

8, 9 族錯体上における金属中心の遠隔転位

Remote Rearrangement of the Metal Center in Group 8 and 9 Metal Complexes

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1. Introduction

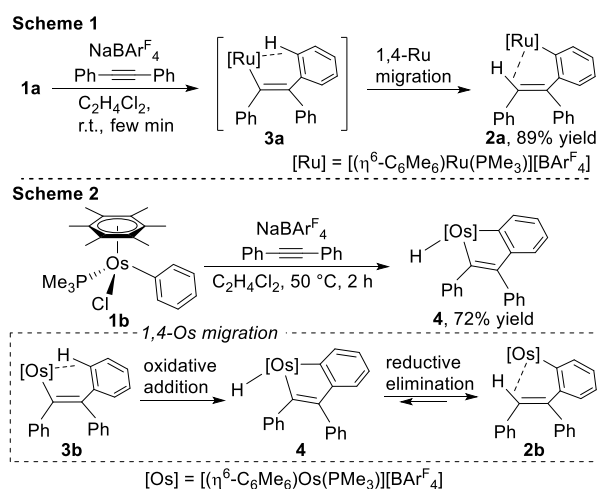
Intramolecular remote metal migration (mostly 1,4-migration), in which the metal center in an alkyl, vinyl, or aryl complex exchanges its position with a remote CH hydrogen, has recently emerged as a potential C–H activation method.¹⁾ Prior to our study,²⁾ only d^8 and d^9 metal complexes of group 9 and 10 elements have been known to serve as an effective reaction site. We have recently demonstrated that the vinyl complexes, which are formed from the reactions of $[\text{Cp}^*\text{M}(\text{Ph})(\text{PMe}_3)]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) with $\text{PhC}\equiv\text{CPh}$, are transformed to the *o*-(vinyl)aryl complexes by the intramolecular 1,4-metal migration, which clearly indicates that metal centers with a d^6 electron configuration can promote the remote metal migration.^{2a,c)} On the other hand, Gunnoe recently reported that treatment of $[\text{Cp}^*\text{FePh}(\text{CO})(\text{NCMe})]$ with $\text{MeC}\equiv\text{CMe}$ led to the formation of $[\text{Cp}^*\text{Fe}(\eta^5\text{-1-hydroxy-2,3-dimethylindenyl})]$, where the 1,4-migration of the Fe(II) center was suggested to be involved, although no experimental evidence has been obtained.³⁾ To broaden the scope of the remote metal migration, this study was aimed at developing 1,4-metal migration in $[(\eta^6\text{-arene})\text{M}(\text{Ph})(\text{PMe}_3)]^+$ type group 8 metal complexes.

2. Results and Discussion

Reaction of $\eta^6\text{-C}_6\text{Me}_6$ complexes with $\text{PhC}\equiv\text{CPh}$ ⁴⁾

When $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{Ph})(\text{PMe}_3)]$ (**1a**) was allowed to react with $\text{PhC}\equiv\text{CPh}$ in the presence of $\text{NaBAR}^{\text{F}_4}$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) at room temperature for a few minutes, *o*-(vinyl)aryl complex **2a** was obtained as the sole product (Scheme 1). In the ¹H NMR spectrum, the vinyl proton of **2a** appeared as a doublet at $\delta -4.47$ (d, $^2J_{\text{PH}} = 13.7$ Hz),

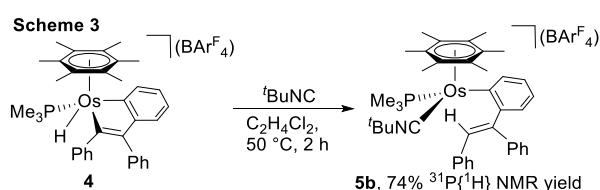
indicating the presence of an agostic interaction. The molecular structure of **2a** determined by a single-crystal X-ray diffraction study confirmed that **2a** was formed by the 1,4-Ru migration from the vinylruthenium intermediate **3a** which was generated by the insertion of $\text{PhC}\equiv\text{CPh}$ into the Ru–Ph bond in **1a**. Thus, the present reaction provides the first experimental evidence of remote rearrangement of a group 8 metal center. A preliminary DFT study suggests that the present 1,4-Ru(II) migration proceeds via the σ -complex assisted metathesis process (σ -CAM).



By contrast, the reaction of **1b** with $\text{NaBAR}^{\text{F}_4}$ and $\text{PhC}\equiv\text{CPh}$ at 50 °C for 2 h afforded the cyclometallated hydrido complex **4** (Scheme 2). The ¹H NMR spectrum of **4** showed a doublet at $\delta -12.3$ (d, $^2J_{\text{PH}} = 47.3$ Hz) diagnostic of a hydrido complex, and its molecular structure was further established by an X-ray diffraction study. **4** is considered to be generated by the alkyne insertion into the Os–Ph bond in **1b** to form the vinyl complex **3b** and the subsequent oxidative addition of an *ortho* C–H bond of the Ph group. While **4** may be viewed as an intermediate in 1,4-Os migration, no further structural change of **4** was observed

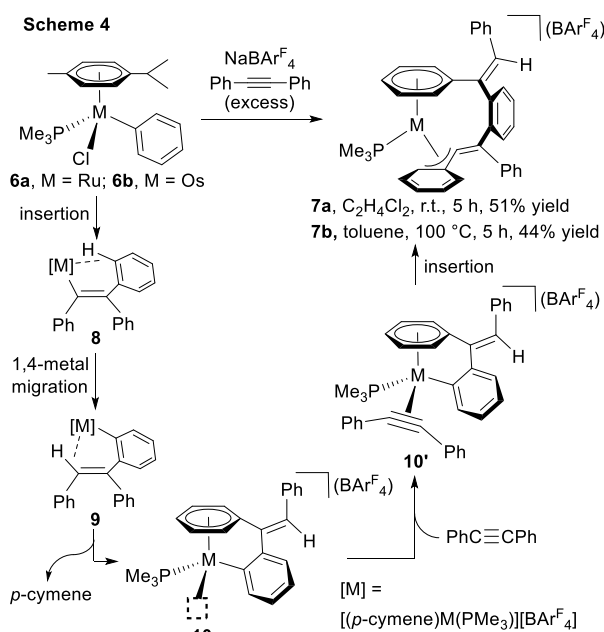
even by heating at 100 °C.

Interestingly, when **4** was reacted with ^tBuNC at 50 °C for 2 h, **5b** which corresponds to the 1,4-Os migration product was formed (Scheme 3). Complex **5b** could not be isolated in a pure form but was characterized by ¹H NMR measurement (δ 6.28 (s), vinyl CH) as well as a single-crystal X-ray diffraction study. It should be pointed out that, unlike in the 1,4-Ru migration, the oxidative addition–reductive elimination mechanism is operative in the 1,4-Os migration.



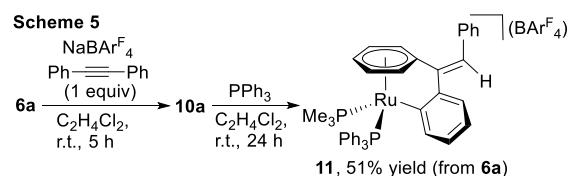
Reaction of η^6 -*p*-cymene complexes with $\text{PhC}\equiv\text{CPh}$

To examine the effects of the η^6 -arene ligand, a similar reaction of the *p*-cymene complex $[(\eta^6\text{-}i\text{-p-cymene})\text{RuCl}(\text{Ph})(\text{PMe}_3)]$ (**6a**) was performed (Scheme 4). When **6a** was allowed to react with $\text{PhC}\equiv\text{CPh}$ in the presence of $\text{NaBAR}^{\text{F}_4}$ at room temperature, tether-type complex **7a** was obtained via incorporation of two $\text{PhC}\equiv\text{CPh}$ molecules concomitant with η^6 -arene ligand exchange. Similarly, Os complex **7b** was obtained from the reaction of **6b** with $\text{NaBAR}^{\text{F}_4}$ and $\text{PhC}\equiv\text{CPh}$. These reactions may be viewed as a unique model for the “merry-go-round” multiple alkylation reaction.⁵⁾



A plausible mechanism for the formation of **7a** is shown in Scheme 4. Initially, the *o*-(vinyl)aryl complex **9a** is formed by way of the insertion of one alkyne molecule into the Ru–Ph bond to generate the vinyl intermediate **8a** followed by the 1,4-Ru migration. The subsequent dissociation of the *p*-cymene ligand and the η^6 -coordination of a Ph group give rise to a coordinatively undersaturated species **10a**. Then the insertion of a second $\text{PhC}\equiv\text{CPh}$ molecule followed by the haptotropic change at the η^1 -(α -styryl) ligand to a η^3 -mode completes the formation of tether-type complex **7a**.

To confirm the above mechanism, isolation of an intermediate complex was attempted (Scheme 5). Although complexes **10a** and **10a'** were failed to be isolated, complex **11**, the stabilized form of **10a** with PPh_3 , was isolated from a reaction of in situ generated **10a** (**6a**, $\text{NaBAR}^{\text{F}_4}$, and one equivalent of $\text{PhC}\equiv\text{CPh}$) with PPh_3 and structurally characterized. This result is in full accordance with the mechanism shown in Scheme 4.



3. Conclusion

The first experimental evidence for the remote rearrangement of a group 8 metal center was provided by the reaction of **1** with $\text{PhC}\equiv\text{CPh}$. In addition, the tether-type complex **7** was formed from the reaction of **6** with $\text{PhC}\equiv\text{CPh}$ through the second alkyne insertion accompanied by dissociation of the *p*-cymene ligand.

4. References

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