

# イリジウム錯体上での内部アルキンのビニリデン転位

## Vinylidene Rearrangement of Internal Alkynes in an Iridium Complex

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### 1. Introduction

Vinylidene rearrangement of terminal alkynes in transition metal complexes has been utilized for transformation of alkynes into various organic compounds.<sup>1</sup> In contrast, similar rearrangement of internal alkynes is still recognized as an unusual process. Previously our group has reported that the vinylidene rearrangement of *general* internal alkynes can proceed at group 8 metal complexes.<sup>2</sup> These findings prompted us to examine whether vinylidene rearrangement of internal alkynes takes place at transition metals other than those of group 8. In fact, our group has recently succeeded in expanding the reaction site to group 9 metal (Ir) complexes; that is, the reaction of [Cp\*IrCl<sub>2</sub>(PPh<sub>3</sub>)] (**1**) with diarylalkynes led to the formation of the corresponding vinylidene complexes. In this study, the author has investigated reactions of **1** with acyl-, thio-, and sulfonylalkynes to expand the scope of the vinylidene rearrangement at an iridium center, which resulted in the formation of unexpected iridacycle complexes.

### 2. Experimental Section

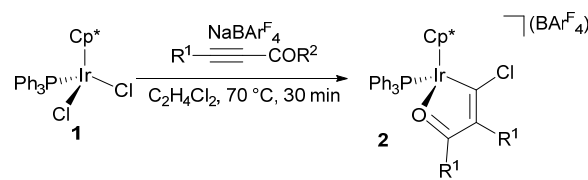
All manipulation were carried out under an inert atmosphere by using standard Schlenk techniques. Organometallic products were characterized by NMR, IR, X-ray diffraction, and elemental analyses.

### 2. Results and Discussion

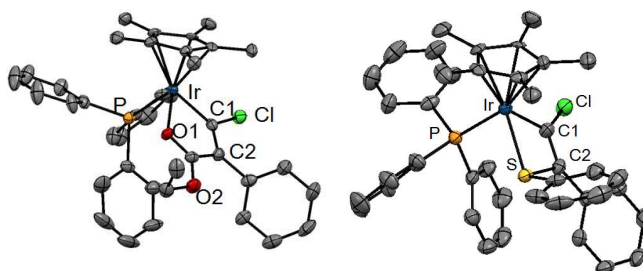
When **1** was allowed to react with Ph-C≡C-CO<sub>2</sub>Et in the presence of NaBAR<sup>F</sup><sub>4</sub> (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) at 70 °C for 30 min, the vinyliridium complex **2a** was obtained as the sole product (Table 1, entry 1). Complex **2a** exhibits a

<sup>13</sup>C{<sup>1</sup>H} NMR signal at δ 186.3 characteristic of the α carbon of the vinyl ligand. The structure determined by X-ray diffraction analysis revealed that the Ph and CO<sub>2</sub>Et groups of **2a** are bound to the same β carbon atom (Figure 1, left), indicating that either of the substituents in Ph-C≡C-CO<sub>2</sub>Et has migrated across the C≡C bond during the reaction. Similar products were obtained in high yields with various acylalkynes (Table 1).

**Table 1.** Reactions of **1** with acylalkynes



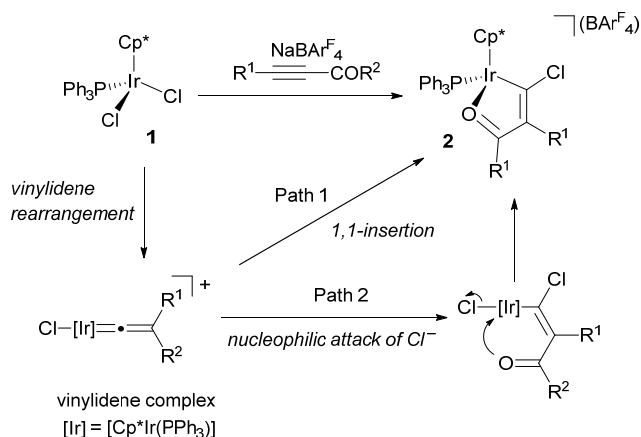
entry	R <sup>1</sup>	R <sup>2</sup>	product	yield (%)
1	Ph	OEt	<b>2a</b>	69
2	<sup>t</sup> Bu	OEt	<b>2b</b>	53
3	Ph	Ph	<b>2c</b>	95
4	Ph	<i>p</i> -Tol	<b>2d</b>	80
5	Ph	Me	<b>2e</b>	66
6	C <sub>3</sub> H <sub>5</sub>	Ph	<b>2f</b>	67
7	<sup>n</sup> Bu	Me	<b>2g</b>	63
8	Ph	H	<b>2h</b>	73
9	Ph	NMe <sub>2</sub>	<b>2i</b>	61



**Figure 1.** ORTEP drawing for the cationic part of **2a** (left) and **3** (right). Selected bond lengths (Å): **2a**, Ir1–C1, 2.029(5); C1–C2, 1.368(7); O1–Ir1, 2.136(3). **3**, Ir1–C1, 2.056(7); C1–C2, 1.349(9); S1–Ir1, 2.389(2).

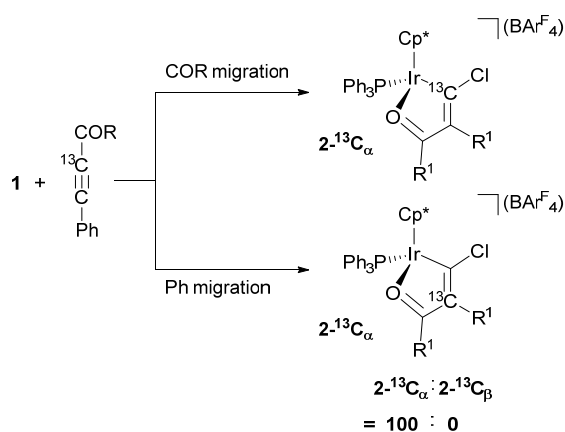
In this transformation, the vinylidene ligand, which is formed from the alkyne at an early stage of the reaction, is considered to undergo the 1,1-insertion into the Ir–Cl bond (Scheme 1, Path 1) or the nucleophilic addition of a chloride anion from the outer-coordination sphere at the vinylidene  $\alpha$  carbon (Path 2).

**Scheme 1.** Mechanism for the formation of **2**



To gain deeper insight into the reaction mechanism, the  $^{13}\text{C}$ -enriched alkyne,  $\text{Ph-C}\equiv^{13}\text{C-COR}$  ( $\text{R} = \text{OEt}$ ,  $p\text{-Tol}$ ) was used as substrates. (Scheme 2). Detailed  $^{13}\text{C}\{^1\text{H}\}$  NMR analysis of the reaction product disclosed that the migration ratio of the COR and Ph groups is essentially 100:0. This result is in full accordance with both experimental and theoretical results that the electron-withdrawing group has higher migrating aptitude in vinylidene rearrangement at a group 8 metal center.<sup>3</sup>

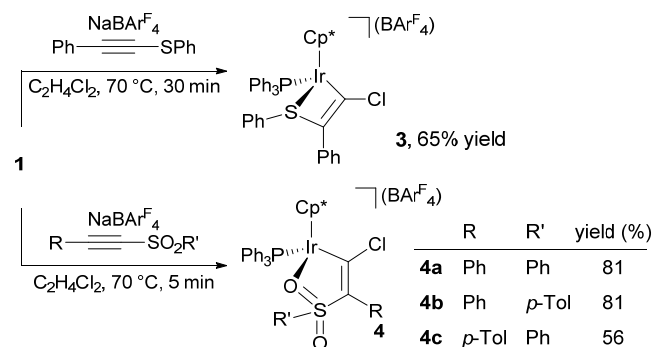
**Scheme 2.** Results of the  $^{13}\text{C}$ -labeling experiments



The author next turned his attention to reactions of thio-

and sulfonylalkynes, because vinylidene rearrangement of heteroatom-substituted internal alkynes remain relatively undeveloped except for that of silylalkynes. When  $\text{Ph-C}\equiv\text{C-SPh}$  or  $\text{R-C}\equiv\text{C-SO}_2\text{R}'$  is allowed to react with **1** in the presence of  $\text{NaBAR}_4^{\text{F}}$ , the corresponding iridacycles **3** and **4** were obtained via vinylidene rearrangement (Scheme 2). The four-membered iridathiacyclobutene in **3** (Figure 1) is a relatively rare structure and found to be almost planar with the sum of the interior bond angles of  $359.6^\circ$ . It should be pointed out that formation of complexes **4** is the first example of vinylidene rearrangement of sulfonylalkynes. It is currently assumed that the thio and sulfonyl groups have migrated in this rearrangement due to the smaller C–S bond energies than those of C–Ar.

**Scheme 3.** Reactions of **1** with S-substituted internal alkynes



### 3. Conclusion

Various internal acyl-, thio-, and sulfonylalkynes have shown to undergo vinylidene rearrangement in an iridium complex. These reactions provide interesting examples of C–C and C–S bond activation with iridium.

### 4. Reference

- 1) C. Bruneau, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2006**, *45*, 2176.
- 2) Ishii, Y. *et al J. Am. Chem. Soc.* **2008**, *130*, 16856.
- 3) Ishii, Y. *et al J. Am. Chem. Soc.* **2012**, *134*, 17746.

### 5. Announcement List

- 1) 97th CSJ Annual Meeting 3G2-30 (2017).
- 2) Kuwabara, T.; Takamori, S.; Ishii, Y. *et al. Synlett* **2018**, in press.