

ジフェノール類の CH 結合活性化によるメタラ芳香族化合物のワンステップ合成

One-Step Synthesis of Metallaaromatic Compounds via CH Activation of Diphenol Derivatives

応用化学専攻 鈴木 美香

Suzuki Mika

1. Introduction

Metallaaromatic compounds, metal complexes in which the metal center is incorporated in an aromatic system, have recently gained considerable interest as a unique class of aromatic molecules. As a result of extensive synthetic efforts combined with sophisticated theoretical studies, many kinds of metallaaromatics have been reported so far. However, study of π -extended metallaaromatics still remains rare due to the lack of efficient synthetic methods.

Cyclometallation via CH bond activation is now recognized as an indispensable method for the synthesis of elaborated organometallic compounds. Recently, a novel double CH-bond activation has been discovered in this laboratory in the reaction of $[\text{Cp}^*\text{Ir}(\text{OAc})_2]$ with methylene-bridged diphenols.¹ During the course of this study, the author has designed ethylene- and ethylidene-bridged diphenol derivatives as substrates and found that cyclometallations of these compounds affords two types of iridaoxacycles **1** and **2**, respectively, both of which are doubly fused with benzo and benzofurane units (Figure 1). Details of synthesis, characterization and metallaaromaticity of **1** and **2** are described below.

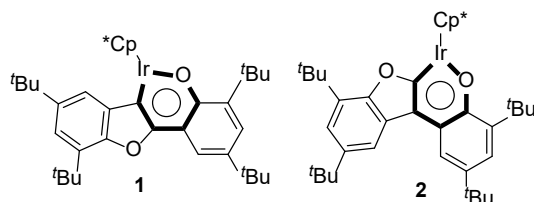
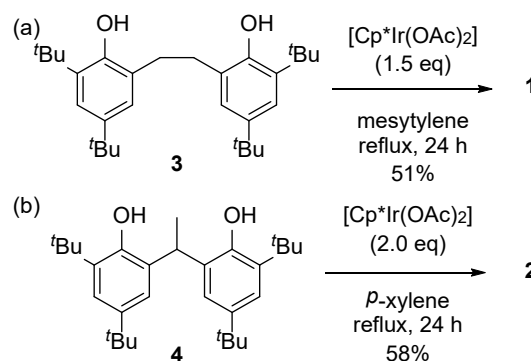


Figure 1. Structures of benzo- and benzofuran-fused iridaoxabenzenes.

2. Results and Discussion

The author first examined a reaction of ethylene-bridged diphenol **3** with $[\text{Cp}^*\text{Ir}(\text{OAc})_2]$ in mesitylene under reflux (Scheme 1a). Purification by silica gel

column chromatography and recrystallization afforded black crystals, which were identified as the target iridaoxacycle **1** in 51% yield. It would also be noteworthy that use of the tetramethyl analog of **3** failed to afford the corresponding iridaoxacycle. The analogous reaction with ethylidene-bridged bisphenol **4** under the optimal condition provided iridaoxacycle **2** in 58% yield (Scheme 1b). Both complexes **1** and **2** were thermally stable, and decomposition was not observed below 270 °C.

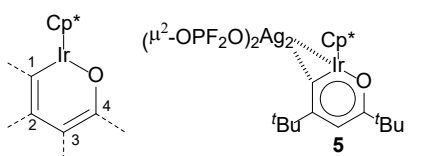


Scheme 1. Syntheses of complex **1** and **2**.

The structures of complex **1** and **2** were determined by X-ray single crystal analyses, although fully refined structures could not be obtained due to low quality of crystals. Both complexes had a planer iridaoxacycle as shown by the sum of angles in the six-membered ring (719.3° for **1** and 719.6° for **2**). In both complexes, Ir–C1 and Ir–O were shorter than those of normal Ir–C and Ir–O single bonds, and lengths of all C–C and C4–O1 bonds in the iridaoxacycle lie between typical single and double bonds (Table 1). These results suggests that the π -electrons on each six-membered iridaoxacycle are highly delocalized. The above-mentioned structural features are similar to those of complex **5**, which is widely accepted as a family of metallabenzene,² and therefore, both complexes **1** and

2 can be reasonably considered as a family of metallaaromatics.

Table 1. Structural parameters of complex **1**, **2**, and **5**. The bond lengths are given in Å.



	1	2	5
Ir–O	2.009(5)	1.990(8)	1.998(3)
Ir–C1	2.013(8)	1.962(11)	2.000(4)
C1–C2	1.391(11)	1.400(15)	1.417(5)
C2–C3	1.442(11)	1.443(15)	1.412(5)
C3–C4	1.407(10)	1.423(14)	1.389(5)
C4–O	1.324(9)	1.343(13)	1.309(5)

Nucleus-independent chemical shifts (NICS) calculations also supported the aromatic character of these complexes; NICS(1)_{ZZ} values of complex **1** and **2** are estimated to be sufficiently negative (-10.3 for **1** and -12.8 for **2**), and these values are within a comparable range with that of complex **5** (-17.0).

Calculated molecular orbitals show that each complex **1** and **2** has a π -conjugated system delocalized over the whole molecular skeleton, and the Ir atom participates in the delocalized π -conjugation (Figure 2). For instance, the HOMO of **1** and **2** involve a π -bonding interaction between the Ir d orbital (one of three t_{2g} orbitals) and the π^* orbital of the organic fragment, and the corresponding antibonding interaction is found in the LUMO.

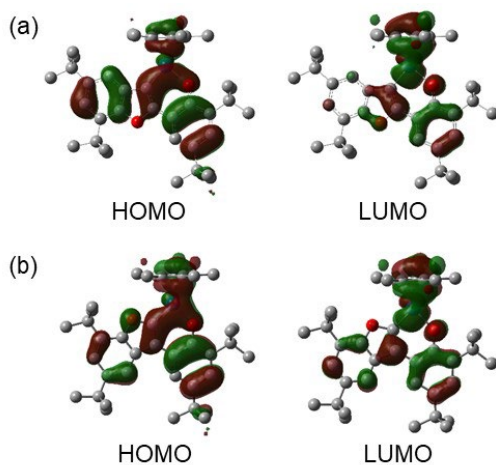


Figure 2. Frontier orbitals of (a) **1** and (b) **2**.

Reactivities of complexes **1** and **2** were next

investigated. In both complexes, the iridium center can be considered as a formal 16e metal. Thus, we examined reactions of complex **1** and **2** with 2-electron donor ligands. To a degassed solution of **1** in CDCl_3 , CO gas was introduced at room temperature to afford the CO-coordinated iridium complex **6** (Figure 3a). An X-ray crystallographic analysis of **6** showed that the Ir atom is significantly deviated from the mean plane defined by C1, C2, C3, C4, and O atoms, which eventually leads to the nonplanar geometry of the iridacycle. This structural change strongly suggests the loss of the metallaaromaticity. Interestingly, by Ar bubbling to the solution of CO-coordinated complex **6**, the starting complex **1** was completely recovered. This labile nature of the CO ligand might be thermodynamically induced by the recovery of the aromatic stabilization energy in complex **1**. Complex **2** also exhibited reversible coordination of CO to give **7** (Figure 3b).

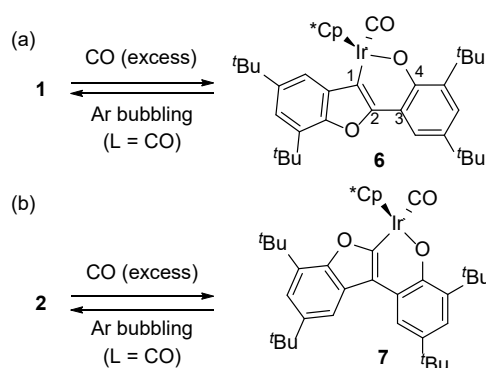


Figure 3. Reactions of complexes **1** and **2** with CO.

3. Conclusion

The author has accomplished the syntheses of novel benzo- and benzofuran-fused iridaoxabenzenes through one-pot cyclometallations including CH bond activations of C_2 bridged diphenol substrates. From the structural analyses and theoretical calculations, both complexes can be considered as metallaaromatics with highly delocalized π -conjugated systems.

4. References

- (1) Ishii, Y. *et al. Organometallics* **2020**, *39*, 4500–4509.
- (2) Paz-Sandoval, M. A *et al. Organometallics* **2002**, *21*, 4696–4710.

5. Presentations

- (1) 101th CSJ Annual Meeting **2021**.
- (2) The 71th JSCC Conf **2021**.
- (3) ref 1.