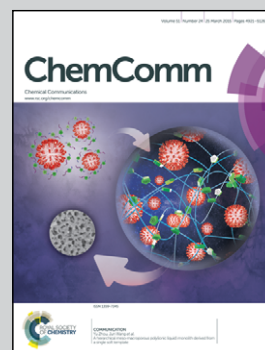


Showcasing work from the laboratory of Prof. Youichi Ishii at the Department of Applied Chemistry, Chuo University, Japan

Remote rearrangement of the metal center in a ($\eta^6\text{-C}_6\text{Me}_6$)Ru(II) complex

Ruthenium jumps! Reaction of a phenylruthenium complex with internal alkynes gives rise to the 1,4-Ru migration to form the *o*-vinylaryl complex, providing the first example of remote migration of a group 8 metal center.

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Reaction of $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{Ph})(\text{PMe}_3)]$ with internal alkynes in the presence of $\text{NaBAR}^{\text{F}}_4$ gave rise to the 1,4-Ru migration to form the *o*-vinylaryl complex, providing the first example of 1,4-metal migration of a group 8 metal center; in one case further isomerization to an η^3 -allyl complex was observed.

C–H bond activation by intramolecular 1,4-metal migration has recently attracted considerable attention as the key step in the transition metal catalyzed synthetic reactions.¹ In this process, a transition metal center is at first introduced into the carbon atom four bonds away from the ‘target’ C–H group by a standard organometallic method, and then exchanges its position with the hydrogen atom to complete the C–H activation. This chemistry was established by Miura, Larock, and others using $\text{Rh}(\text{I})^2$ and $\text{Pd}(\text{II})^3$ complexes, and since then 1,4-migration reactions of these metals have been investigated actively from synthetic as well as mechanistic points of view. Although 1,4-migration of other metals such as cobalt,⁴ iridium,⁵ nickel⁶ and platinum^{3f} was also reported, only group 9 and 10 metal centers with a d^8 electron configuration have served as the effective reaction sites throughout these studies, which limits generality of the 1,4-metal migration.

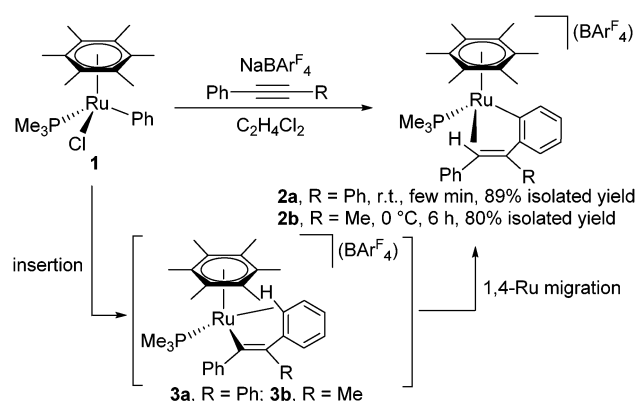
In the course of our investigation into the activation of internal alkynes by using group 9 d^6 metal complexes, we have recently disclosed that the $\text{Rh}(\text{III})$ center in $[\text{Cp}^*\text{Rh}(\text{CR}^1=\text{CR}^2\text{Ph})(\text{PR}_3)][\text{BAR}^{\text{F}}_4]$ ($\text{R} = \text{Ph}, \text{Me}$; $\text{R}^1, \text{R}^2 = \text{alkyl, aryl}$; $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$), which is formed from the reactions of $[\text{Cp}^*\text{RhCl}(\text{Ph})(\text{PR}_3)]$ with $\text{R}^1\text{C}\equiv\text{CR}^2$ in the presence of $\text{NaBAR}^{\text{F}}_4$, takes part in the vinyl-to-aryl 1,4-migration to form the *o*-(vinyl)aryl complexes $[\text{Cp}^*\text{Rh}\{o\text{-C}_6\text{H}_4\text{CR}^2=\text{CHR}^1\}(\text{PR}_3)][\text{BAR}^{\text{F}}_4]$ under very mild conditions.^{7a,b,8} Furthermore, similar reactions of the iridium analog complex $[\text{Cp}^*\text{IrCl}(\text{Ph})(\text{PMe}_3)]$ with

Remote rearrangement of the metal center in a $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{II})$ complex†

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internal alkynes result in not only 1,4- but also direct 1,3-Ir(III) migration, providing the first experimental evidence for the direct 1,3-metal migration accompanied by the C–H bond activation.^{7c,9} To broaden the scope of the 1,4-metal migration, we have now aimed to expand the reaction site to group 8 metal complexes. Herein we describe the first example of the 1,4-migration of a Ru(II) center.

When $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{Ph})(\text{PMe}_3)]$ (**1**), which was prepared by the reaction of $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2(\text{PMe}_3)]$ with PhMgCl , was allowed to react with $\text{PhC}\equiv\text{CPh}$ in the presence of $\text{NaBAR}^{\text{F}}_4$ in $\text{C}_2\text{H}_4\text{Cl}_2$ at room temperature for a few min, the color of the reaction mixture turned red from orange, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a new singlet at $\delta -0.58$. After recrystallization, the *o*-(vinyl)arylruthenium complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{o\text{-C}_6\text{H}_4\text{C}(\text{Ph})=\text{CHPh}\}(\text{PMe}_3)][\text{BAR}^{\text{F}}_4]$ (**2a**) with a Ru–(vinyl CH) agostic interaction was obtained in 89% yield as the sole product (Scheme 1). In the ^1H NMR spectrum, the vinyl proton of **2a** appears as a doublet at $\delta -4.47$ (d, $^2J_{\text{PH}} = 13.7$ Hz), confirming the presence of an effective agostic interaction. In fact, this vinyl signal exhibits considerably large high-field shift compared with those of closely related $\text{Rh}(\text{III})$ and $\text{Ir}(\text{III})$ complexes such as $[\text{Cp}^*\text{M}\{o\text{-C}_6\text{H}_4\text{C}(\text{Ph})=\text{CHPh}\}(\text{PMe}_3)][\text{BAR}^{\text{F}}_4]$ ($\text{M} = \text{Rh}$, δ 0.38; $\text{M} = \text{Ir}$, $\delta -0.30$).⁷



Scheme 1 Reaction of **1** with $\text{PhC}\equiv\text{CR}$ and $\text{NaBAR}^{\text{F}}_4$.

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† Electronic supplementary information (ESI) available: Text, figures and CIF files giving experimental procedures and crystallographic data. CCDC 1036838 and 1036845. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc09699a



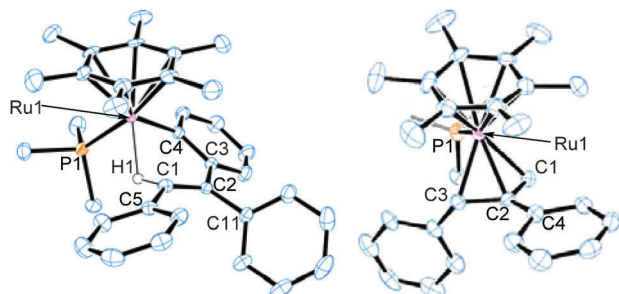
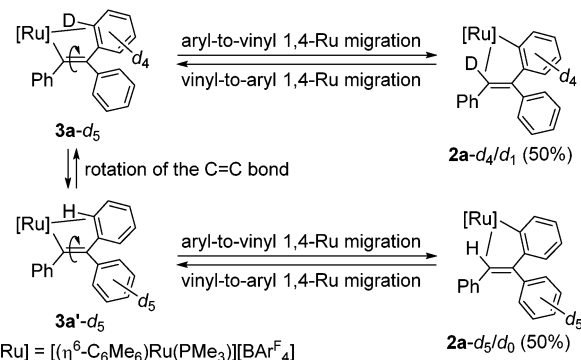


Fig. 1 ORTEP drawings of **2a** (left) and **4** (right). The anionic part and hydrogen atoms except for H1 of **2a** are omitted for clarity. Selected bond lengths (Å): **2a**, Ru1–P1, 2.3190(10); Ru1–C1, 2.426(4); Ru1–C4, 2.065(4); Ru1–H1, 1.87(4); C1–C2, 1.354(5). **4**, Ru1–P1, 2.3517(16); Ru1–C1, 2.201(5); Ru1–C2, 2.165(5); Ru1–C3, 2.168(5); C1–C2, 1.452(6); C2–C3, 1.459(7).

The molecular structure of **2a** has been determined unambiguously by a single-crystal X-ray diffraction study (Fig. 1, left). Complex **2a** displays a three-legged piano-stool structure with the $\eta^6\text{-C}_6\text{Me}_6$, PMe_3 , and *o*-(vinyl)aryl ligands as well as the agostic vinyl C–H group. The Ru1–C1 distance is obviously longer than regular ruthenium–carbon σ -bond lengths but comparable with common agostic Ru–CH distances.¹⁰ This structure clearly indicates that **2a** was formed by the vinyl-to-aryl 1,4-Ru migration from the vinyl-ruthenium intermediate $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{C}(\text{Ph})=\text{CPh}_2\}(\text{PMe}_3)][\text{BAR}^{\text{F}}_4]$ (**3a**) with a Ru–(*o*-CH of Ph) agostic interaction, which was too reactive to be characterized.¹¹ Considering the isoelectronic nature of $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{II})$ and $\text{Cp}^*\text{Rh}(\text{III})$ fragments, the present 1,4-Ru(II) migration is presumed to proceed *via* the σ -complex assisted metathesis process (σ -CAM).^{7,12,13}

Similarly, the reaction of **1** with $\text{PhC}\equiv\text{CMe}$ at 0 °C afforded $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{o-C}_6\text{H}_4\text{C}(\text{Me})=\text{CHPh}\}(\text{PMe}_3)][\text{BAR}^{\text{F}}_4]$ (**2b**) in 80% isolated yield,¹⁴ and its structure was also confirmed by a preliminary X-ray diffraction study. **2b** exhibits a singlet at $\delta -0.26$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR and a high-field shifted vinyl signal at $\delta -4.24$ (d, $^2J_{\text{PH}} = 10.3$ Hz) in the ^1H NMR, the latter of which is diagnostic of an agostic interaction.¹⁵

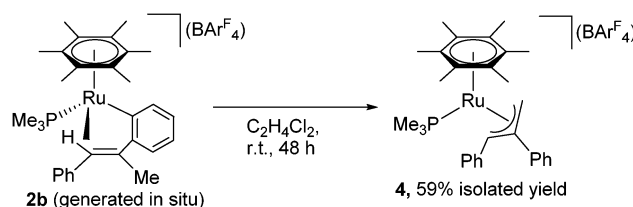
It would be interesting to note that a deuterium labeling experiment using $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{C}_6\text{D}_5)(\text{PMe}_3)]$ (**1-d₅**) and $\text{PhC}\equiv\text{CPh}$ failed to give the product fully deuterated at the vinyl CH group; instead we observed the vinyl CH signal with 0.5 H intensity in the ^1H NMR, suggesting the formation of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{o-C}_6\text{D}_4(\text{Ph})=\text{CDPh}\}(\text{PMe}_3)][\text{BAR}^{\text{F}}_4]$ (**2a-d₄/d₁**) and $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{o-C}_6\text{H}_4(\text{C}_6\text{D}_5)=\text{CHPh}\}(\text{PMe}_3)][\text{BAR}^{\text{F}}_4]$ (**2a-d₅/d₀**) in a 1 : 1 ratio (see ESI[†]). This result clearly demonstrates that **3a-d₅** is rapidly interconverting between **3a-d₅** and **3a'-d₅** by the C=C bond rotation,¹⁶ and the subsequent 1,4-Ru migration can proceed from both structures to give **2a-d₄/d₁** and **2a-d₅/d₀** (Scheme 2). In addition, according to our previous study, vinyl-to-aryl 1,4-metal migration is a reversible process, and it is reasonable to consider that **2a-d₄/d₁** and **2a-d₅/d₀** are in equilibrium at room temperature.^{7b,c,17} It should also be mentioned that the C=C bond rotation of **3a** is even more facile than that of the rhodium system; only transfer of a D atom to the vinyl position was observed in the reaction of $[\text{Cp}^*\text{Rh}(\text{C}_6\text{D}_5)(\text{PPh}_3)]^+$ with $\text{PhC}\equiv\text{CPh}$.^{7a}



Scheme 2 Interconversion between **2a-d₄/d₁** and **2a-d₅/d₀**.

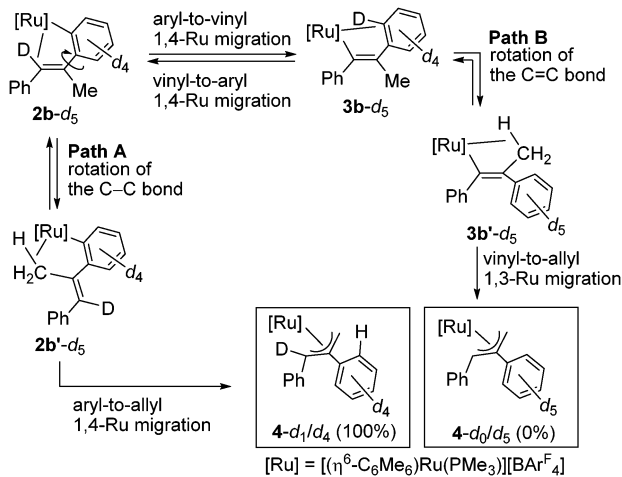
Although a considerable number of C–H activation reactions utilizing the 1,4-metal migration have been described in the literature,¹ they are exclusively performed at group 9 and 10 complexes. Very recently, Gunnoe reported that the reaction of $[\text{Cp}^*\text{FePh}(\text{CO})(\text{NCMe})]$ with $\text{MeC}\equiv\text{CMe}$ ends in the formation of $[\text{Cp}^*\text{Fe}(\eta^5\text{-1-hydroxy-2,3-dimethylindenyl})]$, where a novel coupling reaction of the Ph, CO and $\text{MeC}\equiv\text{CMe}$ ligands leads to an indenyl skeleton. For this transformation, 1,4-migration of the iron(II) center was suggested to be involved,¹⁸ while no experimental evidence for 1,4-migration of group 8 metals has been reported. The present reaction provides the first example of 1,4-metal migration in a structurally well-defined group 8 metal complex and reinforces Gunnoe's proposal.

Complex **2a** is stable at 50 °C, and no further reaction was observed at this temperature. In contrast, **2b** was further isomerized slowly at room temperature (Scheme 3). When an *in situ* generated $\text{C}_2\text{H}_4\text{Cl}_2$ solution of **2b** was stirred at room temperature for 48 h, the color of the reaction mixture turned orange from red, and formation of a new complex showing a $^{31}\text{P}\{^1\text{H}\}$ NMR signal at $\delta 3.03$ was observed. Purification of this reaction mixture by column chromatography and recrystallization afforded the η^3 -allyl complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CHPh}\}(\text{PMe}_3)][\text{BAR}^{\text{F}}_4]$ (**4**) in 59% yield as pale yellow crystals. The ^1H NMR of **4** shows a set of CH signals of the η^3 -allyl ligand at $\delta 5.29$ (br, $\text{CH}_2\text{C}(\text{Ph})\text{CHPh}$), 3.61 (d, $^2J_{\text{HH}} = 3.7$ Hz, *syn*- $\text{CH}_2\text{C}(\text{Ph})\text{CHPh}$), and 1.91 (dd, $^3J_{\text{PH}} = 18.3$ Hz, $^2J_{\text{HH}} = 3.7$ Hz, *anti*- $\text{CH}_2\text{C}(\text{Ph})\text{CHPh}$), and the molecular structure of **4** has been determined unambiguously by a single-crystal X-ray diffraction study (Fig. 1, right). The bond lengths and angles of the η^3 -allyl ligand in **4** are comparable to those of known η^3 -allyl ruthenium complexes.¹⁹ It should be pointed out that the transformation of **2b** into **4** can be viewed as a formal 1,3-metal migration accompanied by CH activation.



Scheme 3 Isomerization of **2b** to **4**.





Scheme 4 Plausible mechanisms of formation of **4**.

To gain mechanistic information regarding this isomerization, we have performed deuterium labeling experiments by using **1-d₅** and examined the destination of the deuterium atoms in **4** by means of ¹H NMR. According to our previous study,^{7c} we have hypothesized two mechanisms for the isomerization of **2b** into **4** as illustrated in Scheme 4. Path A is constituted of the rotation of the C_{aryl}-C_{vinyl} bond in **2b** and the subsequent aryl-to-allyl 1,4-Ru migration, and this route would lead to **4-d₁/d₄** in which one deuterium atom is introduced into the C3 atom (see Fig. 1) of the η³-allyl ligand. On the other hand, path B includes the direct vinyl-to-allyl 1,3-Ru migration from **3b'** which is in turn generated from **2b** through the aryl-to-vinyl 1,4-Ru migration (*vide supra*) followed by the rotation of the C=C bond. In path B, **4-d₀/d₅**, which has no deuterium atom in the η³-allyl moiety, is expected to be formed. The ¹H NMR of the actual reaction product showed selective formation of **4-d₁/d₄**, indicating that only path A is operative in the present reaction system, and the 1,3-Ru migration is not included (see ESI[†]).

This result is in stark contrast to a related reaction with an iridium complex. Thus, we have recently reported the formation of a similar η³-allyliridium complex, [Cp*Ir{η³-CH₂C(Ph)CHPh}(PMe₃)][BARF₄], by the reaction of [Cp*IrCl(Ph)(PMe₃)] with PhC≡CMe and NaBARF₄, and its deuterium labeling experiment with [Cp*IrCl(C₆D₅)(PMe₃)] demonstrated that both path A and B are operative with the iridium system, where path B (direct 1,3-Ir migration) is the major reaction route (30 : 70).^{7c} It is interesting to point out that the reaction mechanism for the present formal 1,3-metal migration is strongly dependent on the metal center involved, although we must await further investigation including DFT calculations to clarify the origin of such metal dependency.

In conclusion, we have revealed that the reaction of [(η⁶-C₆Me₆)Ru(Ph)(PMe₃)]⁺ with PhC≡CR (R = Ph, Me) afforded the *o*-(vinylaryl) complex **2a,b** by way of the alkyne insertion into the Ru-Ph bond to generate **3a,b** followed by the vinyl-to-aryl 1,4-migration. Complex **2b** was further isomerized to η³-allyl complex **4**, and the deuterium labeling experiments

disclosed that this isomerization proceeds through the rotation of the C_{aryl}-C_{vinyl} bond in **2b** and the second aryl-to-allyl 1,4-Ru migration. These reactions provide the first example of 1,4-migration of a Ru(II) center. A mechanistic study involving DFT calculations and synthetic applications of this reaction are now in progress.

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