

博士論文（要約）

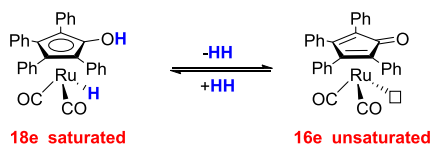
Synthesis and Catalytic Function of  
Hydroxycyclopentadienyl Group 9 Metal Complexes  
(ヒドロキシシクロペンタジエニル9族金属錯体の  
合成と触媒機能)

Shuhei Kusumoto

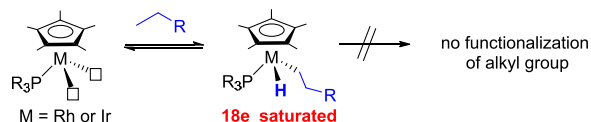
楠本周平

[Introduction] Hydrogenation is one of the most fundamental organic transformations. It is a reaction to add dihydrogen to any bonds to reduce their multiplicity. Dehydrogenation reaction is the reverse reaction of hydrogenation to deprive dihydrogen from bonds to increase their multiplicity. The key steps in these two transformations are cleavage of hydrogen–hydrogen bond and its reverse reaction, hydrogen–hydrogen bond formation. Three types of hydrogen–hydrogen activation mechanisms are so far reported. The first is oxidative addition of dihydrogen to low-valent metal. The second is  $\sigma$ -bond metathesis with metal alkyl bonds. The third is metal–ligand cooperative heterolytic hydrogen–hydrogen bond cleavage into hydride on the metal and proton on the ligand. A pioneering work in metal–ligand cooperative heterolytic hydrogen–hydrogen bond formation and cleavage was reported by Shvo in 1989 with hydroxycyclopentadienyl ruthenium complex (Scheme 1).<sup>1</sup> On the other hand, Cp\* rhodium and iridium complexes have been known to undergo oxidative addition of  $sp^3$  C–H bonds in simple alkane (Scheme 2).<sup>2</sup> Combining these two pioneering works, the author focused his attention on the synthesis and catalytic function of hydroxycyclopentadienyl group 9 metal complexes with metal–ligand cooperative heterolytic hydrogen–hydrogen bond formation and cleavage. Hydroxycyclopentadienyl group 9 metal complexes would show a metal–ligand cooperative unique catalytic function as shown in Scheme 3. After the oxidative addition of C–H bond to 16-electron hydroxycyclopentadienyl complex **A**, the formed 18-electron alkyl hydrido complex **B** can undergo heterolytic H–H bond formation by metal–ligand cooperation to make a vacant site. From the resulting unsaturated 16-electron alkyl complex **C**,  $\beta$ -hydride elimination affords an alkene and hydrido complex **E**, which would exist in equilibrium between **A**. With this function, the first direct acceptorless  $\alpha,\beta$ -unsaturation of various functional groups has been achieved.

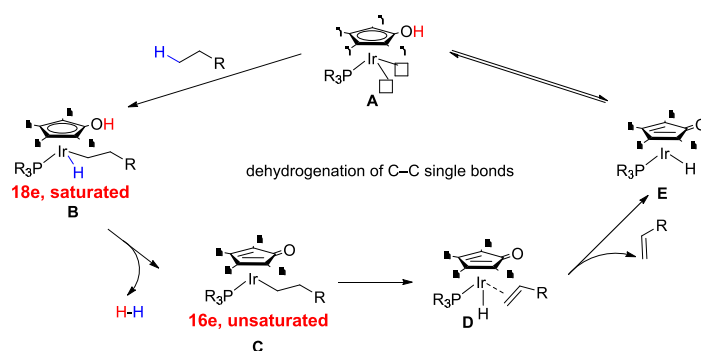
**Scheme 1** Heterolytic H–H bond formation/cleavage by Shvo's ruthenium complex



**Scheme 2** C–H oxidative addition to cyclopentadienyl group 9 metal complexes



**Scheme 3** Catalytic functions of hydroxycyclopentadienyl group 9 complexes



[1] Synthesis and characterization of hydroxycyclopentadienyl group 9 metal complexes Hydroxycyclopentadienyl rhodium and iridium dihydride monophosphine complex **4a<sub>1</sub>**, **4a<sub>2</sub>** and **4b** were synthesized over 3 steps from cyclopentadienone chloride dimer **1a** or **1b** (Scheme 2). Reduction of cyclopentadienone di-*tert*-butylmethylphosphine iridium chloride **2a<sub>1</sub>** resulted in formation of anionic cyclopentadienone iridium dihydride complex **3a<sub>1</sub>**. After protonation of carbonyl oxygen, desired hydroxycyclopentadienyl iridium dihydride **4a<sub>1</sub>** was obtained. Rhodium complex **4b** was also synthesized by the same procedure without isolation of unstable anionic intermediate **3b<sub>1</sub>**. The structures of complexes **3a<sub>1</sub>** and **4a<sub>1</sub>** were elucidated by X-ray crystallography (Figure 1).

## Scheme 2 Synthesis of hydroxy cyclopentadienyl complexes

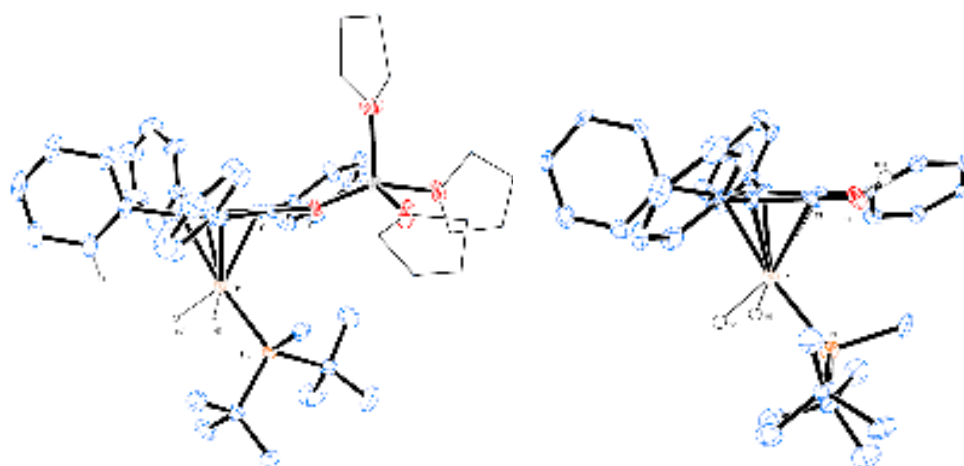
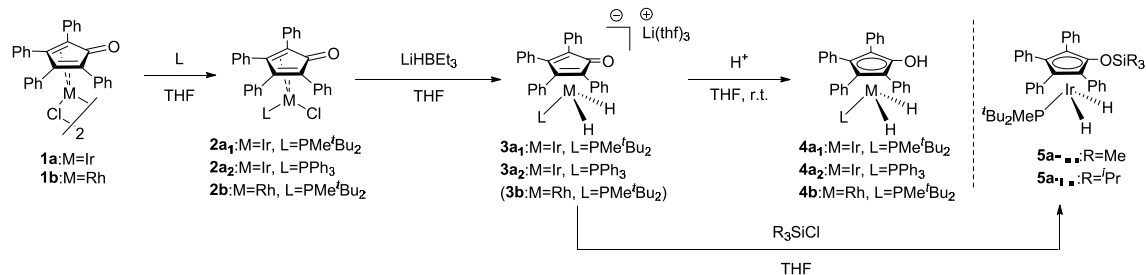
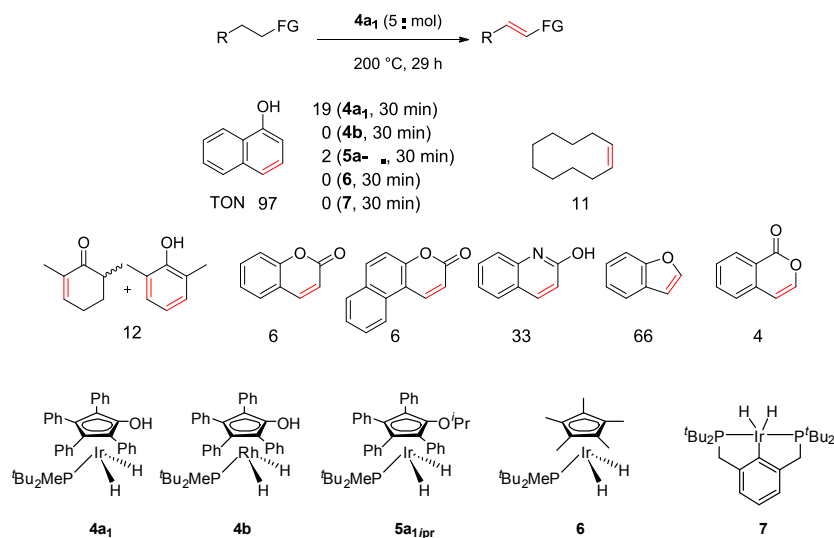


Figure 1 X-ray structures of **3a<sub>1</sub>** (left) and **4a<sub>1</sub>** (right)

### [2] Dehydrogenation of C–C single bonds

Complex **4a<sub>1</sub>** was found to catalyze dehydrogenation of C–C single bonds in simple alkane and to be uniquely active in dehydrogenation of C–C single bond adjacent to various functional groups (Table 1). In dehydrogenation of  $\alpha$ -tetralone to 1-naphthol, complex **4a<sub>1</sub>** showed 19 turnovers in 30 minutes while Cp\* complex **6**, PCP-pincer iridium complex **7** or rhodium complex **4b** showed no activity. This catalysis was strongly suppressed by the protection of hydroxy group on the ligand by triisopropyl group (**5a<sub>1ipr</sub>**) suggesting that free hydroxy group plays an important role in this catalysis. The applicable substrates were not limited to simple alkane and ketones but lactones, lactams, ethers and alkylester were also converted to the corresponding  $\alpha,\beta$ -unsaturated compounds (Table 1).

Table 1 Dehydrogenation of C–C single bonds



Although various functional groups are tolerant in this dehydrogenation reaction, there exists strict substrate limitations. For example, cyclooctanone, 5-nonanone or linear ester showed no activity at all.  $\beta$ -Hydride elimination was proposed to be a turnover limiting step for this catalysis by H/D exchange reaction and DFT calculation on the  $\beta$ -hydride elimination.

[Summary] The author achieved the first direct acceptorless dehydrogenation of C–C single bond adjacent to functional groups by developing a novel hydroxycyclopentadienyl iridium catalyst.

#### [Publications]

1) Kusumoto, S.; Akiyama, M.; Nozaki, K. *J. Am. Chem. Soc.* **2013**, *135*, 18726.

not included in this thesis

2) K. Nozaki, S. Kusumoto, S. Noda, T. Kochi, L. W. Chung, K. Morokuma *J. Am. Chem. Soc.* **2010**, *132*, 16030-16042.

3) S. Kusumoto, S. Ito, K. Nozaki *Asian J. Org. Chem.* **2013**, *2*, 977..

---

#### References

<sup>1</sup> Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

<sup>2</sup> Shvo, Y.; Czarkie, D. *J. Organomet. Chem.* **1989**, *368*, 357–365.