Ir(III)に配位したカリックス[4]アレーンへの末端アルキン挿入による環拡大反応と環拡大カリックス[4]アレーンの配位挙動

Ring Expansion of an Ir-calix[4]arene Complex via Insertion of Terminal Alkynes and Coordination Behaviors of the Ring Expanded Calix[4]arene

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1. Introduction

Calixarenes have been investigated extensively in a wide range of fields including supramolecular and metal complex chemistry owing to their unique coordination behavior derived from the characteristic cavity and multi binding sites. To modify their functionalities, substantial effort has been devoted to the design and synthesis of calixarene derivatives. From this view point, a potentially fascinating approach to induce a dramatic change of their properties is an expansion of the macrocyclic ring. However, in spite of tremendous synthetic studies on calixarene functionalizations, there is no facile method to achieve ring expansion of the parent calixarenes.

Recently, this laboratory has succeeded in the synthesis of calix[4]arene iridium complex **1**, in which the iridium is attached to a methylene carbon (Chart 1).[1] This type of *C*-metalated calix[4]arene complex has rarely been investigated so far,[2] and their reactivities remain undeveloped. In this study, the author investigated the reactivity of complex **1** to find that reaction with terminal alkynes provided ring-expanded calix[4]arene complexes. Isolation of the metal-free ring-expanded calix[4]arenes and their reactions with several transition metal complexes were also studied.

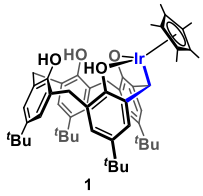


Chart 1.

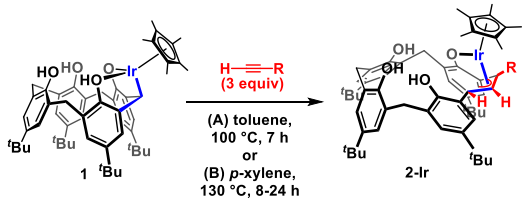
2. Experimental Section

All reactions were carried out under an inert atmosphere by using standard Schlenk techniques. New organometallic compounds were characterized by NMR, X-ray diffraction, and elemental analysis.

3. Results and Discussion

First, we examined reactions of complex **1** with a variety of terminal alkynes (Table 1). When complex **1** was reacted with phenylacetylene, ring-expanded calixarene complex **2a** was obtained in 95% yield. Notably, NMR analysis of the reaction mixture showed formation of a single product, indicating that insertion of phenylacetylene proceeded with excellent regioselectivity. The present reaction could be applied to diverse aryl alkynes HC≡CR (R = *p*-C_6H_4Me, *p*-C_6H_4OMe, *p*-$C_6H_4CF_3$, 1-Naph), to afford the corresponding ring-expanded calixarene complexes **2b**–**2e** in moderate to high yields. Other alkynes such as alkynoates or alkylacetylenes also provided the desired products by employing harsher reaction conditions albeit in lower is isolated yields (**2f**–**2i**).

Table 1. Ring expansion of calix arene with various alkynes.



condition	R	yield (%)
A	Ph (**2a**)	95
A	*p*-Tolyl (**2b**)	95
A	*p*-$MeOC_6H_4$ (**2c**)	84
A	*p*-$CF_3C_6H_4$ (**2d**)	56
A	1-Naphthyl (**2e**)	82
B	MeOOC (**2f**)	41
B	EtOOC (**2g**)	37
B	Hexyl (**2h**)	15
B	Ferrocenyl (**2i**)	26

The structure of complex **2e** was unambiguously determined by X-ray crystallographic analysis (Figure 1). The iridium center is coordinated with the Cp*, one

phenoxy oxygen atom and the η^3-allylic ligand. Thus, 1-naphthylacetylene is selectively inserted into the C(methylene)−C(aryl) bond of **1**, in which the naphthyl group is connected to the terminal carbon of the allyl group. Although details of the reaction mechanism is still obscure, DFT calculations implied that the reaction would proceed via the δ-carbon elimination of complex **1** and the subsequent insertion of an alkyne. It showed also be pointed out that these ring-expanded complexes have a planar chirality derived from the unsymmetrically substituted macrocyclic structures.

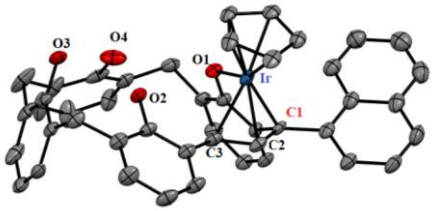
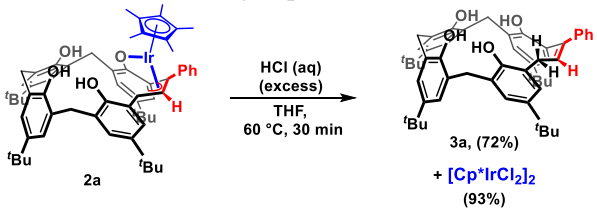


Figure 1. ORTEP drawings of **2e**. Me groups of the Cp* ligand, ^{t}Bu groups, and hydrogen atoms are omitted for clarity.

The author next examined removal of the iridium metal from the ring-expanded calix[4]arene complex (Scheme 1). When complex **2a** was treated with excess amounts of HCl at 60 °C in THF, a mixture of the desired calixarene **3a** and $[Cp^*IrCl_2]_2$ in 72 and 93% yields, respectively. These products were readily separated by washing the crude mixture with ether to give the metal-free ring-expanded calixarene **3a**.



Scheme 1. Protonolysis of complex **2a**.

The molecular structure of **3a** is shown in Figure 2. Although all OH groups are involved in a hydrogen-bonding network as was usually seen in the parent calix[4]arenes, O4–H3 distance is obviously longer in comparison with other hydrogen bonds. Thus, the ring expansion significantly affect the macrocyclic structure of the metal-free ring-expanded calixarenes.

In order to explore coordination behavior of **3a**, reactions with several transition metal complexes were examined (Scheme 2). Treatment of **3a** with metal acetate complexes such as $[Cp^*M(OAc)_2]$ (M = Rh, Ir)

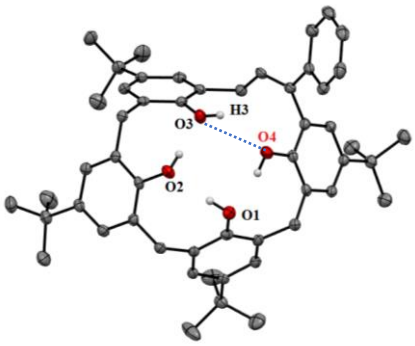
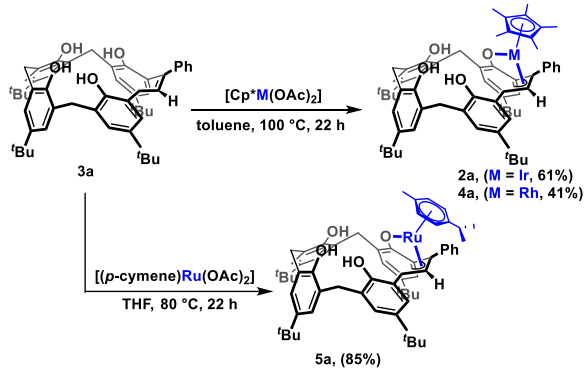


Figure 2. ORTEP drawing of **3a**. Selected bond lengths (Å): O1–H4, 1.904; O2–H1, 1.869; O3–H2, 1.861; O4–H3, 2.278(6); O1–O2, 2.696(3); O2–O3, 2.698(3); O3–O4, 2.852(3); O4–O1, 2.728(3)

and $[(p\text{-cymene})Ru(OAc)_2]$ resulted in the selective formation of the corresponding η^3-allyl complexes **2a**, **4a** and **5a**, respectively. These results indicated that compound **3a** has a potential to serve as a novel macrocyclic ligand by utilizing the allylic moiety.



Scheme 2. Reaction of **3a** with transition metals.

4. Conclusion

Ring-expanded calix[4]arene complexes have been synthesized from the *C*-metallated calix[4]arene complex **1** via insertion of a terminal alkyne in accompany with the inert C−C bond cleavage. Transformation into the metal-free ring-expanded calixarenes was readily achieved by protonolysis of complex **2**. Furthermore, the ring-expanded calixarenes have shown to possess a potential to serve as novel macrocyclic ligands.

5. References

1) Ishii, Y. *et al*. *Organometallics* **2018**, *37*, 1829–1832.
2) For another example, see; Parkin, G. *et al*. *J. Am. Chem. Soc*. **2006**, *128*, 16358–16364.

6. Presentations

1) 100th CSJ Annual Meeting 2H2-46 (**2020**).
2) 70th Conf. Jpn. Soc. Coord. Chem. 2PD-01 (**2020**).