<div align="center">

ピリジルフェニル配位子をもつ 9 族金属錯体上での
アルキンの酸素酸化および関連反応

Oxygenation and Related Reactions of Alkynes at Group 9 Metal Complexes with a Pyridylphenyl Ligand

</div>

応用化学専攻　難波　孝行

NAMBA Takayuki

1. Introduction

Transition-metal-mediated transformation of alkynes provides a useful synthetic tool in organic chemistry. Especially, the metal-catalyzed oxygenation of alkynes to the corresponding diketones have drawn notable attention. For instance, Lo has reported the catalytic transformation of alkynes to the 1,2-diketone derivatives via a coordinatively unsaturated Ru(II) alkynylvinyl complex.[1] However, the reactivity of such 16-electron alkynylvinyl complexes still remains to be investigated.

In the course of our investigation into the vinylidene rearrangement of internal alkynes at a cationic Ir(III) pyridylphenyl complex [Cp*Ir(ppy-F_4)]$^+$ (ppy-F_4 = 2,3,4,5-tetrafluoro-6-pyridylphenyl), we have observed a competition between vinylidene rearrangement and 1,2-insertion of the alkynes.[2] Importantly, it was revealed that the fluorine substituents on the ppy ligand strongly favor the vinylidene formation. On the contrary, when 1,4-diferrocenyl-1,3-butadiyne was used as a substrate, selective 1,2-insertion proceeded to give the alkynylvinyl complex. In this study, the author investigated the reactivity of such alkynylvinyl complexes toward various oxidants. Effects of the metal center (Ir, Rh) and the fluorine substituents on the oxidation were studied.

2. Experimental Section

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

3. Results and Discussion

Oxygenation of 2-F_n

When complexes 1-F_n (n = 2, 4) were allowed to react with FcC≡C–C≡CFc in the presence of NaBAr$^F_4$ (Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$) at r.t. for 1 h, the alkynylvinyl complexes 2-F_n were obtained as dark red crystals in good yields via 1,2-insertion (Scheme 1). In contrast, non-fluorinated complexes $2a$-F_0 and $2b$-F_0 could not be isolated due to their instability. Further treatment of a CH$_2$Cl$_2$ solution of $2a$-F_n with O$_2$ gas at r.t. for 1 h resulted in the formation of the corresponding 1,2-diketone complexes $3a$-F_n, which were isolated in moderate yields after purification by column chromatography and recrystallization. As shown in the table, the reaction of the iridium complexes $2a$ completed within 1 h, and $2a$-F_0 generated *in situ* was also able to be converted into $3a$-F_0. In contrast, the rhodium complexes $2b$ are much less reactive toward O$_2$ and required longer reaction time. $3b$-F_0 could not be obtained even by the direct oxygenation of $2b$-F_0 generated in solution.

Scheme 1
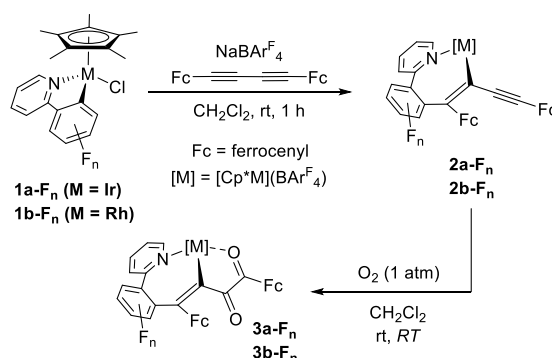
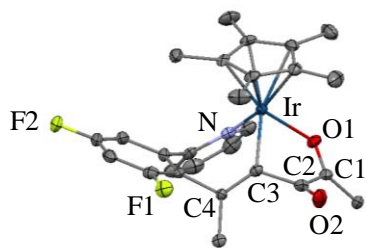| M	n	2-F_n (% yield)	3-F_n (% yield)	*RT* (h)
Ir	0	Not isolated	56	1
	2	77	41	1
	4	68	62	1
Rh	0	Not isolated	Not detected	24
	2	80	48	9
	4	77	34	30

Figure 1. ORTEP drawing for the cationic parts of **3a-F₂**. The ferrocenyl substituents are omitted. Selected bond lengths (Å): C1–O1, 1.259(5); C2–O2, 1.219(5).

The molecular structure of **3a-F₂** is shown in Figure 1. The C1−O1 and C2−O2 bond lengths are 1.259(5), 1.219(5) Å respectively, which suggest the C1–O1 bond is elongated on coordination to the Ir center.

Interestingly, the Ir complex **2a-F₂** was so reactive that it underwent oxygenation even in the solid state (Scheme 2). The yield was improved to 76%, probably because side-reactions were suppressed in the crystal state. In contrast, Rh complex **2b-F₂** failed to react with O₂ without a solvent.

Scheme 2
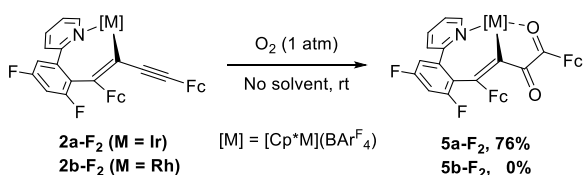
Reactions of 2a-F₂ with other oxidants

To gain insight into the oxidation of **2a-F₂**, other oxidants were examined (Scheme 3). **2a-F₂** was successfully oxidized by N₂O, although longer reaction time of 24 h was required to complete the reaction. On the other hand, mCPBA and S₈ failed to serve as the O/S source to transform **2a-F₂** into the desired diketone/ dithioketone complexes.
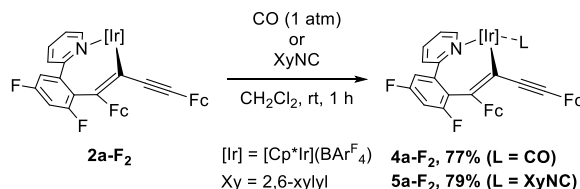
Scheme 3
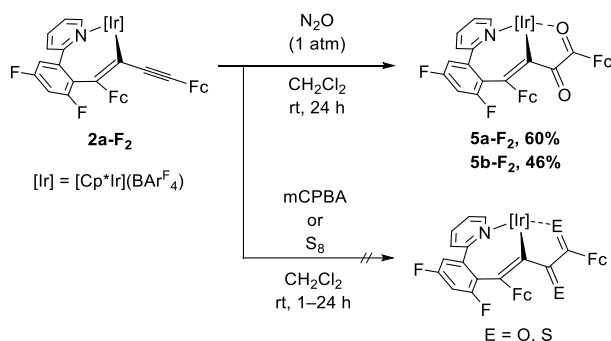
Unsaturated nature of 2a-F₂

The oxygenation of **2-Fₙ** is considered to start with coordination of O₂ at the potentially unsaturated metal center of **2-Fₙ**. Unfortunately, the O₂ complexes could

not be detected by NMR measurements, while CO and 2,6-xylylisocyanide adducts, **4a-F₂** and **5a-F₂**, respectively, were successfully synthesized (Scheme 4). The molecular structure of **5a-F₂** was determined unambiguously by an X-ray diffraction study revealing its three-legged piano stool structure. As expected, **4a-F₂** and **5a-F₂** are not reactive toward O₂.

Scheme 4

C–H activation reaction of 4a-F₂

Finally, reactivities of **4a-F₂** were investigated (Scheme 5). When **4a-F₂** was heated at 70 °C in C₂H₄Cl₂, complex **6a-F₂** was obtained as black crystals in 46% yield. The ^{1}H NMR spectrum of **6a-F₂** shows a singlet signal at δ 6.29 assignable to the vinyl proton. Although the mechanism for the formation of **6a-F₂** is still unclear, the vinyl proton is presumed to be supplied from one of the Cp groups, and a mechanism involving the ferrocenyl C–H activation promoted by a pyridine base located nearby (CMD mechanism) is postulated.

Scheme 5
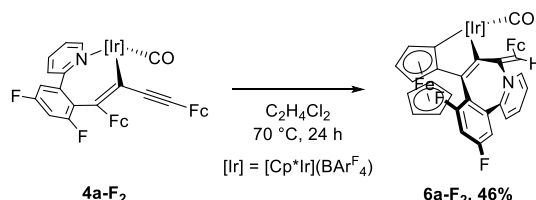
4. Conclusion

A series of complexes **2-Fₙ** were synthesized via 1,2-insertion of internal diynes, which were further oxygenated to give **3-Fₙ**. The oxidation of Rh complex was slower than that of the Ir systems. Interestingly, the O₂ oxidation of **2a-F₂** took place even in the solid state. A unique C–H activation reaction of **4a-F₂** was also developed.

5. References

1) Lo, Y-H. *et al*. *Dalton Trans*. **2011**, *40*, 12663–12666.
2) Ishii, Y. *et al*. *Dalton Trans*. **2015**, *44*, 17448–17452.

6. Presentations

1) 99th CSJ Annual Meeting 2D1-16 (**2018**).
2) 69th Conf. Jpn. Soc. Coord. Chem. 3PD-014 (**2019**).