

## 論文の内容の要旨

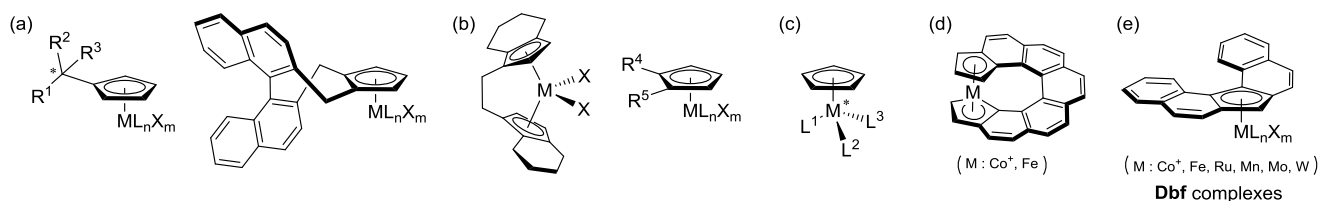
### 論文題目 Synthesis and Properties of [7]Helicene Metallocenes with Group 8 Metals

(8 族金属を有する[7]ヘリセンメタロセンの合成と性質)

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## 1. Introduction

Since the discovery of ferrocene in 1950,<sup>1</sup> a variety of cyclopentadienyl (Cp) metal complexes have been synthesized in this 60 years. There are also lots of examples of chiral Cp complexes and they can be divided into three representative families:<sup>2-4</sup> (i) complexes with Cp ligand(s) bearing substituent(s) with central or axial chirality (Figure 1a), (ii) complexes composed of prochiral Cp ligand(s) arranged in either  $C_2$  or  $C_1$  symmetry (Figure 1b), and (iii) metal-centered chiral complexes with three different ligands other than Cp (Figure 1c). In contrast, only a few examples of chiral Cp complexes with chirality originating from the helicity of the Cp ligand are known.<sup>5</sup> Katz *et al.* reported Co and Fe complexes with a helicene ligand with Cp moieties at the edge of its skeleton (Figure 1d).<sup>6-11</sup> The complexes exhibited a large absorption in the visible region and a strong signal in its circular dichroism (CD) spectra. From 2007, Thiel *et al.* made great contributions in the synthesis of a series of metal complexes with dibenzo[*c,g*]fluorenyl (**Dbf**) ligand (Figure 1e).<sup>12-16</sup> Although the Cp-ligand in the complexes showed a helical-chiral conformation in the crystal state due to the axial-chirality of the binaphthyl backbone, racemization proceeded rapidly at room temperature in solution.<sup>12</sup>



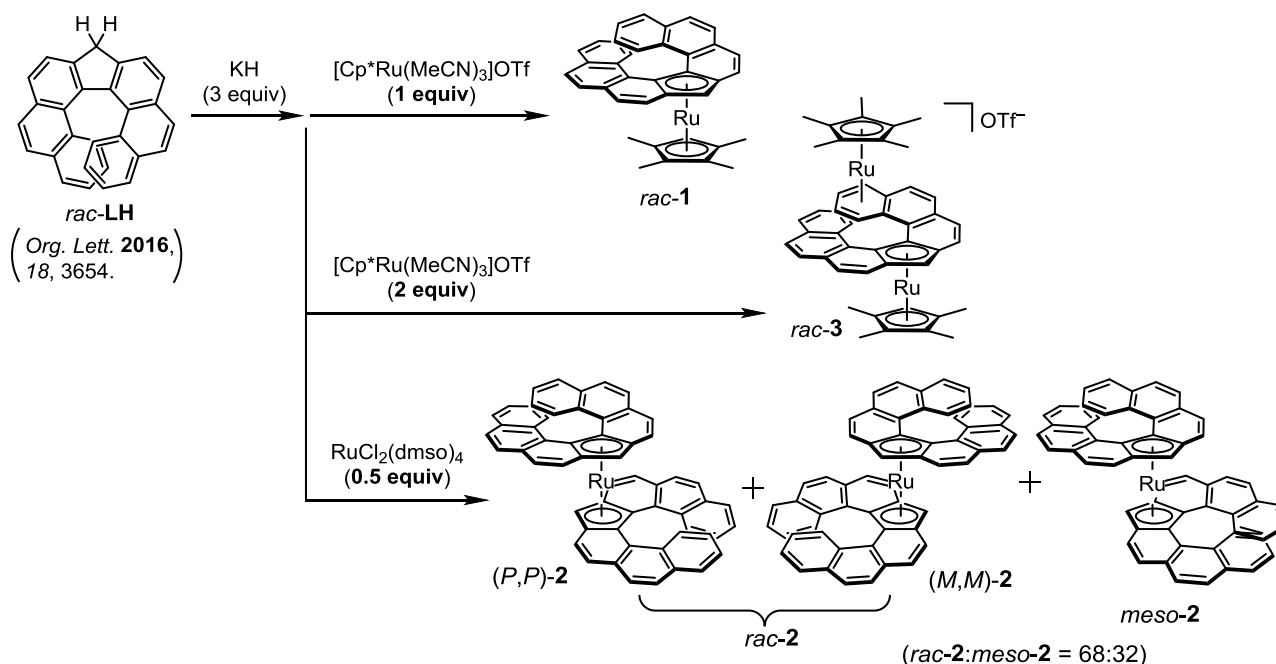
**Figure 1.** Representative examples of chiral Cp metal complexes.

In this thesis, the author developed a new [7]helicene ligand with a Cp moiety at the middle of its skeleton, and synthesized three types of ruthenocenes; complex **1** has one [7]helicene ligand and one ruthenium atom, complex **2** is a ruthenocene possessing two [7]helicene ligands, and complex **3** has two ruthenium atoms on one [7]helicene ligand. Structures, isomerization behaviours, and optical and chiroptical properties of the ruthenocenes will be discussed based on both experimental and theoretical study.

## 2. Synthesis and structural analysis of [7]helicene ruthenocenes

Three ruthenocene derivatives **1**, **2**, and **3** were synthesized in the procedure described in Scheme 1. First, a racemic mixture of **LH**<sup>17</sup> was used as a precursor, which was readily deprotonated after the addition of potassium hydride. The following reaction with an equimolar amount of [Cp\**Ru*(MeCN)<sub>3</sub>]OTf afforded a mono-helicene ruthenocene bearing one helicene ligand, *rac*-**1**, in 76% yield. When two equivalence of [Cp\**Ru*(MeCN)<sub>3</sub>]OTf was added, a bimetallic ruthenium complex *rac*-**3** was obtained in 49% yield. The reaction of deprotonated *rac*-**LH** with a half equimolar of RuCl<sub>2</sub>(dmsO)<sub>4</sub> gave bis-helicene ruthenocene **2** as a mixture of (*P,P*)- and (*M,M*)-**2** (*rac*-**2**), and (*P,M*)-

**2** (*meso*-**2**) in a 7:3 ratio, in 26% total yield. Next, the complexes were synthesized in their optically pure forms. Enantiopure (*P*)-**LH** obtained by separation of a racemic mixture using chiral HPLC was converted to optically pure (*P*)-**1**, (*P,P*)-**2**, and (*P*)-**3** by the same procedure with the case when synthesizing their racemic mixture. The opposite enantiomers were also prepared from (*M*)-**LH**. Notably, the [7]helicene ligand afforded enantiopure helicene ruthenocenes, while optically pure complexes with [5]helicene **Dbf**, reported by Thiel *et al.*,<sup>12</sup> could not be isolated due to the rapid racemization of **Dbf**.



**Scheme 1.** Synthesis of the [7]helicene ruthenocenes.

Single crystals of the obtained complexes were analyzed by X-ray diffraction. Focusing on the bond length of the five-membered ring, it was found that the cyclopentadiene moiety of **LH** was aromatized to Cp anion. The ruthenium atom coordinated to the Cp moiety in an  $\eta^5$  manner, and the additional metal in complex **3** was bound to the arene ring at the end of the [7]helicene in an  $\eta^6$  manner. The distance between the metal and the five-membered ring was almost the same as that of unsubstituted ruthenocene.<sup>18</sup> The distortion of the helical structure became smaller than that in **LH**. The racemic and meso forms of **2** were slightly more twisted than **1**, probably because of the steric repulsion between the two helicene ligands.

### 3. Isomerization behavior of the metal-bound [7]helicene

It was found that *rac*-**2** slowly converted to *meso*-**2** in solution at more than 100 °C. The ratio of *rac*- and *meso*-**2** converged into a specific value depending on temperature. There should be an equilibrium between the two isomers, in which the racemic form was 0.7 kcal mol<sup>-1</sup> more stable than its meso form, estimated from the Van't Hoff plot. According to the Eyring plot, the activation energy of isomerization from *rac*-**2** to *meso*-**2** was determined to be 33.9 kcal mol<sup>-1</sup>, which was nearly the same as racemization barrier of [6]helicene composed of only 6-membered rings (36.2 kcal mol<sup>-1</sup>).<sup>19</sup> For the conversion of *rac*-**2** to *meso*-**2**, there are two possible pathways: a flip of one of the helicene units, and/or exchange of ligands between (*P,P*)- and (*M,M*)-**2**. To clarify the mechanism, we tested if the thermal isomerization could occur with enantiopure **2**. Upon heating (*P,P*)-**2** at 122 °C, *meso*-**2** and (*M,M*)-**2**

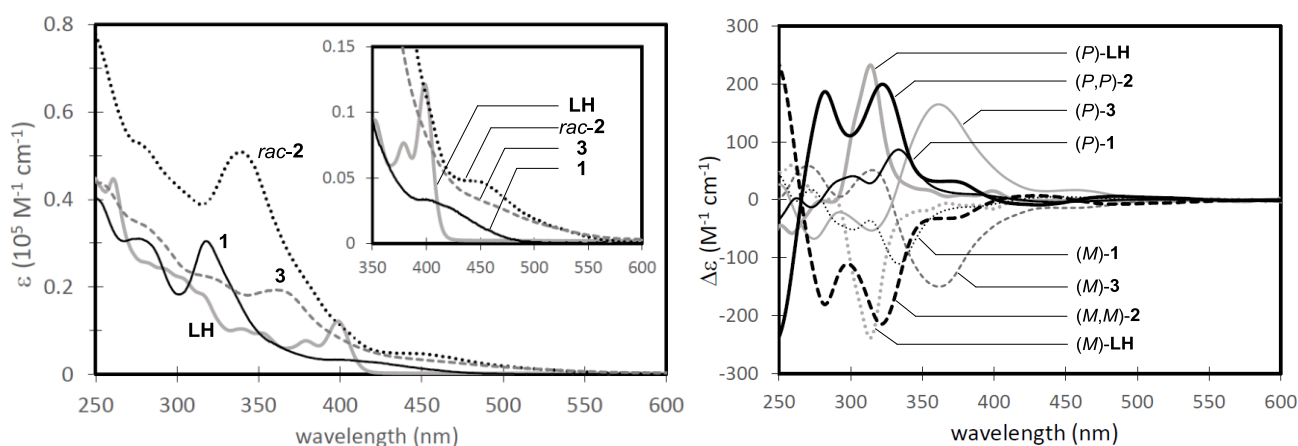
were generated, suggesting that the epimerization occurred through the helical inversion of the ligand.

#### 4. Optical and chiroptical properties

Helicenes, large aromatic molecules with helical shape, show unique optical and chiroptical properties, which can be changed by the coordination of metal(s).<sup>5</sup> In each UV-vis absorption spectrum of the obtained [7]helicene ruthenocenes, a weak broad peak was observed at longer wavelength than 400 nm, while the ligand precursor **LH** did not show any peak at the low-energy range (Figure 2). When comparing the three complexes, the absorption edge was more red-shifted in the spectra of *rac*-**2** and **3** than in that of complex **1**.

Enantiomerically pure helicene ruthenocenes showed large optical rotations and strong CD signals (Figure 2). Specific rotation of (*M*)-**1** showed  $[\alpha]_D^{23}$  of  $-1.0 \times 10^3$  ( $c = 0.1$ ,  $\text{CHCl}_3$ , the same hereinafter), whose absolute value was smaller than that of enantiopure **LH** ( $2.7 \times 10^3$ ), which could be attributed to the less distorted structure of helical moieties in the complexes than in **LH**, as mentioned in section 2. As was the case with the complexes possessing two helicene ligands reported by Katz<sup>10</sup> and Crassous,<sup>20</sup> (*M,M*)-**2** exhibited larger optical rotation than (*M*)-**1**,  $-2.8 \times 10^3$ . Optical rotation of (*M*)-**3** was  $-2.9 \times 10^3$ , which was also greater than that of (*M*)-**1**. The CD spectra of the complexes were mirror images to each enantiomer. Each complex showed large cotton effect in the shorter wavelength range, and small one at longer wavelength area than 400 nm.

These experimental results will be discussed based on DFT and TD-DFT calculations in the thesis.



**Figure 2.** UV-vis absorption and CD spectra of [7]helicene ruthenocenes and the ligand precursor **LH**.

#### 5. Phosphorescence from a bimetallic [7]helicene ruthenocene

Phosphorescent transition-metal complexes attract much attention as candidates for functional materials such as organic light emitting diodes, chemical sensors, photovoltaics, and bio-imaging.<sup>21–23</sup> Although there are a number of ruthenium complexes showing phosphorescence, represented by  $\text{Ru}(\text{bpy})_3^{2+}$ ,<sup>24,25</sup> to the best of the author's knowledge, there is no precedents without any  $\text{sp}^2$ -nitrogen based ligand such as pyridine, phenanthroline, quinoline, and so on. For example, non-substituted ruthenocene showed very weak phosphorescence, in less than 3% quantum yield even at 25 K.<sup>26</sup>

With regard to the [7]helicene metallocenes, monometallic complexes **1** and *rac*-**2** showed no luminescence at all even at 77 K like non-substituted ruthenocene. On the other hand, the bimetallic complex **3** was found to exhibit a strong broad emission peak at around 650 nm at 77 K both in a butyronitrile solution and in a

solid state. The lifetime of this emission was in 10  $\mu$ s order, which was long enough to be characterized as phosphorescence. The quantum yield was 31% in a butyronitrile solution, and 18% in a solid state, respectively. These values were much higher than that of ruthenocene derivatives which have been reported so far.

## 6. Summary

In this thesis, the author achieved the synthesis of optically-pure ruthenium complexes with a new [7]helicene ligand, **1**, **2**, and **3**. According to their X-ray structures, the helical part was aromatized and worked as an  $\eta^5$  ligand like Cp. Successful isolation of each enantiomer of [7]helicene ruthenocenes enabled the investigation of their helical structures, isomerization behaviors, and chiroptical properties. Theoretical calculations suggested that the d-orbitals of the coordinated metals hybridized to the [7]helicene's  $\pi$ -orbitals, which led to unique optical and chiroptical properties. Furthermore, the bimetallic complex **3** was found to exhibit phosphorescence in much higher yield than other reported ruthenocene derivatives.

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## Publications included in this thesis

- [1] **Akiyama, M.**; Nozaki, K. *submitted*.  
[2] **Akiyama, M.**; Tsuchiya, Y.; Ayumi, I.; Hasegawa, M.; Kurashige, Y.; Nozaki, K. *manuscript in preparation*.

## Other publications

- [1] Kusumoto, S.; **Akiyama, M.**; Nozaki, K. *J. Am. Chem. Soc.* **2013**, *135*, 18726–18729.  
[2] **Akiyama, M.**; Akagawa, K.; Seino, H.; Kudo, K. *Chem. Commun.* **2014**, *50*, 7893–7896.  
[3] Akagawa, K.; **Akiyama, M.**; Kudo, K. *Eur. J. Org. Chem.* **2015**, *18*, 3894–3898. (Highlighted in Cheminform)  
[4] **Akiyama, M.**; Nakano, K.; Nozaki, K. in *Chemical Science of  $\pi$ -Electron Systems*, Akasaka, T., Osuka, A., Fukuzumi, S., Kadori, H., Aso, Y. (Eds.), Springer, 2015, 37–46. (Review)  
[5] Oyama, H.; **Akiyama, M.**; Nakano, K.; Naito, M.; Nobusawa, K.; Nozaki, K. *Org. Lett.* **2016**, *18*, 3654–3657.