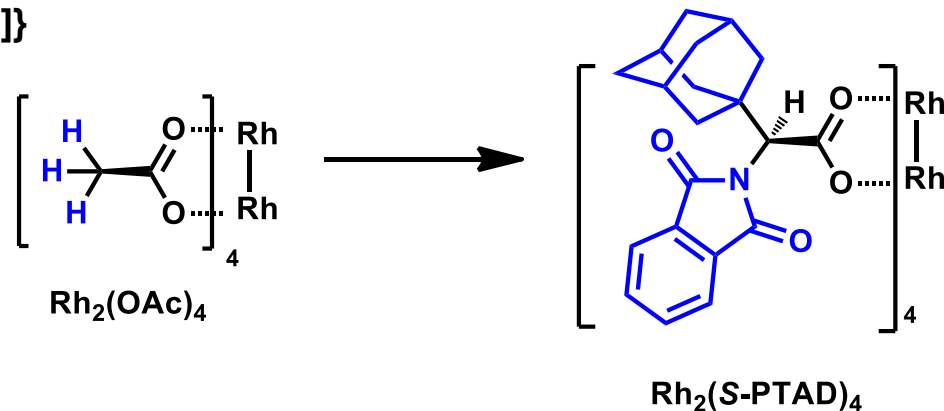
Morokuma, K. et al *THEOCHEM*, **1999**, 461, 1

Morokuma, K. et al *JCTC.*, **2006**, 2, 8151

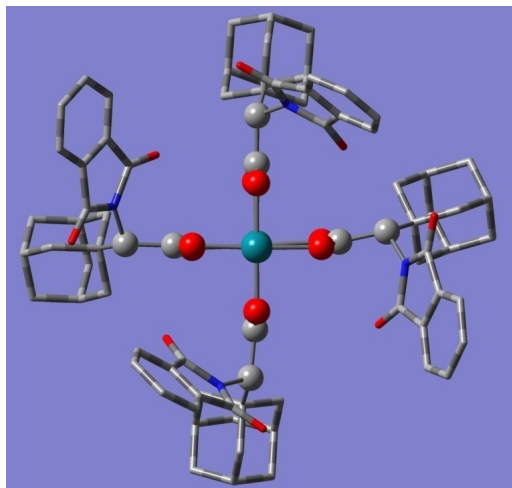
ONIOM Set Up: DiRh-tetracarboxylate Catalyst

High-Level: B3LYP/{LANL2DZ + [6-31G(d,p)]}

Low-Level: AMBER WITH ESP CHARGES FROM B3LYP/{LANL2DZ + [6-31G(d,p)]}

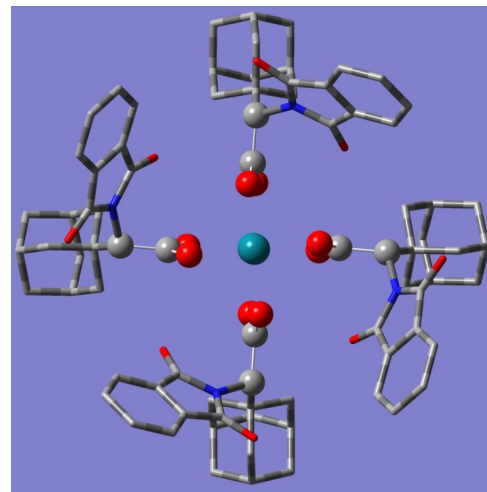


X-ray structure



ONIOM Structure

	X-RAY	ONIOM
<u>Rh-Rh</u>	2.38 Å	2.40 Å
<u>Rh-O</u>	2.03 Å	2.05 Å



1835:

J.J. Berzelius coined the word “catalysis”

Greek words “**cata**” means “**down**”
“**lysis**” means “**split**” or “**break**”



Jöns Jacob Berzelius
(1779-1848)

“some reactions between seemingly inert chemicals may occur in the presence of a ‘third’ substance called **catalyst**”

Jahresberichte für Chemie, March/1835

“This new force, which is unknown until now, is common to both organic and inorganic nature. I do not believe that it is a force completely independent of electrochemical affinities; ... It is more convenient to give this force a separate name. I would therefore call this the catalytic force. I would furthermore, call the decomposition of substances resulting from this force catalysis, just as the decomposition of substances resulting from chemical affinity is called analysis.”

Three Classes of Catalysts

- **Homogeneous**- The catalyst and the reactants are in the same phase
- **Heterogeneous**- The catalyst and the reactants are in different phases
- **Biological** - Enzymes

Effect of Catalyst on Reaction Profile and Activation Energy

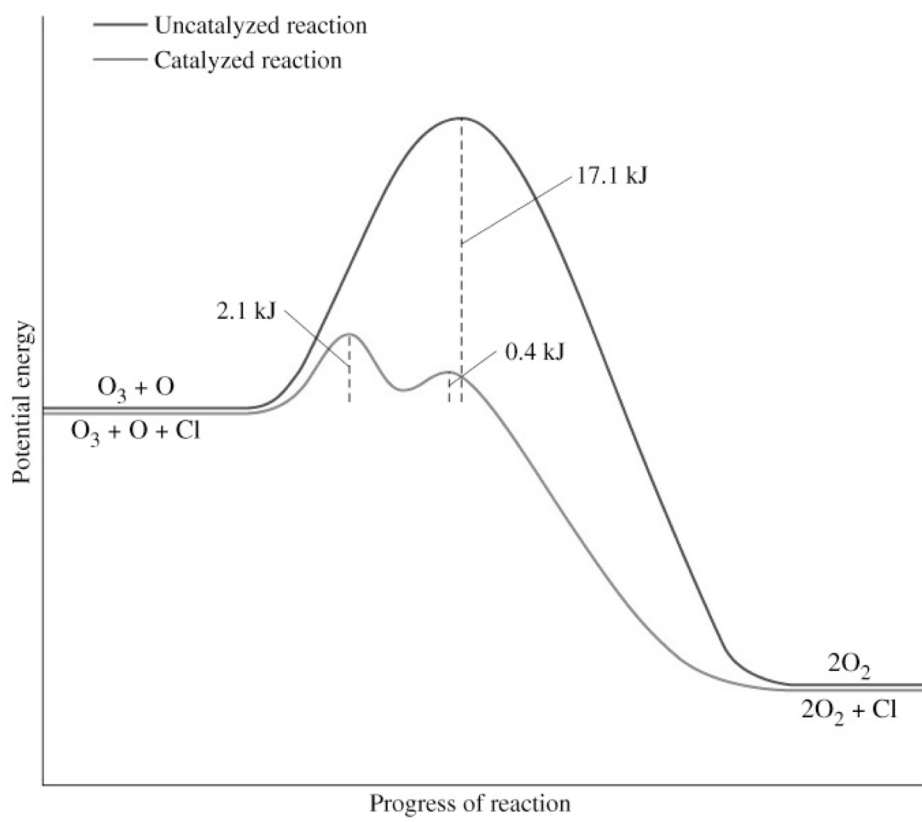


Wilhelm Friedrich Ostwald (1853-1932)

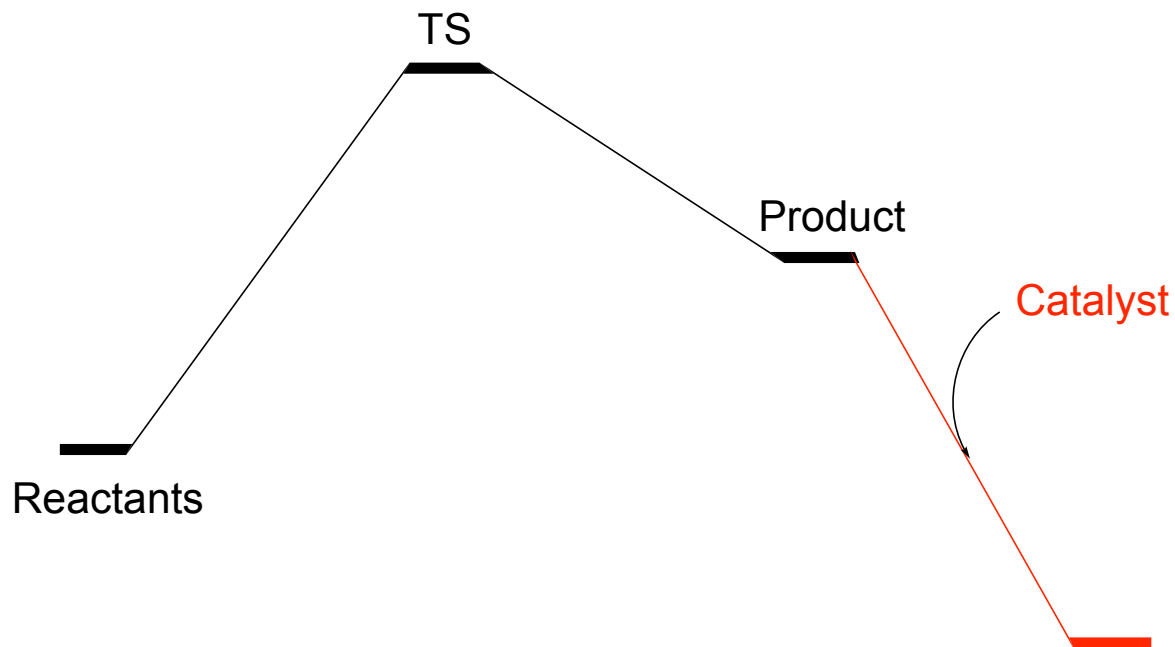
Thermodynamics and Catalysis (1909):
 catalyst does not shift equilibrium, but accelerates only thermodynamically allowed reactions

1909: Ostward **received Nobel Prize** (for Ostward process):

(1903)
 $2\text{NH}_3 + 7/2 \text{O}_2 \rightarrow 2\text{NO}_2 + 3 \text{H}_2\text{O}$ (Pt sponge as catalyst)



Effect of Catalyst on Reaction Profile: As a Facilitator to Improve Thermodynamics of the Reaction



What we should do:

We should optimized GEOMETRY and Calculated Energy:

Every Reactants
Catalyst
Intermediate Structures
Transition States
Products

Frequency Calculations:

To confirm nature of
the calculated structures:
Reactants (no Imaginary Freq.)
Intermed. (no Imaginary Freq.)
Products. (no Imaginary Freq.)
TS: (ONE Imaginary Freq.)

All calculations should be done at the same level of theory:

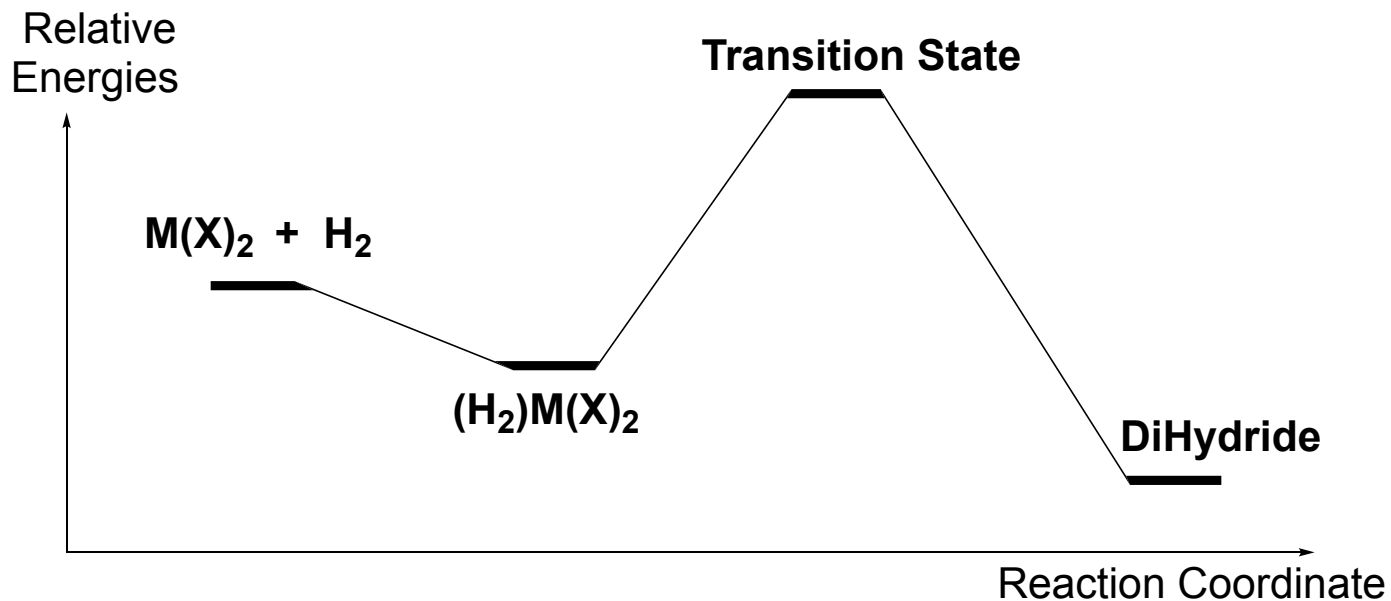
Methods and
Basis Sets

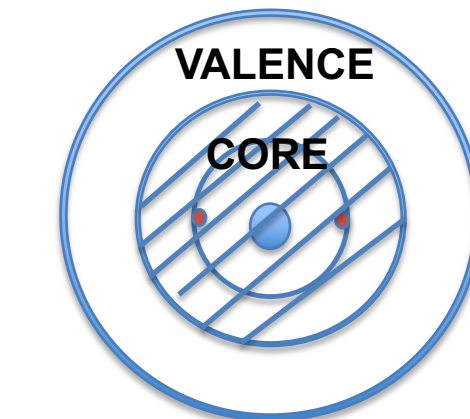
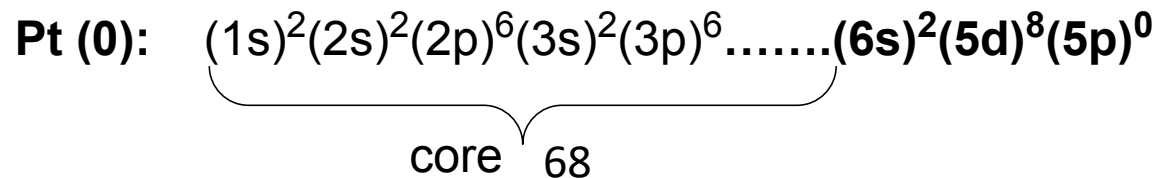
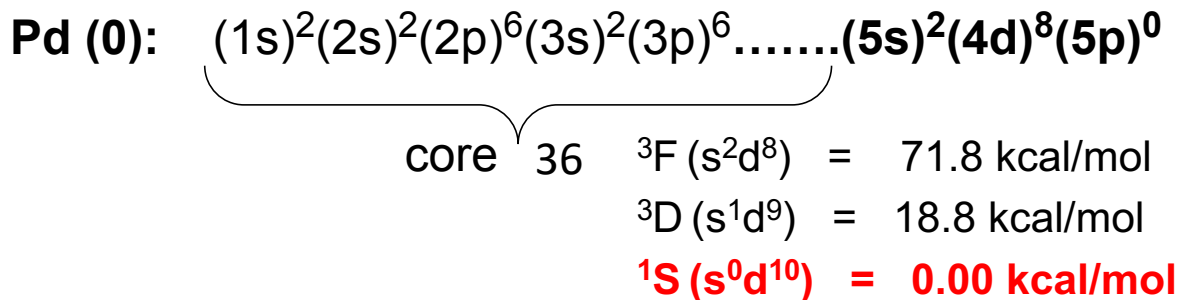
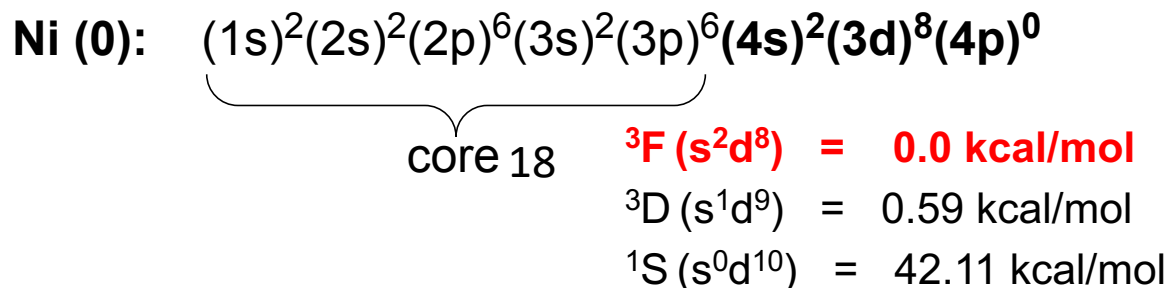
Use the calculated energies to obtain:

Barriers
Thermodynamic parameters
Resting State
Kinetic Parameters
ee, Selectivity of the Reaction,
more

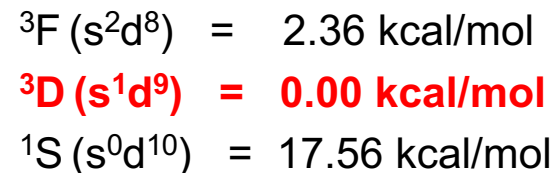


X = none and PH₃





Effective core potential (ECP) method allows to replace core electrons by an effective potential, thus reducing # of electrons & # of basis functions.



Method: (B3LYP – D3BJ)

Basis Sets: M lanl2dz: also ECP: lanl2dz
H 6-31G(d,p)

Relative energies: in kcal/mol

Total energies: in hartree

Ni: (s¹d⁹)
Triplet

$E_{\text{tot}} = -169.247761118$
 $E_{\text{tot}} + \text{ZPEC} = -169.247761$
 $H = -169.245401$
 $G = -169.264536$

0.0
0.0

Ni: (s¹d⁹)
Singlet

35.1
35.8

$E_{\text{tot}} = -169.247761118$
 $E_{\text{tot}} + \text{ZPEC} = -169.247761$
 $H = -169.245401$
 $G = -169.264536$

Pd: (s¹d⁹)
Triplet

$E_{\text{tot}} = -126.675269824$
 $E_{\text{tot}} + \text{ZPEC} = -126.67527$
 $H = -126.672909$
 $G = -126.692899$

19.8
19.1

Pd: (s⁰d¹⁰)
Singlet

0.00
0.00

$E_{\text{tot}} = -126.706763485$
 $E_{\text{tot}} + \text{ZPEC} = -126.706763$
 $H = -126.704403$
 $G = -126.723356$

Pt: (s¹d⁹)
Triplet

$E_{\text{tot}} = -119.0776387$
 $E_{\text{tot}} + \text{ZPEC} = -119.077639$
 $H = -119.075278$
 $G = -119.096132$

0.0
0.0

Pt: (s⁰d¹⁰)
Singlet

13.0
13.7

$E_{\text{tot}} = -119.056880224$
 $E_{\text{tot}} + \text{ZPEC} = -119.056880224$
 $H = -119.05452$
 $G = -119.074337$



Total energies: in hartree

H₂ molecule

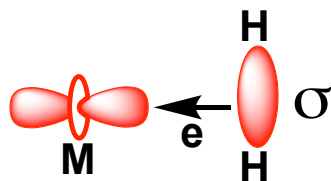


$$E_{\text{tot}} = -1.17868007631$$

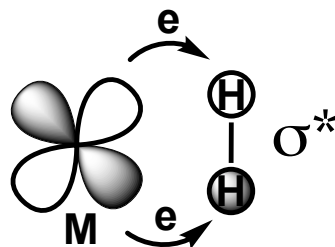
$$E_{\text{tot}} + \text{ZPEC} = -1.168515$$

$$H = -1.16521$$

$$G = -1.180002$$



Donation

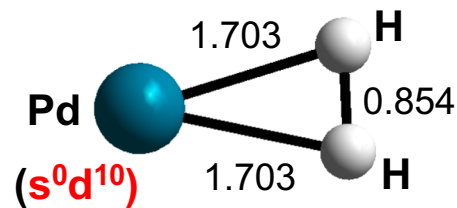
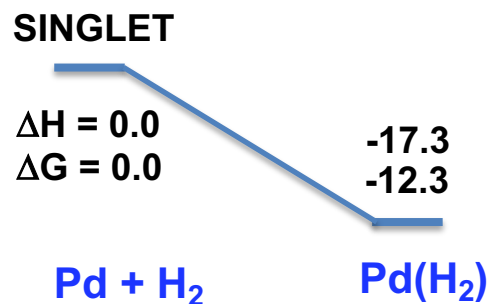
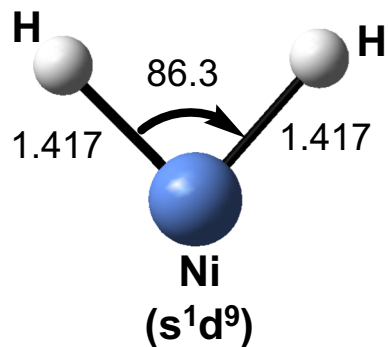
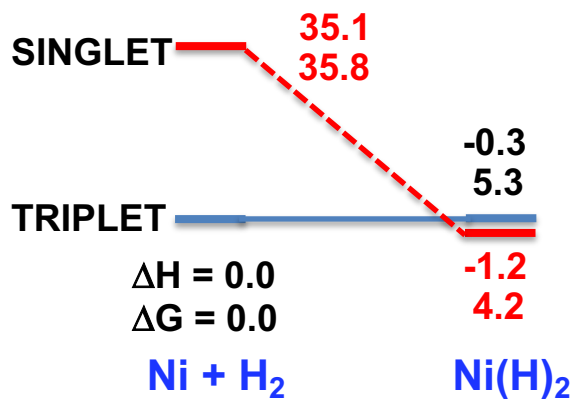


Back-donation

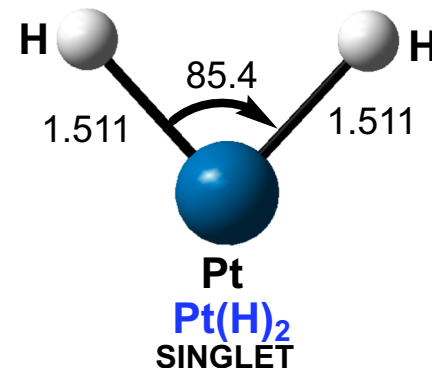
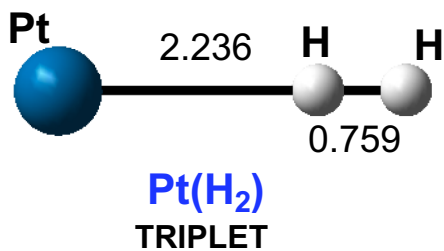
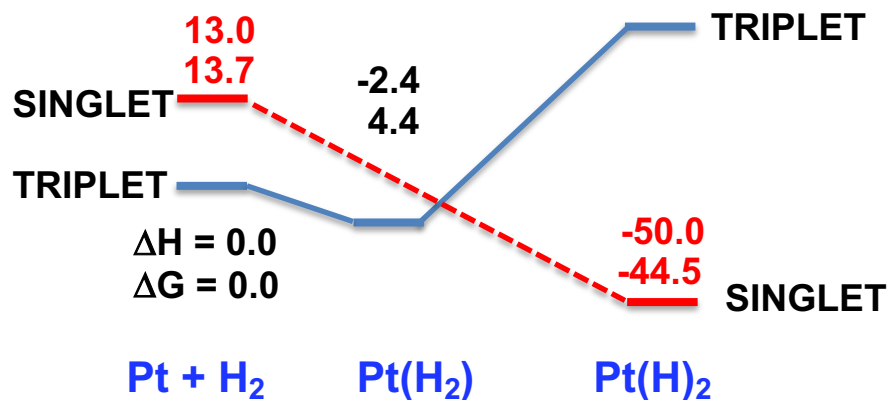
Thus, in order to reaction proceed:

- Metal center should have empty $d(\sigma)$ -orbital
- Metal center should have doubly occupied d_{π} -orbital

Energy Surfaces of the reactions:



Energy Surfaces of the reactions:

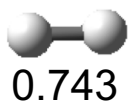
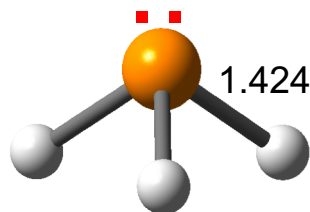




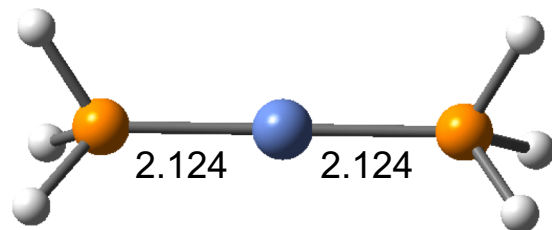
Method: (B3LYP – D3BJ)

Basis M lanl2dz: also ECP: lanl2dz

Sets: P and H: 6-31G(d,p)

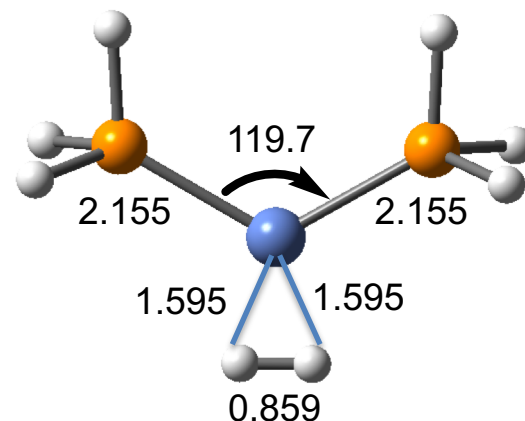


$E_{\text{tot}} = -1.178680$
 $E_{\text{tot}} + \text{ZPC} = -1.168527$
H = -1.165222
 $G = -1.180015$



$E_{\text{tot}} = -855.615061$
 $E_{\text{tot}} + \text{ZPC} = -855.561798$
H = -855.553332
 $G = -855.595677$

Ni-(H)₂ IS NOT STABLE

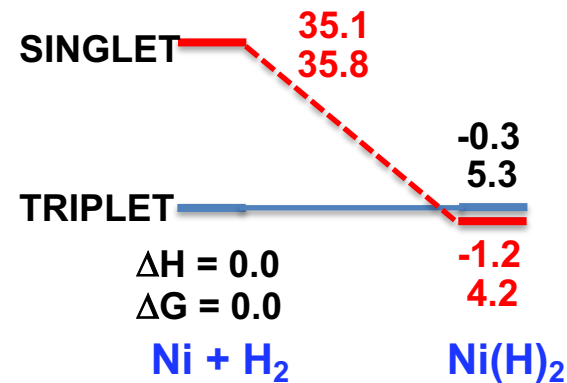
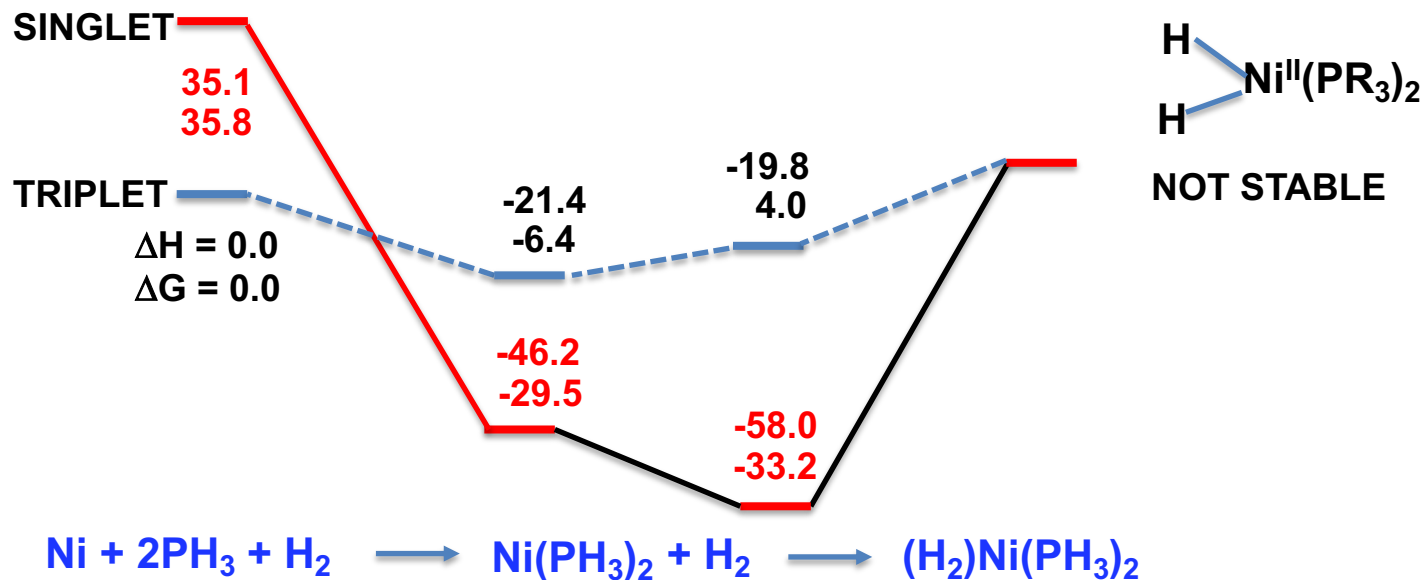


$E_{\text{tot}} = -856.815495$
 $E_{\text{tot}} + \text{ZPC} = -856.746792$
H = -856.737422
 $G = -856.781527$

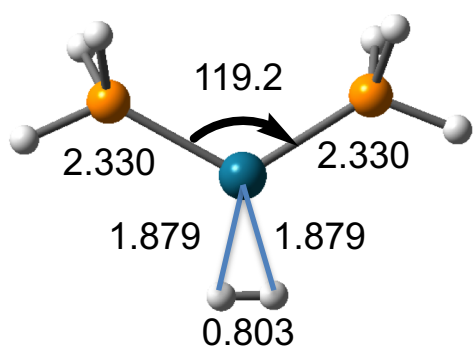
$$E [\text{Ni}(\text{PH}_3)] - \{2E(\text{PH}_3) + \text{Ni}\} = -46.2/-29.5 \text{ kcal/mol}$$

$$E [(\text{H}_2)\text{Ni}(\text{PH}_3)] - \{E(\text{H}_2) + E[\text{Ni}(\text{PH}_3)]\} = -11.8/-3.7 \text{ kcal/mol}$$

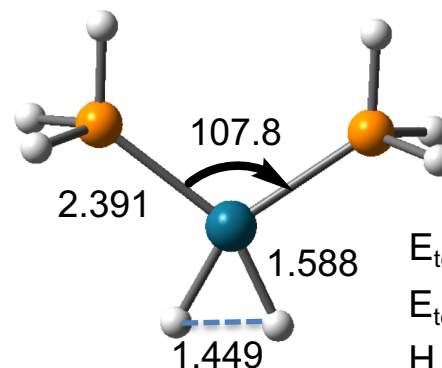
Reaction Profile of Ni(0) + 2 PH₃ + H₂



M = Pd



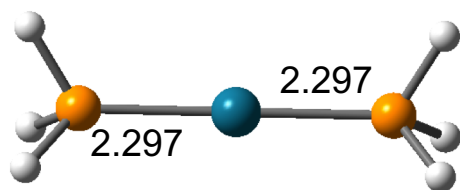
$E_{\text{tot}} = -814.285642$
 $E_{\text{tot}} + \text{ZPC} = -814.218517$
 $H = -814.208263$
 $G = -814.256079$



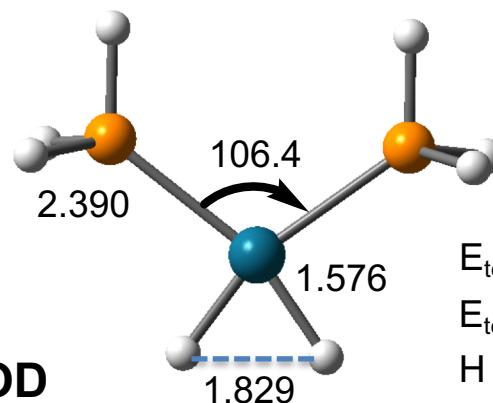
$V_i = -643.58 \text{ cm}^{-1}$

$E_{\text{tot}} = -814.271720$
 $E_{\text{tot}} + \text{ZPC} = -814.206104$
 $H = -814.196675$
 $G = -814.240872$

COMP \longrightarrow TS



$E_{\text{tot}} = -813.104916$
 $E_{\text{tot}} + \text{ZPC} = -813.051396$
 $H = -813.042755$
 $G = -813.085527$



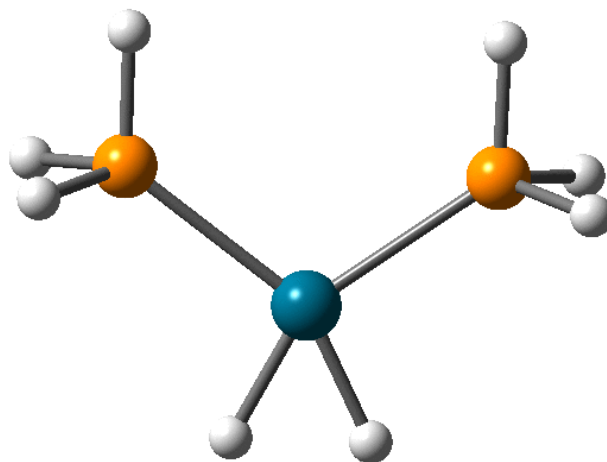
$E_{\text{tot}} = -814.272639$
 $E_{\text{tot}} + \text{ZPC} = -814.205056$
 $H = -814.195637$
 $G = -814.239346$

REAC

PROD

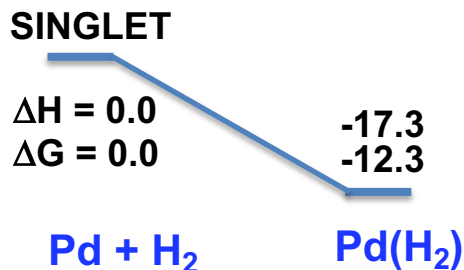
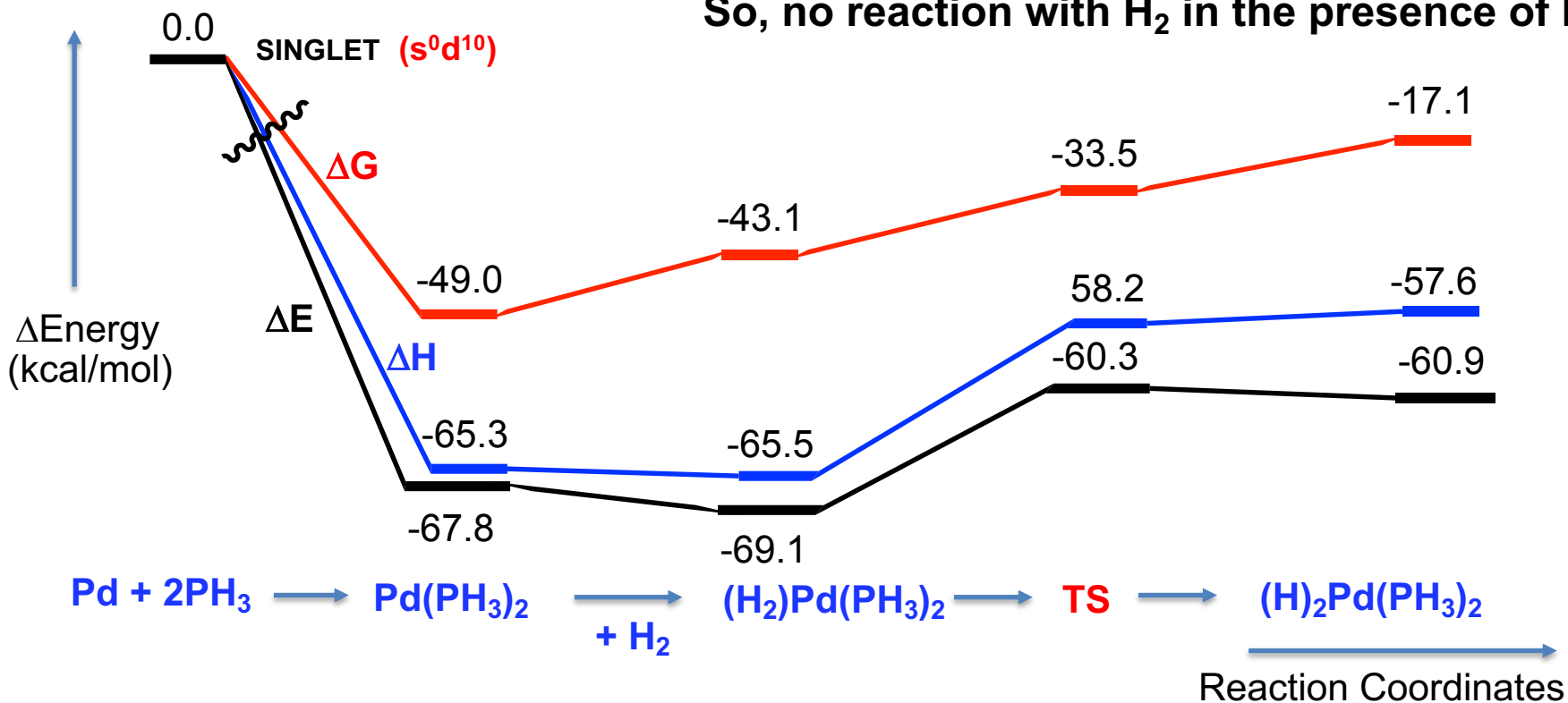
M = Pd: Transition State

$$V_i = -643.58 \text{ cm}^{-1}$$

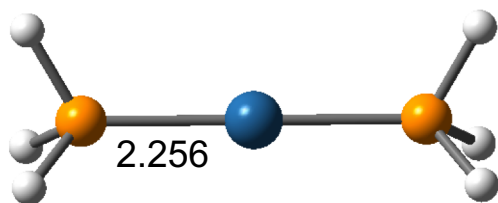


Reaction Profile of Pd(0) + 2 PH₃ + H₂

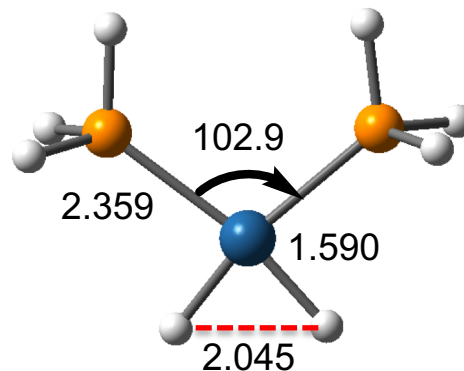
So, no reaction with H₂ in the presence of PH₃



Reaction Profile of Pt(0) + 2 PH₃ + H₂



$E_{\text{tot}} = -805.530345$
 $E_{\text{tot}} + \text{ZPC} = -805.475418$
 $H = -805.467331$
 $G = -805.509018$



$E_{\text{tot}} = -806.723452$
 $E_{\text{tot}} + \text{ZPC} = -806.653179$
 $H = -806.644339$
 $G = -806.687467$

