

## 論文内容の要旨

# Development of Novel Cyclometallated Complexes with Pyridyl-Pendant Corannulenes

(ピリジル基修飾型コラニューレンによる新規シクロメタル化錯体の開発)

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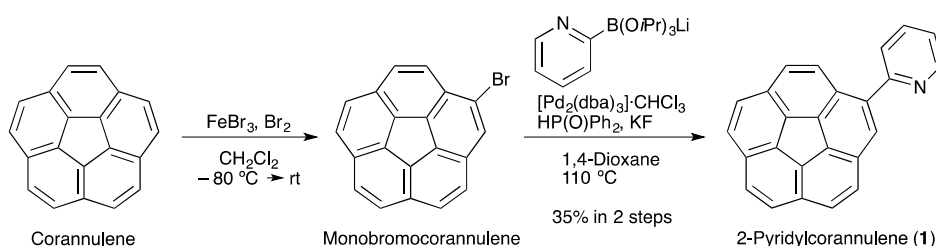
### Introduction

Corannulene  $C_{20}H_{10}$ , a fragment of buckminsterfullerene  $C_{60}$ , has attracted much attention due to its characteristic structure with a curved  $\pi$ -surface and unique features such as bowl-to-bowl interconversion and anisotropic structure. Such bowl-shaped aromatic compounds, namely buckybowls, have recently been extended over not only to organic modification but also to metal complexation. In contrast to planar polycyclic aromatic compounds, corannulene has both concave and convex faces due to its curvature so that it has much potential for forming many types of coordination structures with unique dynamic behaviors. While most of corannulene complexes reported so far are coordinated with  $\pi$ -coordination of their curved  $\pi$ -surfaces, metal complexes with  $\sigma$ -coordination at the rim are still rare.

In this study, I have designed and synthesized a corannulene-based ligand with a pyridyl pendant, 2-pyridylcorannulene (**1**) to construct a new class of corannulene metal complexes to bring out their unique coordination and association properties. Cyclometallation of ligand **1** was expected to produce  $C^{\wedge}N$  type metal complexes which have extended  $\pi$ -conjugated curved surfaces including metals. Moreover, stacked metallated corannulene derivatives would generate metal-metal interactions. Herein, I report two examples of cyclometallated corannulene complexes,  $[Pd^{II}(H-1)(CH_3CN)_2]BF_4$  and  $Ir^{III}(H-1)_3$ , and their structures and chemical properties.

### Synthesis and Structure of 2-Pyridylcorannulene Ligand **1**

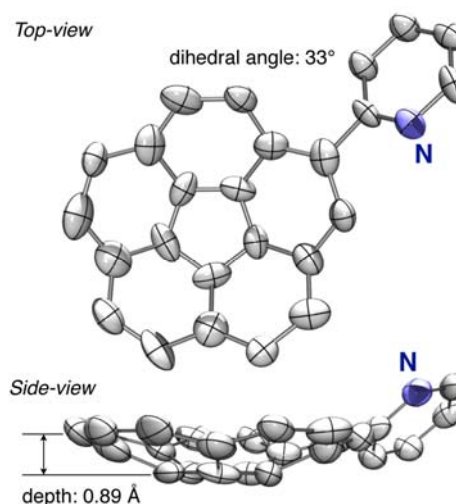
A corannulene ligand **1**, 2-pyridylcorannulene, was synthesized from corannulene in two steps. Firstly, corannulene was brominated to afford monobromocorannulene according to a literature



**Scheme 1.** Synthesis of 2-pyridylcorannulene (**1**) from corannulene in two steps.

previously reported. Ligand **1** was then obtained by Suzuki-coupling between monobromocorannulene and 2-pyridylborate in 35% overall yield in two steps.

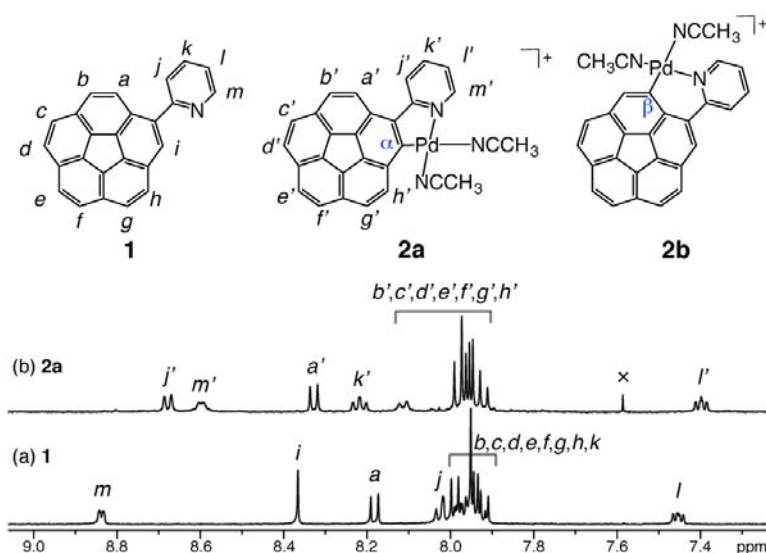
Ligand **1** was characterized by solution-phase NMR spectroscopy and DART mass spectrometry ( $m/z = 328.1$  [ $\text{H}\cdot\mathbf{1}$ ] $^+$  and  $655.2$  [ $\text{H}\cdot\mathbf{1}_2$ ] $^+$ ). A pale-yellow block crystal for X-ray structural analysis was obtained from a solution of **1** in  $\text{CHCl}_3/\text{MeOH}$  (3:1). The single-crystal X-ray analysis revealed that ligand **1** includes two enantiomers arising from the typical asymmetry of a singly substituted corannulene. The bowl depth of **1** (0.89 Å) is almost the same as that of non-substituted corannulene (0.87 Å) (Figure 2). In the crystal, the dihedral angle between corannulene and pyridyl moieties in **1** is relatively large ( $33^\circ$ ), suggesting that  $\pi$ -conjugation between these moieties is not extended. This is also supported by a UV-vis spectrum of **1** showing only a small amount of red shift by 3-6 nm compared with corannulene.



**Figure 2.** Crystal structure of 2-pyridylcorannulene (**1**).

### Synthesis of Cyclopalladated Complex, $[\text{Pd}^{\text{II}}(\text{H}_-1\mathbf{1})(\text{CH}_3\text{CN})_2]\text{BF}_4$ , and Its Self-assembly Behaviors

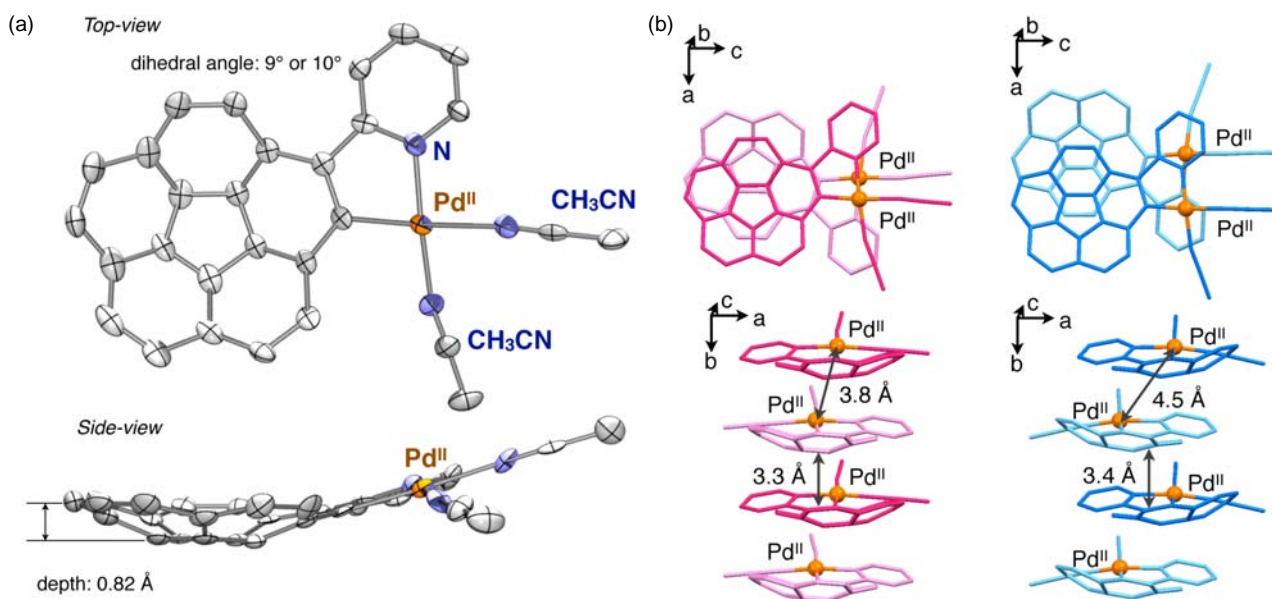
Cyclometallation of **1** was firstly examined using four-coordinate  $\text{Pd}^{\text{II}}$  with a view to a stacked structure. The reaction of **1** with 1 equiv. of  $[\text{Pd}^{\text{II}}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  was conducted in  $\text{CD}_3\text{CN}$  at  $60^\circ\text{C}$  for 8 days. The  $^1\text{H}$  NMR spectrum of the resulting solution suggested that two sets of structural isomers arising from different deprotonation positions (**2a** and **2b**),  $[\text{Pd}^{\text{II}}(\text{H}_-1\mathbf{1})(\text{CH}_3\text{CN})_2]\text{BF}_4$ , were produced in a ratio of 9:1 (Figure 3). A major species without a singlet signal for the  $\alpha$ -position to the pyridyl moiety is assigned to **2a** forming a 5-membered cyclopalladated ring, while the other minor species with two singlet signals is assigned to **2b** forming a 6-membered cyclopalladated ring as the result of  $\beta$ -deprotonation. The ESI-TOF mass spectrum strongly supports the formation of a cyclopalladated  $\text{Pd}^{\text{II}}(\text{H}_-1\mathbf{1})$  structure ( $m/z = 473.0$  [ $\text{Pd}^{\text{II}}(\text{H}_-1\mathbf{1})(\text{CH}_3\text{CN})$ ] $^+$  and  $514.1$  [ $\text{Pd}^{\text{II}}(\text{H}_-1\mathbf{1})(\text{CH}_3\text{CN})_2$ ] $^+$ ).



**Figure 3.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_3\text{CN}$ , 300 K) of (a) **1** and (b) **2a** and chemical structures of **1**, **2a**, and **2b**.

Slow evaporation of a  $\text{CH}_3\text{CN}$  solution containing a mixture of cyclopalladated complexes (**2a** and **2b**) produced two different crystals, plates and needles, in 31% yield in total.  $^1\text{H}$  NMR of the mixed crystals indicated only one species, **2a**. Conversion from **2a** to **2b** was too slow to be observed at room temperature in solution.

In the X-ray structure of **2a** (plate), the central  $\text{Pd}^{\text{II}}$  center is coordinated by a deprotonated C and an N atom of ligand **1** with a 5-membered chelate ring and two  $\text{CH}_3\text{CN}$  molecules (Figure 4a). In the crystal, the  $\text{Pd}^{\text{II}}$  complex is a racemate and two enantiomers arising from the inversion of the corannulene moiety are alternately stacked through  $\pi$ - $\pi$  interactions to form a columnar structure (Figure 4b). The depth of corannulene moiety (0.82 Å) is less

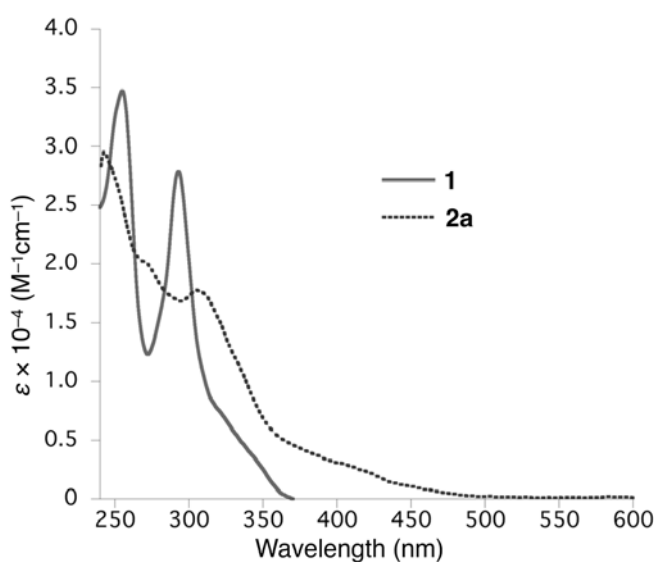


**Figure 4.** X-ray structure of  $[\text{Pd}^{\text{II}}(\text{HL}_1)(\text{CH}_3\text{CN})_2]\text{BF}_4$  (**2a**).  $\text{BF}_4^-$  ions are omitted for clarity.

than that of **1**, and the dihedral angle (9 or 10°) between corannulene and pyridyl moieties is much smaller than that of **1**. In the same column, the corannulene parts are stacked in a concave-convex fashion through  $\pi$ - $\pi$  interactions (3.3 or 3.4 Å). Moreover, there are two kinds of columns alternately arranged parallel to one another. One has a shorter Pd-Pd distance (3.8 Å) while the other has a longer distance (4.5 Å), which indicates there is no bonding between  $\text{Pd}^{\text{II}}$  centers in both cases. The Pd-Pd distances were expected to be adjusted by ligand exchange of the coordination sites bound by  $\text{CH}_3\text{CN}$  ligands. Self-assembly of **2a** with  $\pi$ - $\pi$  stacking in solution was also suggested by upfield shift of  $^1\text{H}$  NMR signals with increasing concentrations of mixed **2a** and **2b** from 0.1 mM to 1 mM.

The electronic state of **2a** in solution was studied by UV-vis spectroscopy (Figure 5). Compared with **1**, an additional broad absorption band was observed with **2a** in the range from 350 to 450 nm, which may be in part assigned to an MLCT transition. The absorption maxima at 271 and 306 nm in  $\text{CH}_3\text{CN}$  are red-shifted from those of **1** (255 and 293 nm), which can be attributed mainly to the extended  $\pi$ -conjugation in the molecular structure of **2a**, because only a small  $\pi$ - $\pi$  stacking effect is expected under the highly dilute condition (9.9  $\mu\text{M}$ ).

Investigation of the bowl-to-bowl inversion of the corannulene ring was conducted by the replacement of two acetonitrile ligands on the  $\text{Pd}^{\text{II}}$  center of **2a** by a chiral bidentate ligand (1*R*,2*R*)-(-)-1,2-diaminocyclohexane (**3**), in



**Figure 5.** UV-vis spectra of **1** ( $\text{CH}_3\text{CN}$ , [**1**] = 10  $\mu\text{M}$ , 293 K) and **2a** ( $\text{CH}_3\text{CN}$ , [**2a**] = 9.9  $\mu\text{M}$ , 293 K).

expectation of the observation of the diastereomeric inversion. Unfortunately, although the ligand exchange quantitatively took place as shown by  $^1\text{H}$  NMR and ESI-TOF mass measurements, the diastereomeric inversion

was not observed even at low temperatures.

### Synthesis of Ir<sup>III</sup> Complex, *mer*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub>, and Its Coordination Structure

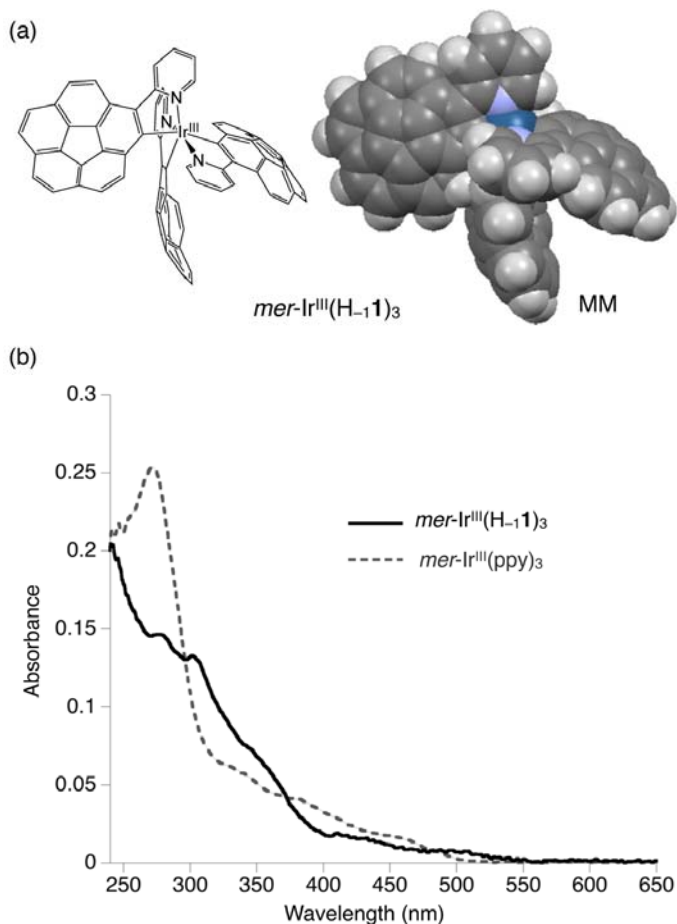
Tris(2-phenylpyridinato) Ir<sup>III</sup> complex, Ir<sup>III</sup>(ppy)<sub>3</sub> (ppyH = 2-phenylpyridine), and its derivatives are attractive luminescent materials. A six-coordinate Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> complex was synthesized by the reaction of the bulky ligand **1** with Ir<sup>III</sup> in two steps according to the synthetic method of Ir<sup>III</sup>(ppy)<sub>3</sub> through [Ir<sup>III</sup>(ppy)<sub>2</sub>(μ-Cl)]<sub>2</sub>. Firstly, a biscyclometallated Ir<sup>III</sup> complex was generated by the reaction of **1** with IrCl<sub>3</sub>·nH<sub>2</sub>O, which was characterized by <sup>1</sup>H NMR spectroscopy and ESI-TOF mass spectrometry. The resulting biscyclometallated Ir<sup>III</sup> complex was then mixed with **1** at 140 °C to obtain Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub>, which was isolated as an orange solid after purification with silica gel column chromatography. The Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> complex was characterized by <sup>1</sup>H NMR and ESI-TOF mass measurements (*m/z* = 1171.3 [Ir(H<sub>1</sub>**1**)<sub>3</sub>]<sup>+</sup>). It should be noted that some NMR signals for protons around the sterically crowded coordination sites were shifted to higher magnetic field by up to 6 ppm, indicating the shielding effect of the large π-surfaces. In the light of the symmetry of the NMR signals, the complex Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> was assigned to its *meridional* (*mer*) isomer (Figure 6a).

A UV-vis absorption spectrum of *mer*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> was significantly red shifted compared to that of *mer*-Ir<sup>III</sup>(ppy)<sub>3</sub> (Figure 6b). Its absorption bands in

the longer-wavelength region than 400 nm suggest the extended π-conjugation of the corannulene moiety due to the cyclometallation of **1** with Ir<sup>III</sup>. According to the previously reported peak assignment for *mer*-Ir<sup>III</sup>(ppy)<sub>3</sub>, the strong absorption from 250 to 400 nm and the weaker absorption in the longer-wavelength region than 400 nm may be assigned to spin-allowed π-π\* transition of the ligand moiety and MLCT, respectively. *mer*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> complex does not have strong luminescence, whereas *facial* (*fac*) isomer of Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> is expected to have strong luminescence as observed with *fac*-Ir<sup>III</sup>(ppy)<sub>3</sub>. Synthesis of *fac*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> is now underway.

### Summary

A novel pyridyl-pendant corannulene ligand, 2-pyridylcorannulene (**1**), was synthesized from corannulene in two steps. Complexation of **1** with Pd<sup>II</sup> and Ir<sup>III</sup> produced [Pd<sup>II</sup>(H<sub>1</sub>**1**)(CH<sub>3</sub>CN)<sub>2</sub>]BF<sub>4</sub> and *mer*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> complexes, respectively, with a cyclometallated structure. Their extended π-conjugation with metal complexation was established by structural and spectrochemical analyses of these complexes in solution and crystal states. The X-ray structure of the Pd<sup>II</sup> complex suggests that the stacking interactions between the corannulene rings would provide



**Figure 6.** (a) Structure and molecular model of *mer*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> and (b) absorption spectra of *mer*-Ir<sup>III</sup>(ppy)<sub>3</sub> (CH<sub>2</sub>Cl<sub>2</sub>, [*mer*-Ir<sup>III</sup>(ppy)<sub>3</sub>] = 8 μM, 293 K) and *mer*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub> (CH<sub>2</sub>Cl<sub>2</sub>, [*mer*-Ir<sup>III</sup>(H<sub>1</sub>**1**)<sub>3</sub>] = 8 μM, 293 K).

an excellent tool to align metals attached around the rim of the rings in an extended  $\pi$ -conjugation system.