

Metal / σ -bond interactions

– toward an understanding of C-H activation –



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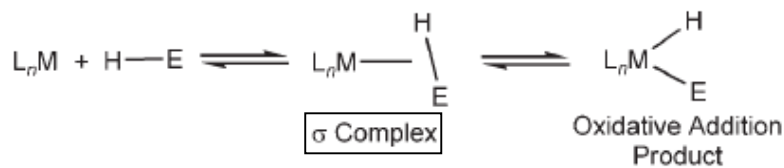
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☉ Main source

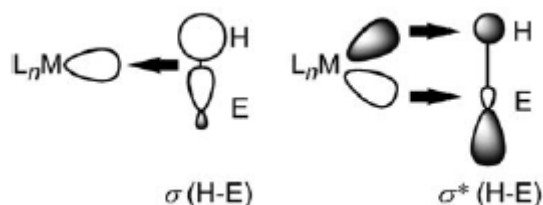
Robin N. Perutz and Sylviane Sabo-Etienne *Angew. Chem. Int. Ed.* **2007**, *46*, 2578

1 σ -complex (η^2 -R-H bonds)

1.1 Formation of σ -complex



- Intermediate of Oxidative addition
- Equilibrium changes by what M, L, E are used



- $\sigma(H-E)$: electron donor
- Three-center two-electron bond

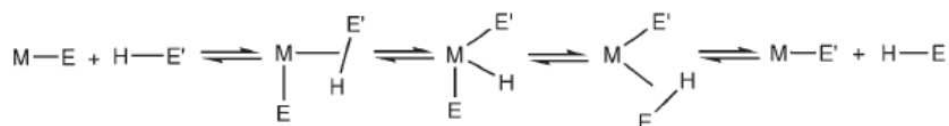
Characterized by X-ray diffraction and NMR: $E = H, Si, B, C$ (etc.?)

1.2 Structure and Dynamics of σ -Complex ($MH_m(\eta^2-E-H)_n$) ($n=m \neq 0$)

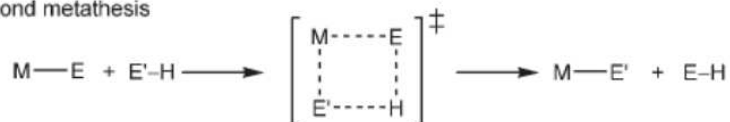
“Classical” interaction of σ -complex

Metathesis

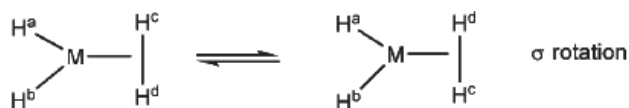
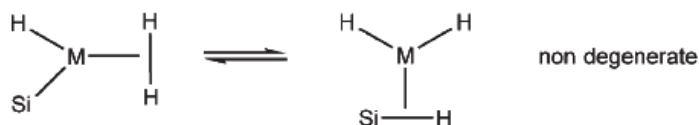
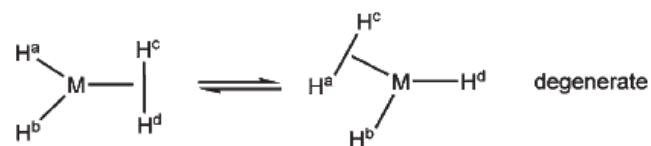
a) oxidative addition / reductive elimination



b) σ -bond metathesis



Another behavior



1.2.1 E = H

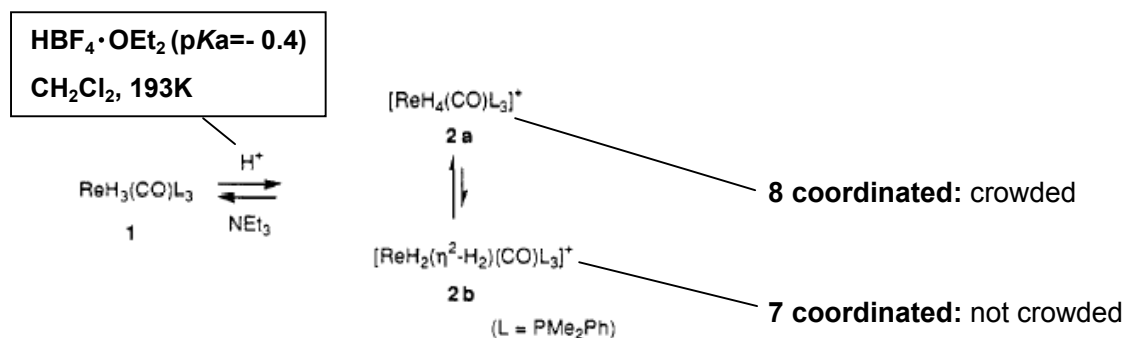
This type of complex is the most studied family.

- ① **First observation of $\eta^2\text{-H}_2$ complex (X-ray diffraction, Neutron diffraction):** $\text{W}(\text{CO})_3(\text{P}^i\text{Pr}_3)_2(\eta^2\text{-H}_2)$
(Kubas. G. J. *et. al JACS* **1984**, 106, 451)

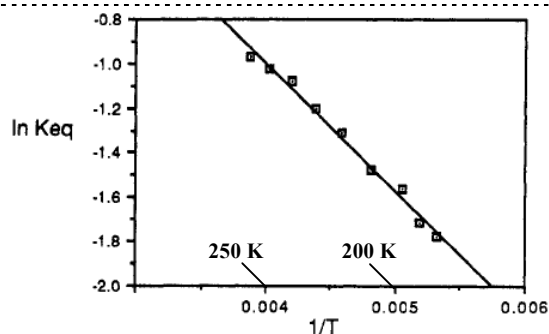
- ② **First observation of the equilibrium between ($\eta^2\text{-H}_2$) and ($\eta^1\text{-H}$)**
(Xiao-Liang Luo *et. al, JACS* **1990**, 112, 6912)

($\eta^2\text{-H}_2$) ligand in multihydride complex is not so stable

→ Forcible introduction of hydrogen into complex using strong acid



^1H NMR analysis



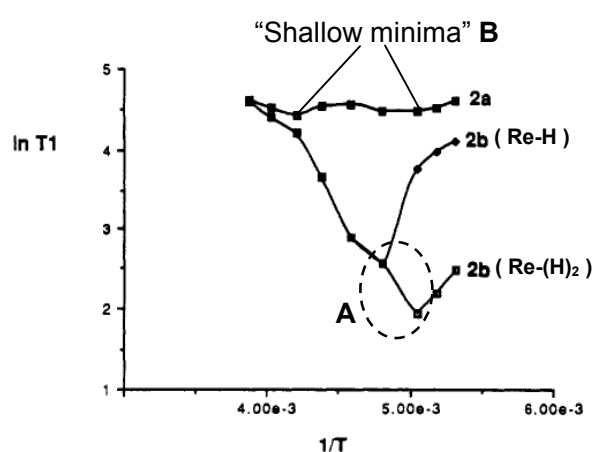
$K_{\text{eq}} = [\mathbf{2b}]/[\mathbf{2a}]$: Determined by the ^1H NMR integration

$$\Delta H = 1.1 \pm 0.2 \text{ kcal mol}^{-1}$$

→ **2b** is slightly less stable than **2a**

$$\Delta S = 2.4 \pm 0.8 \text{ cal mol}^{-1} \text{ K}^{-1}$$

→ Result of the rotation of the $\eta^2\text{-H}_2$ ligand in **2b**
(in CH_2Cl_2)



T_1 (msec): longitudinal relaxation time (縦緩和時間)

(T_1 value mainly depends on temperature and atom density around the target atom)

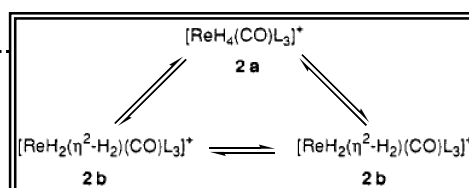
Phenomena A

→ Due to the exchange of $\eta^2\text{-H}_2$ and $(\text{H})_2$ ligands of **2b**

Phenomena B

→ Due to the exchange between **2a** and **2b**

Existence of equilibrium between hydrogen ligands



- ③ How is T_1 observed?: *JACS* **1988**, 110, 4126)

Search for detail exchange mechanism...

- ☉ Gibbs free energy of activation

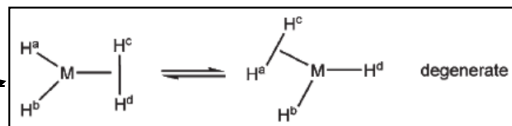


If $2b \rightarrow 2b$ include $2b \rightarrow 2a \rightarrow 2b$ process: $\Delta G_1^\ddagger \geq \Delta G_2^\ddagger$

But this time:

$$\Delta G_1^\ddagger < \Delta G_2^\ddagger$$

➡ $2b \rightarrow 2b$ is not via OA/RE route.



- ☉ Activation enthalpy and activation entropy of $2b \rightarrow 2a$

$$\Delta H_2^\ddagger = 1.0 \pm 0.4 \text{ kcal mol}^{-1}, \quad \Delta S_2^\ddagger = -42 \pm 2 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (1)$$



$$\Delta H^\ddagger = 10 - 12 \text{ kcal mol}^{-1}, \quad \Delta S^\ddagger = -20 \text{ to } -24 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (2)$$

(William H. Saunders, Jr. *et. al JACS* 1985, 107, 8049)

In spite of intramolecular mechanism of (1),

ΔS^\ddagger of (1) is smaller than that of (2) which is intermolecular mechanism.

➡ Direct $2b \rightarrow 2b$ exchange??

- ☉ ...But in this paper, no more direct observation could not achieved.

Their final prediction for $2b \rightarrow 2b$ exchange mechanism

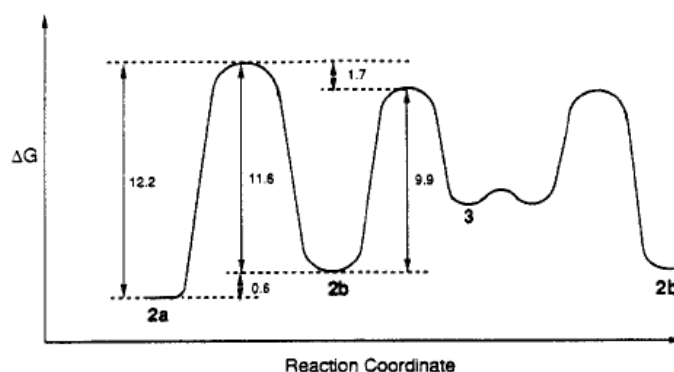
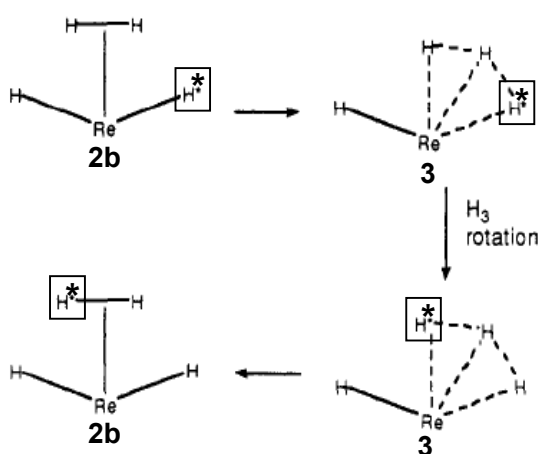


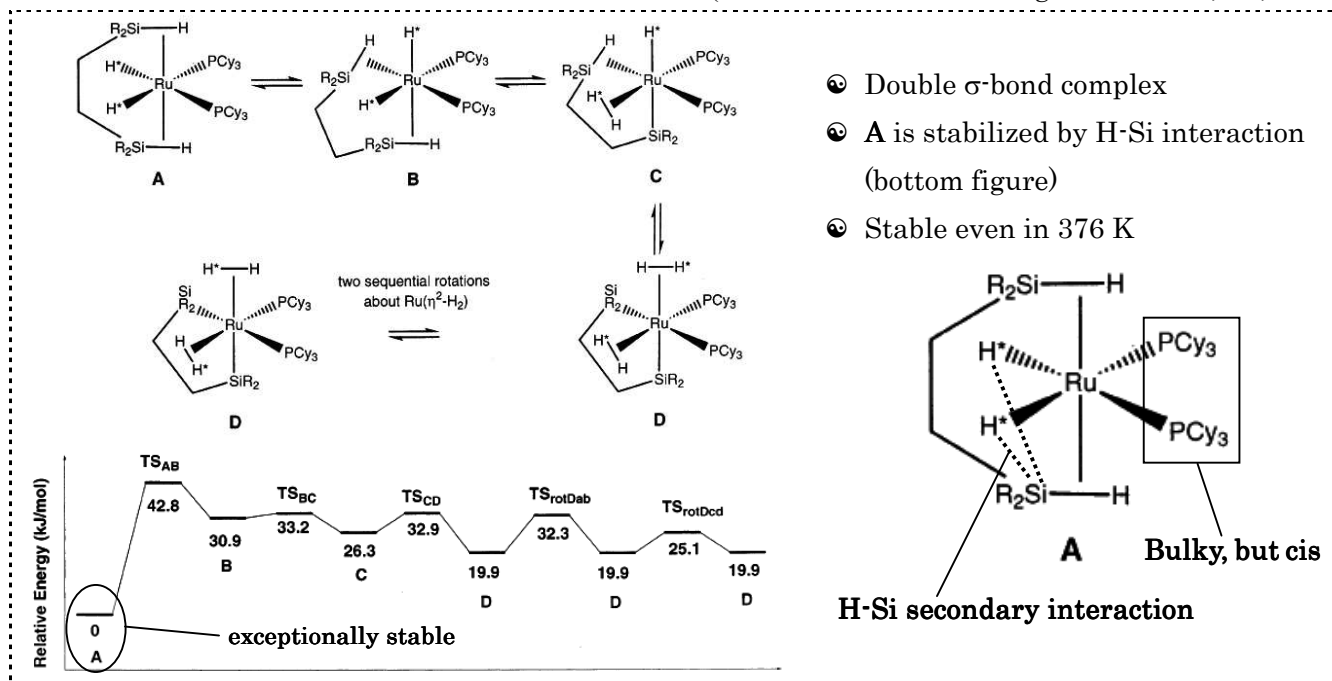
Figure 4. Free energy profile for the intramolecular exchange of dihydrogen and hydride ligands in $2b$ and the interconversion of $2a$ and $2b$ at 213 K, with ΔG^\ddagger values in kilocalories per mole. 3 represents the proposed trihydrogen intermediate.

- ☉ Compound 3 cannot be detected at least NMR because of this middle instability.

- ☉ This is also the first example of having described non-classic σ metathesis mechanism

1.2.2 E = Si

(Robin N. Perutz *et. al Organomet. 2002, 21, 5347*)



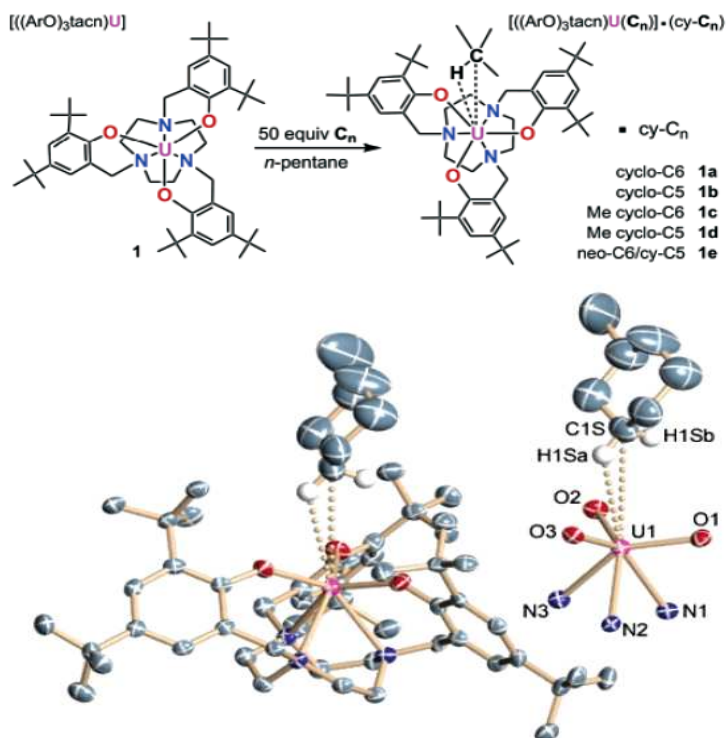
1.2.3 E = C

Direct observation of σ -C-H complex is rare so far.

(ex.1) One of the two example (so far) of

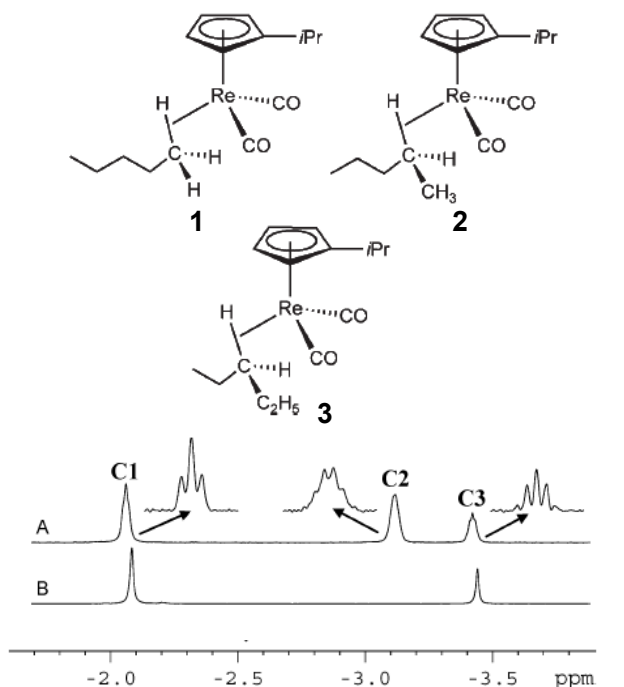
observing σ -C-H complex by X-ray diffraction

(Karsten M. *et. al JACS 2003, 125, 15734*)



(ex.2) NMR study

(Graham E.B. *et. al JACS 2005, 127, 4134*)



B: using 2,2,4,4- d_4 -pentane (500MHz, 163K)

Relative intensities

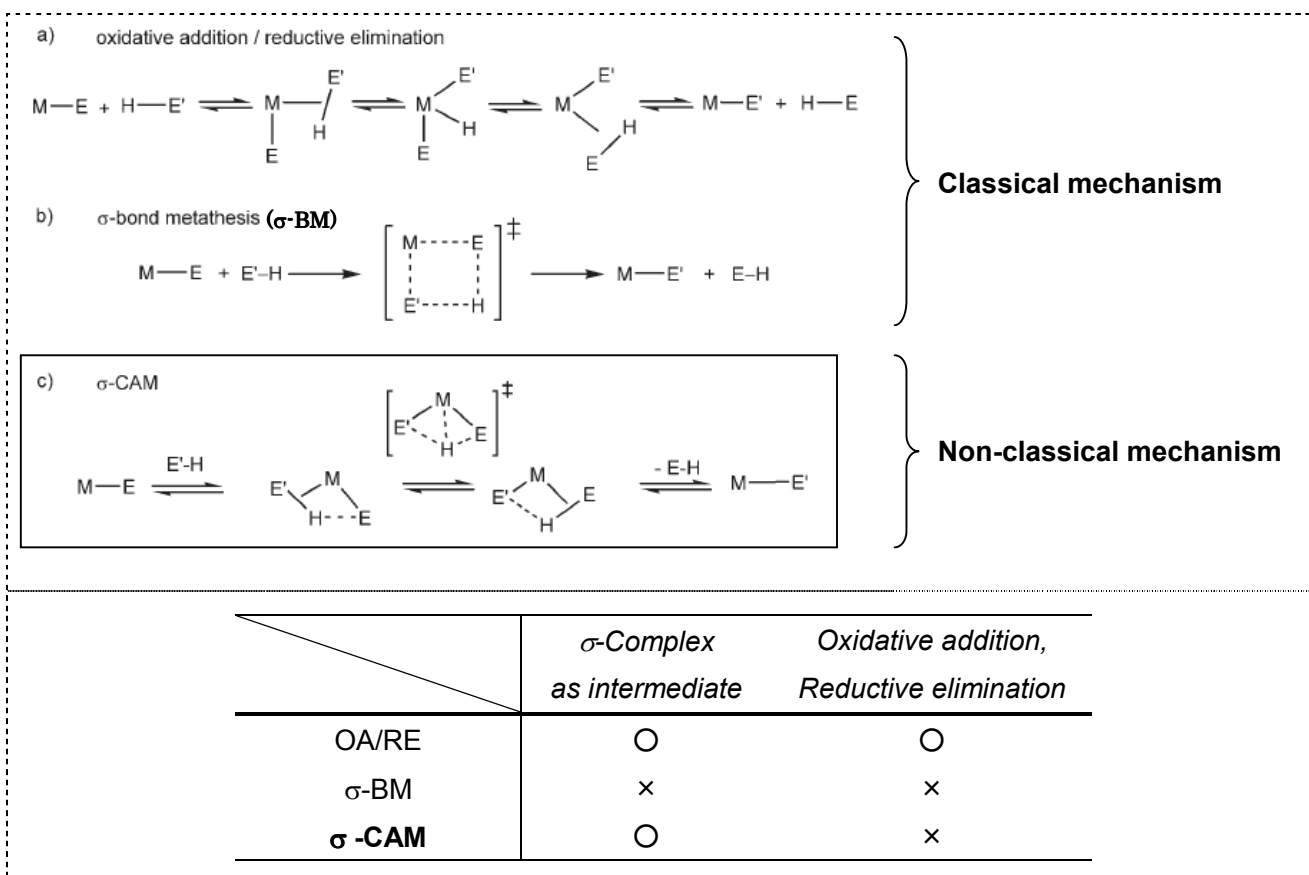
$$C1 / C2 / C3 = 6 / 6.07 / 2.90$$

It is so difficult to observe σ -C-H bonds unless using finely tuned complex, for example, using low-valent, coordinatively unsaturated, tris-aryl oxide uranium(III) complex (ex.1).

2 σ -CAM (σ -bond Complex Assisted Metathesis)

2.1 Non-classical metathesis mechanism

Some of the examples shown in the section 1 are about non-classical behavior of σ -complex. In order to explain these phenomena, another type of metathesis mechanism was invented.

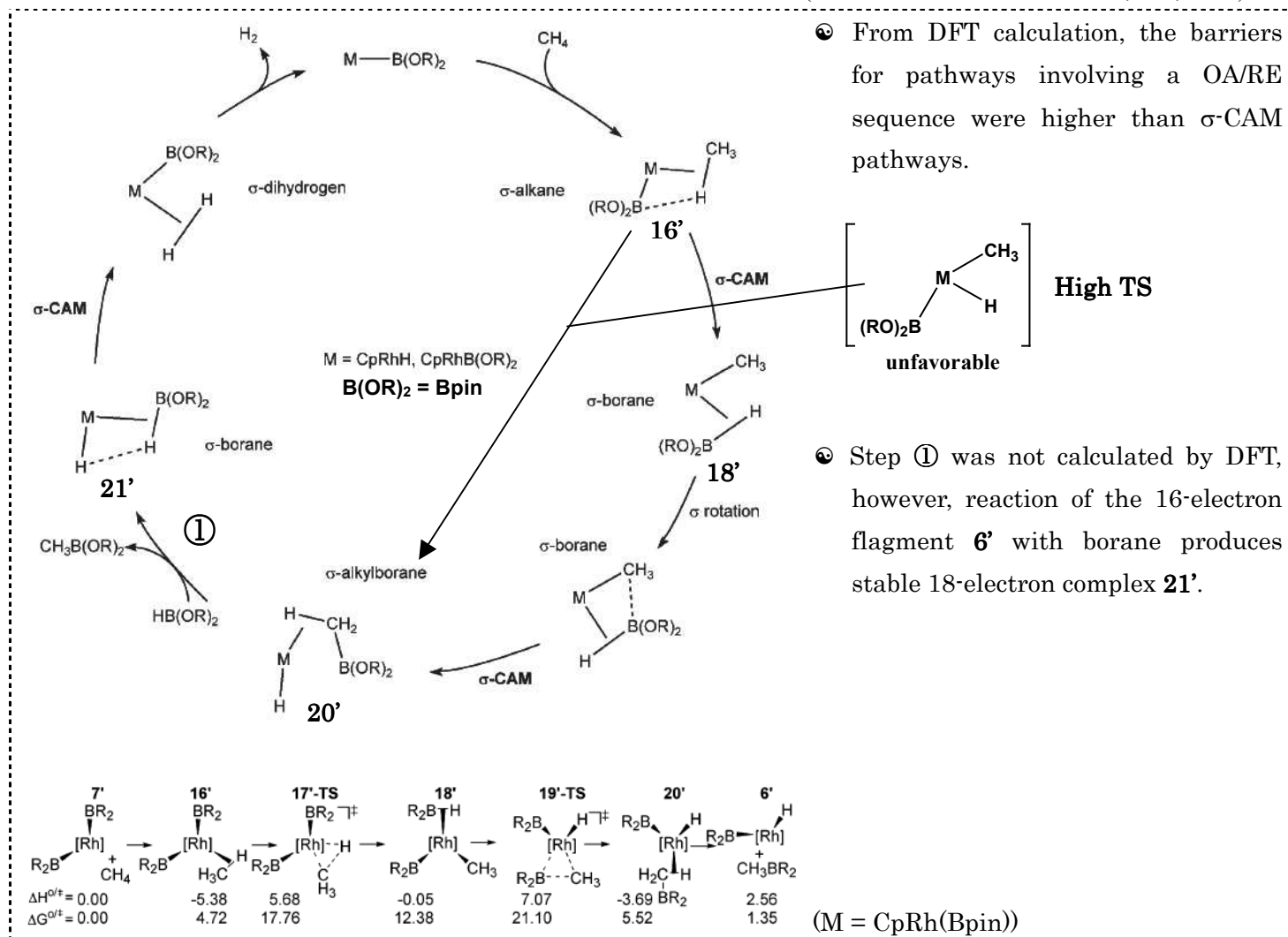


2.2 Catalytic cycle via σ -CAM

Following examples are estimated by experimental evidences and DFT calculation.

2.2.1 Borylation

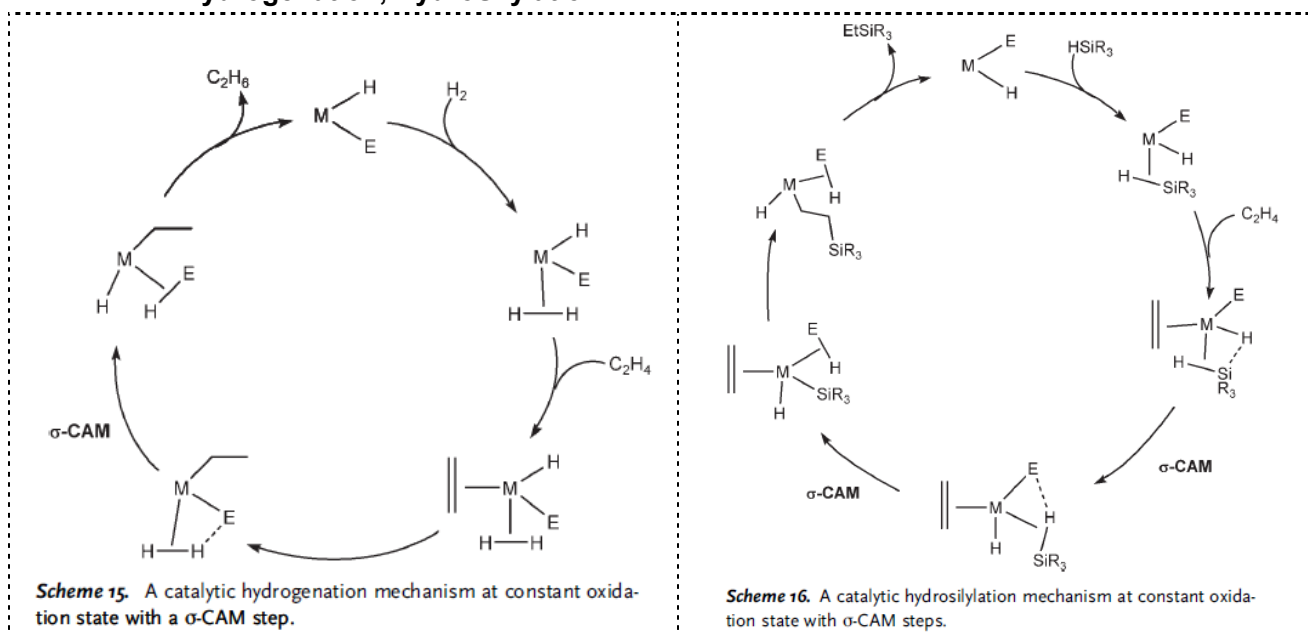
(Michael B. H. *et. al JACS* **2005**, *127*, 2538)



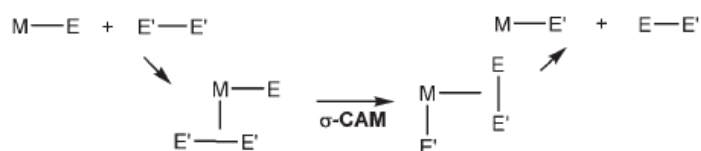
From DFT calculation, the barriers for pathways involving a OA/RE sequence were higher than σ -CAM pathways.

Step ① was not calculated by DFT, however, reaction of the 16-electron fragment **6'** with borane produces stable 18-electron complex **21'**.

2.2.2 Hydrogenation, HydroSilylation



2.3 σ -CAM for the E-E bonds (E \neq H)



Scheme 19. A σ -CAM sequence for the reaction of E-E bonds (E \neq H).

⊙ Ultimate version of σ -CAM.

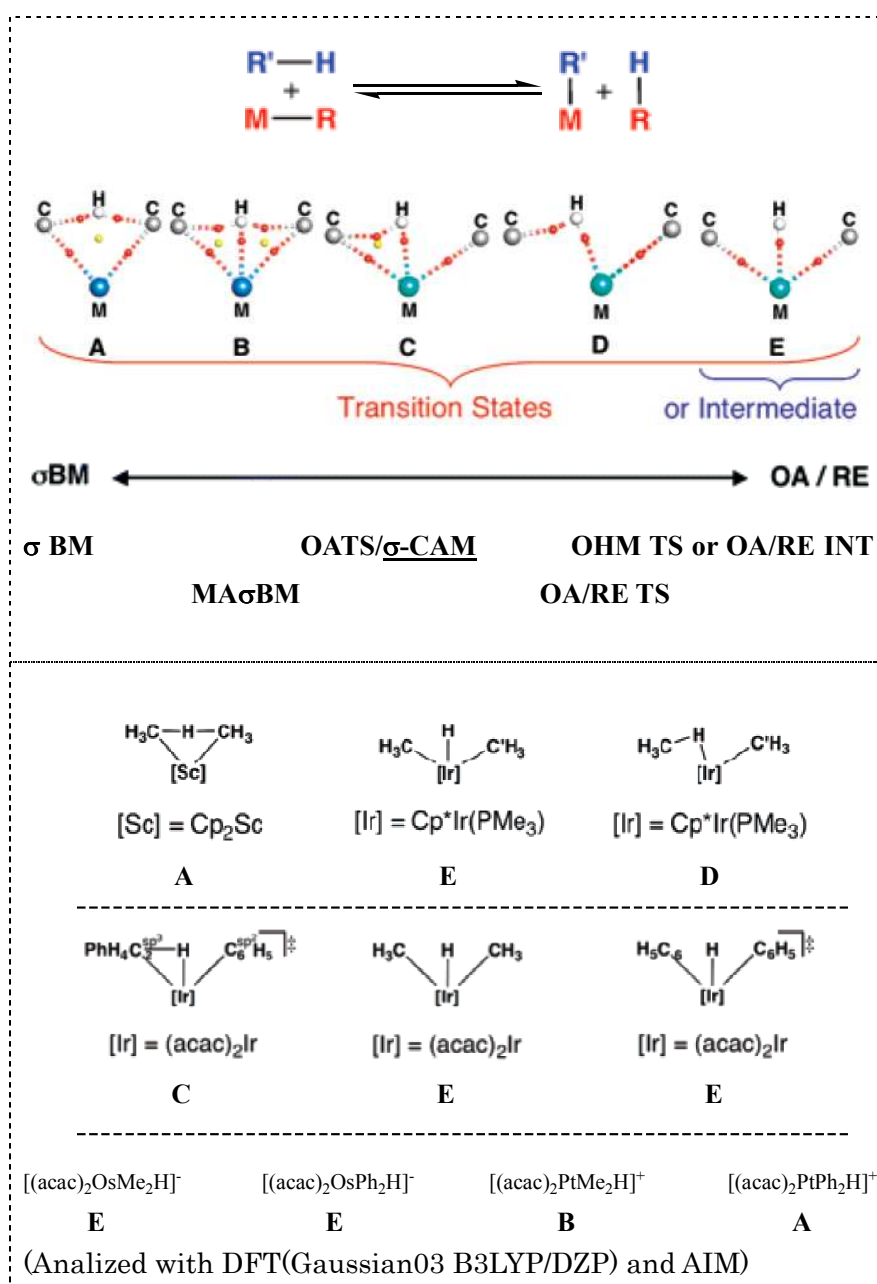
⊙ agostic C-C complex is known, but σ -C-C complexes are not known

3 Various Types of Mechanism ~ or more simple mechanism? ~

3.1 C-H bond activation mechanisms

(Michael B. H. *et. al JACS* 2007, 129, 12068)

Recently, several groups have suggested alternative mechanisms that appear to be in between OA/RE and σ -BM. Michael *et al.* tried to unify this chaotic situation.



Thank you