

# Ru 及び Ir 錯体上でのヘテロ元素置換内部アルキンのビニリデン転位 Vinylidene Rearrangement of Heteroatom-Substituted Internal Alkynes at Ru and Ir Complexes

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## 1. Introduction

The vinylidene rearrangement at a transition metal center, in which a coordinating alkyne is transformed into the corresponding vinylidene ligand, is among the most important transition-metal-promoted reactions of alkynes and has been applied widely to organic synthesis.<sup>1</sup> Although there have been many reports on this type of rearrangement using terminal- and silicon-substituted alkynes,<sup>2</sup> similar transformation of carbon-disubstituted<sup>3</sup> and group 15/16 element-substituted<sup>4</sup> internal alkynes still remains to be explored. Since the discovery of vinylidene rearrangement of simple dialkyl- and diarylalkynes at a ruthenium center,<sup>5</sup> this laboratory has been engaged in expanding the scope of this transformation from both viewpoints of the group migrating and the reaction site.<sup>6</sup> In fact, vinylidene rearrangement of phosphoryl-, sulfonyl-, and arylthio-substituted internal alkynes has recently been achieved at a cationic ruthenium center.<sup>7</sup> In this work, the author has investigated this rearrangement of *N*-substituted internal alkynes at ruthenium and iridium complexes and *S*-substituted internal alkynes at an iridium complex.

## 2. Experimental Section

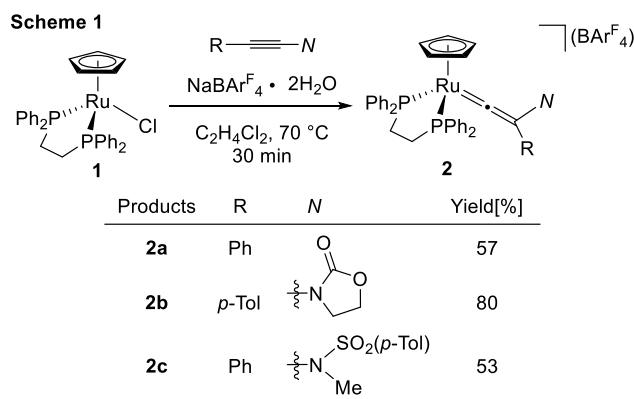
All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. Organometallic products were fully characterized by NMR, IR, X-ray diffraction, and elemental analyses.

## 3. Results and Discussion

### Ru-Promoted Vinylidene Rearrangement of *N*-Substituted Internal Alkynes

When [CpRuCl(dppe)] (**1**) was allowed to react with amide- and sulfonamide-substituted internal alkynes in

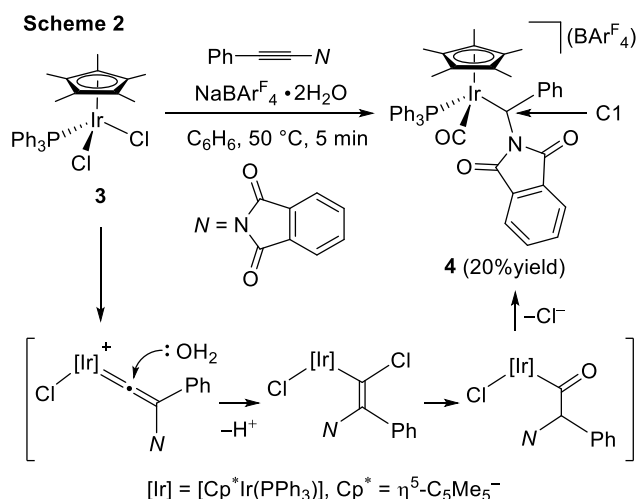
the presence of NaBAR<sup>F</sup><sub>4</sub>·2H<sub>2</sub>O, where Ar<sup>F</sup> = 3,5-bis(trifluoromethyl)phenyl, the corresponding vinylidene complexes **2** were obtained (Scheme 1). Complex **2c** exhibits a <sup>13</sup>C{<sup>1</sup>H} NMR signal at δ 355.4 characteristic of the α carbon of the vinylidene ligand. The Ru–C<sub>α</sub> and C<sub>α</sub>–C<sub>β</sub> bond lengths determined by an X-ray diffraction study of **2c** are 1.835(4) and 1.345(5) Å, respectively, which fall in the normal range for those in Ru-vinylidene complexes.



### Ir-Promoted Vinylidene Rearrangement of *N*-Substituted Internal Alkynes

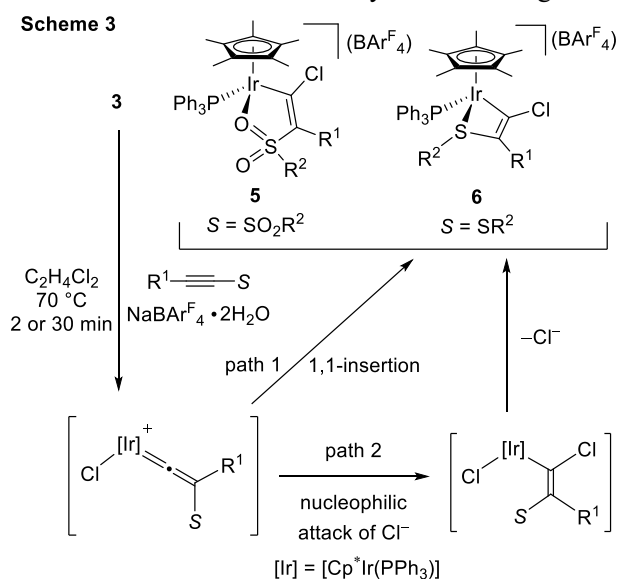
Since vinylidene rearrangement was not observed in the reaction of amide-substituted internal alkynes with a cationic iridium complex generated from [Cp\*IrCl<sub>2</sub>(PPh<sub>3</sub>)] (**3**), the author explored the reaction with *N*-(phenylethynyl)phthalimide. Treatment of **3** and *N*-(phenylethynyl)phthalimide at 50 °C in the presence of NaBAR<sup>F</sup><sub>4</sub>·2H<sub>2</sub>O resulted in the formation of carbonyl complex **4** as the major product (Scheme 2). The molecular structure determined by X-ray diffraction analysis revealed that the Ph and phthalimide groups are bound to the same α-carbon (C1) atom, indicating that either of the Ph or phthalimide group has migrated

to form a vinylidene intermediate. In the  $^1\text{H}$  NMR spectrum, the methine signal of **4** was observed at  $\delta$  6.78, whereas its  $^{13}\text{C}\{^1\text{H}\}$  NMR signal appeared at  $\delta$  20.7 (d,  $^2J_{\text{CP}} = 5.6$  Hz). The Ir–C1 bond length of 2.136(3) Å falls in the normal range for those of Ir–C single bonds. Complex **4** seems to be generated by nucleophilic attack of  $\text{H}_2\text{O}$  at the vinylidene  $\text{C}_\alpha$  atom followed by elimination of HCl and decarbonylation.



### Ir-Promoted Vinylidene Rearrangement of *S*-Substituted Internal Alkynes

When **3** was allowed to react with sulfonyl- and arylthio-substituted internal alkynes at 70 °C in the presence of  $\text{NaBARF}_4 \cdot 2\text{H}_2\text{O}$ , five-membered iridacycle **5** and iridathiacyclobutene **6** were isolated, respectively, as the single product (Scheme 3). On the basis of the structures of **5** and **6** where the  $\text{R}^1$  group is located at the  $\alpha$ -position of the sulfur atom, these complexes are deduced to be formed via the vinylidene rearrangement.



The five-membered iridacycle in **5** is non-planar, whereas the iridathiacyclobutene skeleton in **6** is flat with the sum of the internal angles of 359.9°. Complexes **5** and **6** were generated via either 1,1-insertion of the vinylidene ligand into the Ir–Cl bond (path 1) or nucleophilic attack of  $\text{Cl}^-$  at the  $\text{C}_\alpha$  atom of the vinylidene ligand (path 2).

### $^{13}\text{C}$ -Labeling Experiments

To better understand the mechanism for the rearrangement, the migration aptitude of the alkyne substituents was confirmed by using the  $^{13}\text{C}$ -labeled alkynes. Careful analysis of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra led to the conclusion that the *S*-substituents have migrated in the formation of **5** and **6**, while the *N*-substituents have a low tendency to migrate in the formation of **2** and **4**.

### 4. Conclusion

Ru-promoted vinylidene rearrangement of *N*-substituted internal alkynes and Ir-promoted vinylidene rearrangement of *N*- and *S*-substituted internal alkynes have been investigated. Although, the resulting Ir-vinylidene complexes could not be isolated due to their high reactivity toward nucleophiles, it has been confirmed that iridium acts as an active reaction site for this rearrangement. The migratory aptitude of the alkyne substituents is  $\text{S} > \text{C} > \text{N}$ .

### References

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- 6) a) Ishii, Y. *et al. Synlett* **2018**, *29*, 727–731; b) Ishii, Y. *et al. Organometallics* **2019**, *38*, 1560–1566.
- 7) Ishii, Y. *et al. Organometallics* **2020**, *39*, 711–718.

### Presentation List

- 1) Faraday Discussion P-06 (2019).
- 2) 69<sup>th</sup> Conf. of JSCC 3Da-04 (2019).
- 3) 100<sup>th</sup> CSJ Annual Meeting 2H2-47 (2020).
- 4) 70<sup>th</sup> Conf. of JSCC 2PD-07 (2020) (**Poster Award**).

### Publication List

- 1) Aoki, Y.; Ishii, Y. *et al. Organometallics* **2020**, *39*, 711–718.