

ルテニウムピラー[5]アレーン錯体の合成と物性

Synthesis and Properties of Ruthenium Complexes with a Pillar[5]arene Ligand

応用化学専攻 堤崎 悠飛

TSUTSUMIZAKI Yuhi

1. Introduction

Pillar[*n*]arenes (*n* = 5–15) first reported by Ogoshi in 2008 are macrocyclic compounds composed of electron-rich dialkoxybenzene units connected by methylene bridges at the *para*-positions.¹ Especially, pillar[5]arenes show interesting host properties derived from their rigid pentagonal framework. For example, they can selectively form host–guest complexes with only linear *n*-alkanes, while do not with cyclic and branched alkanes.² Since it is expected that π -complexation of pillar[*n*]arenes with cationic transition metals reduces electron density of the cavity, such π -metalated pillar[*n*]arenes would have unique host properties different from those of unmodified pillar[*n*]arenes. In fact, pillar[5]arene complexes bearing one, two or three [Cp**M*]²⁺ (Cp* = η^5 -C₅Me₅; M = Rh, Ir) units, have been synthesized and revealed to uptake one of the counteranions inside the cavity through anion– π interactions.³ On the other hand, our group independently has synthesized [Cp**M*(η^6 -pillar[5]arene)][BF₄]₂ (M = Rh, Ir) which show strong interaction with polar solvents such as CH₃NO₂ and acetone. In this study, the author reports the synthesis of novel Ru–pillar[5]arenes whose ruthenium units have mono- and dicationic charges. The host–guest chemistry of the dicationic Ru complex is also demonstrated.

2. Experimental Section

All reactions were carried out under an inert atmosphere by using standard Schlenk techniques. New compounds were characterized by NMR, IR and TOF-MS spectroscopy, and for **3**–**5** by X-ray diffraction analysis as well.

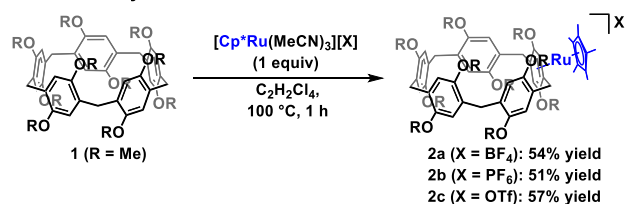
3. Results and Discussion

[Cp**Ru*(η^6 -pillar[5]arene)][X] (**2a–c**)

When 1 equiv of [Cp**Ru*(acetonitrile)₃][X], where X = BF₄, PF₆, and OTf, were allowed to react with

pillar[5]arene (**1**) in C₂H₂Cl₄ at 100 °C for 1 h, pillar[5]arene complexes **2a–c** were obtained as colorless crystals in moderate yields (Scheme 1). In the ¹H NMR spectrum of **2a–c**, five distinct aryl-H signals were observed, one of which appeared at a characteristic high-field region (δ 5.84). The upfield-shifted signal is attributable to the aryl group coordinating to the [Cp**Ru*]⁺ unit.

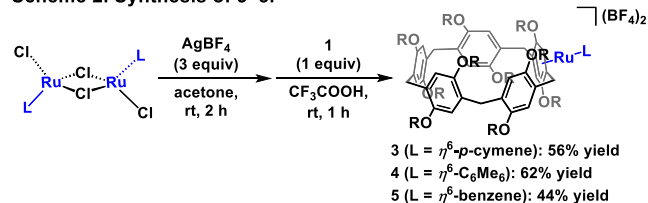
Scheme 1. Synthesis of **2a–c**.



[(η^6 -arene)Ru(η^6 -pillar[5]arene)][BF₄]₂ (**3–5**)

Reaction of *in situ* generated [(η^6 -arene)Ru(acetone)₃][BF₄]₂, where arene = *p*-cymene, C₆Me₆, and benzene, with **1** in CF₃COOH at room temperature yielded the corresponding pillar[5]arene complexes **3–5** (Scheme 2). Single crystals of **3**–CH₃NO₂ suitable for X-ray diffraction analysis were obtained by slow diffusion of ¹PrOH vapor into a CH₃NO₂ solution of **3**. The X-ray diffraction study revealed that one MeNO₂ molecule is embedded within the cavity of **3** (Figure 1). Since the shortest distance between the O1 and C_{arene} atoms (i.e. O1···C1) is 2.86(1) Å which is shorter than the sum of the van der Waals radii of these two atoms (3.22 Å), we infer that there are electrostatic interactions between the CH₃NO₂ molecule and the arene ring coordinating to the Ru atom. Notably,

Scheme 2. Synthesis of **3–5**.



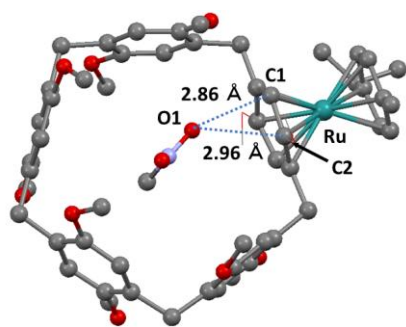


Figure 1. Crystal structure of $3\supset\text{CH}_3\text{NO}_2$. The BF_4 ions and all hydrogen atoms are omitted for clarity.

formation of supramolecular complexes with any solvent molecules has not been reported for $[(\text{Cp}^*\text{M})_n(\eta^6\text{-pillar}[5]\text{arene})][\text{OTf}]_{2n}$ ($\text{M} = \text{Rh}, \text{Ir}; n = 1, 2, 3$).³

¹H NMR Titration Experiments

Motivated by the encapsulation of a CH_3NO_2 molecule inside the cavity of **3** in the solid state, ¹H NMR titration experiments were performed to understand the host–guest interaction of **3** and nitroalkanes.

As shown in Figure 2, the ¹H NMR signal of CH_3NO_2 shifted from δ 4.33 to 4.22 upon addition of an equimolar amount of **3**, which implies the formation of a supramolecular complex from **3** and CH_3NO_2 in CDCl_3 solution. The Job plot shown in Figure 3 revealed that the composition ratio (**3**: CH_3NO_2) in the supramolecular complex is 1:1. Importantly, no upfield shift was detected for a 1:1 mixture of **1** and CH_3NO_2 , revealing that the coordination to the cationic metal changes the host properties of pillar[5]arene. 1-Nitrohexane also showed a notable change of the ¹H NMR chemical shifts on addition of **3**, while 2-nitropropane did not. These findings suggest that the host–guest interaction between **3** and nitroalkanes is highly dependent on the shapes of nitroalkanes.

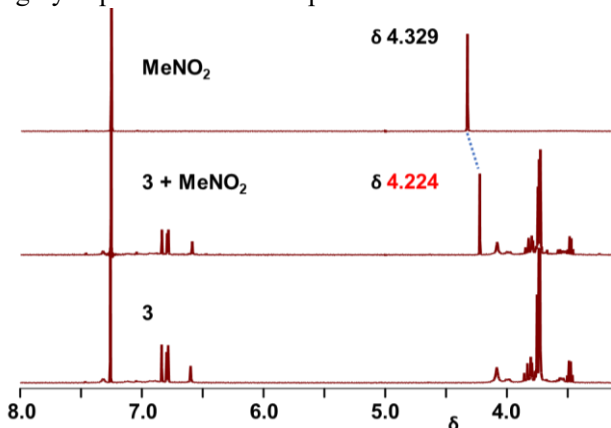


Figure 2. ¹H NMR (CDCl_3) spectra of CH_3NO_2 (top), a 1:1 mixture of $3\supset\text{CH}_3\text{NO}_2$ (middle), and **3** (bottom).

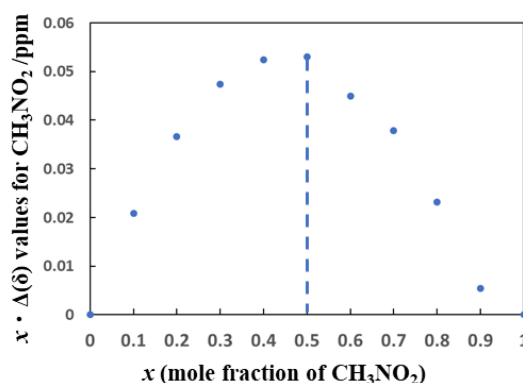


Figure 3. Job plot between **3** and CH_3NO_2 .

Finally, ¹H NMR titration experiments were performed to determine the binding constant (K). Varying amounts of a CDCl_3 solution of **3** (from 0 to 7 equiv) was added to a 1.00 mM solution of CH_3NO_2 in CDCl_3 , and the changes of the chemical shift were recorded (Figure 4). The K value for CH_3NO_2 was calculated to be $72 \pm 12 \text{ M}^{-1}$ by using non-linear curve fitting analysis.

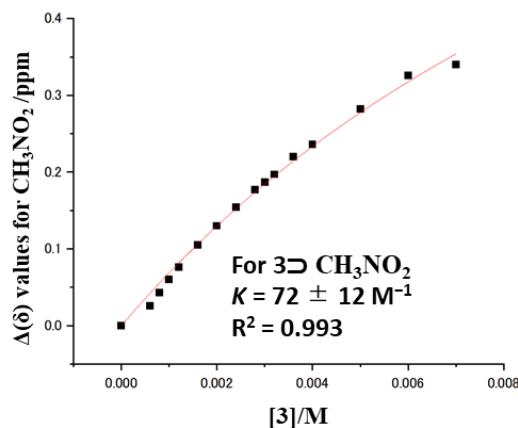


Figure 4. The chemical shift changes of the ¹H NMR signal of CH_3NO_2 .

4. Conclusion

We have synthesized Ru–pillar[5]arene complexes **2–5**. The ¹H NMR titration experiments suggested that **3** selectively uptakes linear nitroalkanes inside the cavity. The binding constant K for the complexation of **3** and CH_3NO_2 was estimated to be $72 \pm 12 \text{ M}^{-1}$.

References

- (1) Ogoshi, T. *et al. J. Am. Chem. Soc.* **2008**, *130*, 5022–5023.
- (2) Ogoshi, T. *et al. Chem. Commun.* **2011**, *47*, 10290–10292.
- (3) Yang, H-B. *et al. Angew. Chem., Int. Ed.* **2017**, *56*, 14438–14442.

Presentations List

- (1) 69th Conf. Jpn. Soc. Coord. Chem. 1PA-007 (2019).