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Reactions of Ruthenium Cp Phosphine Complex with 4,4-Disubstituted-1,6-Enynes: Effect of Methyl Substituents in the Olefinic Fraction

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Abstract: We studied chemical reactions of $Cp(PPh_3)_2RuCl$ with nine 1,6-enyne compounds (**1**−**4**, **8**, **12**, **19**, **21**, and **22**) in which the triple bond is associated with propargylic alcohol and the olefinic group has various substituted methyl groups. For the enyne compounds **1**−**3** with no substituted methyl group, the reaction takes place at the propargylic alcohol first giving the allenylidene complex **6** which could undergo a skeletal rearrangement to yield the disubstituted vinylidene complex **7**. By changing the propargylic alcohol to propargylic ether, the reaction gives the carbene complex **10** as the major product and the butadiene complex **9** by a cyclization reaction as the minor product. For enyne **12** with two methyl groups at the terminal carbon of the olefinic part, formation of either of the carbene complexes **15** and **16** with a substituted cyclopentenyl ring at Cα or the vinylidene complex **17** is controlled by the use of solvent. For the formation of **15** and **16**, a C−C bond-forming cyclization reaction is proposed to occur at Cβ in an intermediate where the triple bond is π-coordinated. However, for the vinylidene intermediate, the reaction may proceed by the formation of the allenylidene, which undergoes a retro-ene reaction to bring about cleavage of the dimethyl substituted allyl group giving **17**. For two enynes **21** and **22** where each olefinic portion is internally substituted with one methyl group, two vinylidene complexes **23** and **24** each with a five-membered ring bonded at Cβ are isolated. The reaction proceeds via formation of an allenylidene intermediate followed by a cyclization at Cγ. Stabilization of the cationic charge by the presence of methyl subsituents clearly controls the reaction pathway to give different products. These chemical reactions and their mechanisms are corroborated by structure determinations of five ruthenium complexes using single crystal X-ray diffraction analysis.

Introduction

Reactions of enynes catalyzed by electrophilic late-transition metal complexes have attracted much attention because a variety of products can be obtained from fairly simple substrates under mild conditions.[1] Various metal vinylidene and allenylidene complexes have been proven to be key intermediates for many alkyne transformations.[2] These have contributed to the rational design of new catalytic reactions. As a result of the compatibility and the utilization of very diverse precursors, the metal-catalyzed cycloisomerization of enyne systems has recently expanded on synthetically versatile developments, including notably applications in the total synthesis of natural products.[3] Metal-catalyzed cycloisomerization of enynes often leads to various skeletal rearrangements because "nonclassical" cations may participate as reaction intermediates.[4] For example, transition-metal catalyzed cycloisomerization of 1,6-enynes represents an efficient strategy for a variety of five-membered and six-membered alkenes and dienes.[5] Recently, the ruthenium-catalyzed carbon−carbon forming reactions between propargylic alcohol and alkenes, which were explained reasonably by proposing a concerted ruthenium-allenylidene-ene reaction process, were reported. However, only phenyl propargylic alcohol derivatives could be employed as starting materials.[6] We have recently described the development of ruthenium-mediated isomerizations of 1,5-enynes to furnish another type of 1,5-enynes and cycloisomerizations to produce alkoxycyclohexenes in the presence of alcohol. This process was supported by the

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ruthenium-mediated skeletal rearrangement via an unusual mechanism involving a formal metathesis process of the terminal vinyl group with the C=C of the vinylidene group.[7]

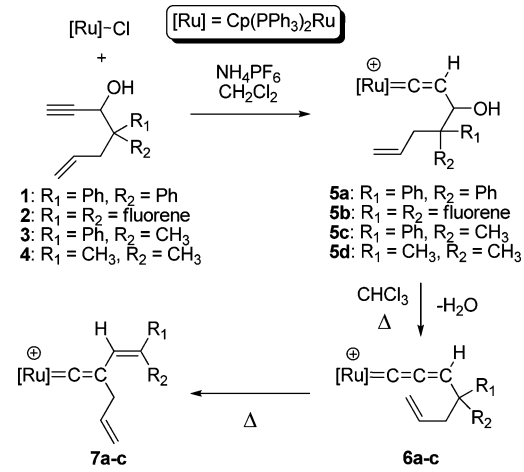
As an extension of our previous study, we have now envisaged to develop the ruthenium-mediated reactions of 1,6-propargyl enynes affording the corresponding skeletal rearrangement and cycloisomerization complexes with an excellent yield. Here, following our previous observation, the reactions are expected to occur between Cα−Cβ or Cβ−Cγ and the terminal allyl group. The present paper describes successful results of these novel reactions via rearrangement from allenylidene intermediates and π-coordinated species by controlling the methyl-substituted-olefinic group of substrates and reaction conditions.

Results and Discussion

Reactions of Enynes with No Methyl Group on the Olefinic Part. Modification of the original preparative procedure of ruthenium vinylidene complexes tethering terminal vinyl group at Cγ[7] has allowed the synthesis of a number of cationic γ-hydroxyvinylidene[8−10] ruthenium complexes from [Ru]Cl ([Ru] = Cp(PPh$_3$)$_2$Ru). For example, treatment of [Ru]Cl with 1,6-enyne **1**, a 4,4-diphenylsubstituted propargylic alcohol tethering a terminal allyl moiety also at C$_4$, in the presence of NH_4PF_6 in CH_2Cl_2 at room temperature in 6 h afforded the cationic γ-hydroxyvinylidene complex **5a** in good yield (Scheme 1). Other γ-hydroxyvinylidene ruthenium complexes **5b**−**d** were similarly prepared form **2**−**4**, respectively.

When left for 1 day in $CHCl_3$ solution at room temperature, the vinylidene complexes **5a**−**c** underwent a slow but spontaneous dehydration to give the allenylidene complexes **6a**−**c** all with the distinctive dark green color. These allenylidene

Scheme 1



complexes **6a**−**c** were obtained with moderate yields and could be characterized by ^{31}P and ^{1}H NMR spectroscopy. Typical ^{1}H resonance of Cγ−H of the allenylidene ligand is more downfield than that of Cβ−H of the corresponding vinylidene precursor. For example, the ^{1}H NMR spectrum of **5a** consist of two doublet resonances at δ 4.45 and δ 5.44 with $^{3}J_{HH}$ = 8.15 Hz assigned to Cβ−H and Cγ−H respectively, and two doublet resonances at δ 42.42 and δ 44.35 with $^{2}J_{PP}$ = 26.13 Hz in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum of **6a** displays a singlet resonance at δ 9.08 assigned to Cγ−H and a singlet signal appears at δ 45.69 in the ^{31}P NMR spectrum.

The dehydration reactions of **5** at room temperature are slow. These reactions are speeded up when heated. However, the conditions to induce dehydration of **5** stimulate a new interesting skeletal rearrangement between the allenylidene ligand and the pending allylic group, see Scheme 1. The rearrangement takes place when a solution of **6a** in chloroform was heated at 60 °C for 3 h, leading to the disubstituted vinylidene complex **7a** as the only product. Heating complex **5a** in $CHCl_3$ at 60 °C for 6 h also generated **6a** and subsequently led to the allyl migration product **7a** in good yield (Scheme 1). Complexes **5b** and **5c** also show the same reactivity to yield the corresponding products **7b** and **7c**.

Transformation of **5a** to **7a** is a result of migration of terminal allylic group to the allenylidene Cβ which could proceed via either a direct 1,3-allyl shift[11] or Cope rearrangement.[12] To ascertain the mechanism, a deuterium labeling experiment was explored (Scheme 2). Treatment of **1**-d_2 with [Ru]Cl afforded complex **5a**-d_2. Interestingly, the mixture of **7a′**-d_2 and **7a″**-d_2 were obtained with a ratio of 2:1 from 99% deuterated **5a**-d_2 at 60 °C in $CHCl_3$ (Figure 1). Obviously, a direct 1,3-allyl shift from Cδ to Cβ gave complex **7a′**-d_2. The Cope rearrangement which involves the interaction between the terminal carbon of

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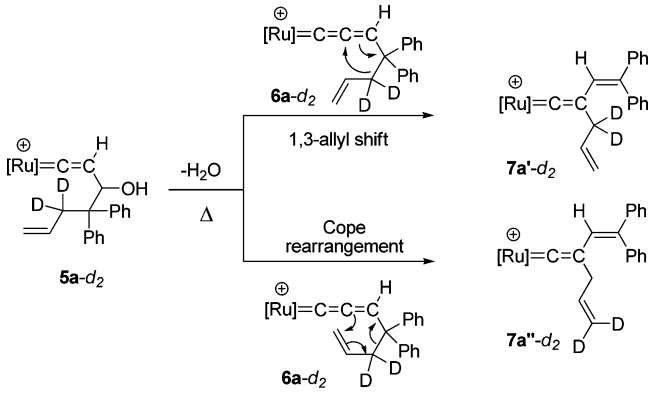
Scheme 2



the allylic double bond and Cβ forming a transition state with a six-membered ring yields the product **7a″**-d_2. At 40 °C, the reaction gave a mixture of **7a′**-d_2 and **7a″**-d_2 in a ratio of 40:9. The 1,3-allyl shift plays the major role for this transformation. However, as the temperature decreases, the product from the Cope rearrangement decreases.

The bulkier the R_1 and R_2 group, particularly in **6a** and **6b**, the easier the approach of the terminal double bond of the allylic group to Cβ and the reaction would occur more readily. The conjugation in the vinyl−vinylidene ligand may be the driving force for the formation of **7a** and **7b**. Thus, for 1,6-enyne **3**, with one phenyl group replaced by a methyl group, transformation of **5c** with a less bulky vinylidene ligand to **6c** required heating to 60 °C with much longer reaction time (12 h). Subsequently, the allyl migration product **7c** with a cis:trans ratio = 1:10 was obtained.

Structures of air stable complexes **7a**−**c** and the ratio of isomers of **7c** have been determined by NMR and NOESY spectroscopy. The solid state structure of **7a** was further determined by a single crystal X-ray diffraction analysis. Single crystals of complex **7a** were obtained from acetone/diethyl ether at 5 °C. An ORTEP type view of the cationic complex **7a** is shown in Figure 2, with selected bond distances and angles. The complex possesses distorted three-legged piano-stool coordination geometry around the ruthenium center which bound to the Cp group and two PPh_3 ligands and the disubstituted vinylidene group. The bond length of Ru(1)−C(1) in **7a** of 1.860(3) Å and the C(1)−C(2) bond length of 1.310(4) Å show a typical Ru═C═C bonding skeletal. The Ru(1)−C(1)−C(2) bond angle of 173.9(2)° also shows almost linear geometry. The bond distances of C(2)−C(3), C(3)−C(4) and C(4)−C(5) are 1.521(4), 1.497(8) and 1.305(11), respectively, confirming that the allylic group is tethering at Cβ of the vinylidene ligand.

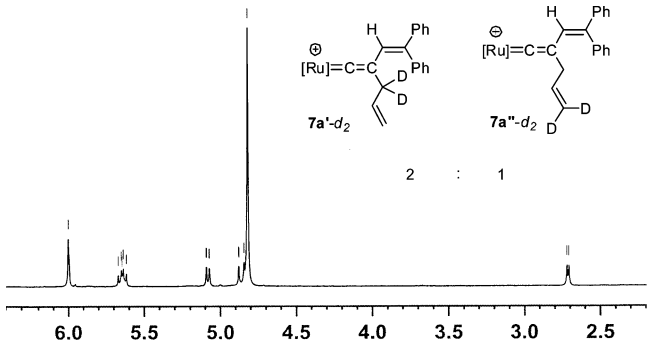


Figure 1. Part of the ^{1}H NMR spectrum of the mixture containing **7a′**-d_2 and **7a″**-d_2 obtained from 99% deuterated **5a**-d_2 at 60 °C.

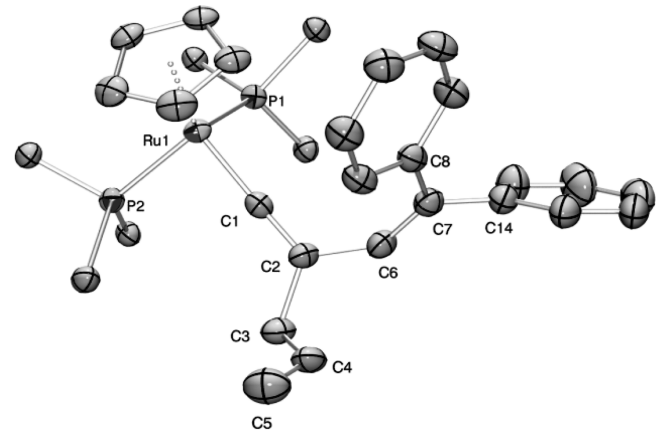


Figure 2. ORTEP drawing of the cationic complex **7a**. For clarity, aryl groups of the triphenylphosphine ligands on Ru except the ipso carbons and PF_6^- are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)−C(1), 1.860(3); C(1)−C(2), 1.310(4); C(2)−C(3), 1.521(4); C(3)−C(4), 1.497(8); C(4)−C(5), 1.305(11); C(2)−C(6), 1.479(4); C(6)−C(7), 1.344(4); Ru(1)−C(1)−C(2), 173.9(2);C(1)−C(2)−C(3),122.1(3);C(1)−C(2)−C(6),120.0(3);C(2)−C(6)−C(7), 131.2(3); C(6)−C(7)−C(8), 125.5(3); C(6)−C(7)−C(14), 117.5(3); C(3)−C(4)−C(5), 123.2(12).

No rearrangement was observed for complex **5d** with two methyl groups at Cδ even under forced reaction condition at 60 °C for 48 h. Under NMR monitoring, 50% of complex **5d** would undergo dehydration reaction to yield the allenylidene complex **6d** after thermal treatment for 1 h at 60 °C. However, Cγ of the allenylidene complex **6d** was easily reacted with trace of water molecule possibly because of the steric effect and slowly went back to **5d** at room temperature. Therefore, no skeletal rearrangement product was observed. Although transition metal promoted sigmatropic rearrangement[3,13] and Claisen-rearrangement of enynes[14] are reported in the literature, the [1,3]-sigmatropic *C*- to *C*-rearrangement are still rare, and the allenylidene-ene reaction we described here is the first example of an intramolecular C−C bond formation in a metal complex via the rearrangement. It is known that most of cationic vinylidene complexes react with alcohol to give alkoxycarbene complexes.[15] However, the vinylidene complexes **7a**−**c** containing two PPh_3 ligands are inert to various alcohols even under refluxing condition perhaps due to the electron-rich character and the bulkier fragment of the disubstituted vinylidene ligand.

Interestingly, when 1,6-enyne **8**, with a propargylallylether group, was reacted with [Ru]Cl in the presence of NH_4PF_6 in CH_2Cl_2, typical reaction to form vinylidene complex did not

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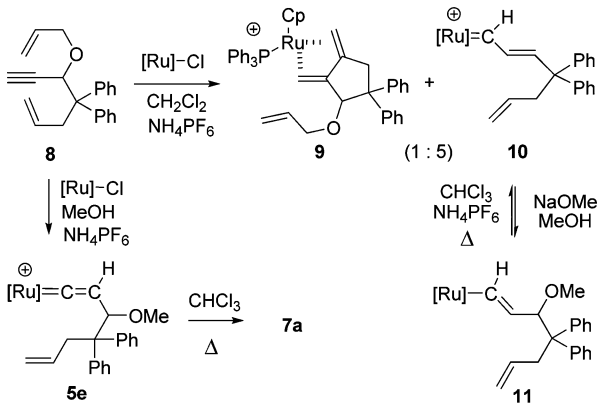
Scheme 3



occur; instead, the η^4-butadiene complex **9** and the carbene complex **10** (Scheme 3) were obtained in a ratio of 1:5. To separate two products, the mixture containing **9** and **10** was treated with excess NaOMe in methanol. Addition of a methoxy group to Cγ of the carbene ligand of **10** generated the vinyl complex **11**. Then this mixture was passed through a neutral Al_2O_3 column eluted with ether/CH_2Cl_2. Collecting the first and the second bands separately resulted in the yellow vinyl product **11** and the light-yellow butadiene product **9**. The reaction through path A was inhibited by performing the reaction in the presence of additional PPh_3 and produced **10** as the only product. Demethoxylation of complex **11** could proceed spontaneously in the presence of NH_4PF_6 salt at 60 °C and reversed back to complex **10**. However, when the reaction of **8** with [Ru]Cl was carried out in methanol, the expected vinylidene complex tethering an allyloxy group at Cγ was not observed; instead, the reaction produced the methoxyvinylidene complex **5e** as the only product with no **9** or **10** detected. Formation of **5e** proceeds via an allenylidene intermediate by elimination of allyl alcohol followed by addition of methanol. Then under thermal condition in $CHCl_3$, methanol elimination of **5e** giving **6a** was followed by the rearrangement mentioned above to yield **7a**.

The structures of **9**, **10**, and **11** were determined by NMR spectroscopy and both complexes **9** and **11** were characterized by single crystal X-ray diffraction analysis. Complex **9** shows several unusual resonances in its ^{1}H NMR spectrum.[16] Two doublet resonances at δ 0.16 and 0.05 coupled with the phosphine ligand with $^3J_{PH} = 17.03$ and 18.50 Hz, respectively, are assigned to two separate terminal methylene protons of the butadiene ligand. Resonances of other two hydrogen atoms of the same terminal methylene groups appear as two singlet peaks at δ 4.10 and 3.94. The two terminal carbons of the butadiene ligand show two doublet resonances at δ 43.41 and 42.24 both with $^2J_{CP} = 4.65$ Hz in its ^{13}C NMR spectrum. In the ^{1}H NMR spectrum of **10**, a characteristic doublet of triplet resonance at

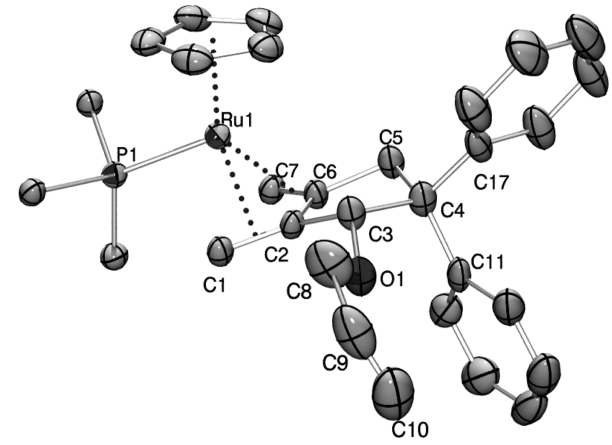


Figure 3. ORTEP drawing of the cationic ruthenium complex **9**. For clarity, aryl groups of the triphenylphosphine ligands on Ru except the ipso carbons and PF_6^- are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)−C(1), 2.210(4); Ru(1)−C(2), 2.196(4); Ru(1)−C(6), 2.193(4); Ru(1)−C(7), 2.207(4); C(1)−C(2), 1.408(5); C(2)−C(6), 1.416(5); C(6)−C(7), 1.395(5); C(1)−C(2)−C(6), 121.7(3); C(2)−C(6)−C(7), 122.1(3).

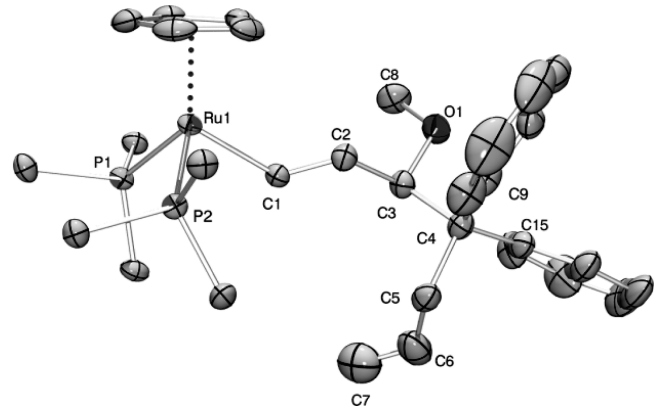


Figure 4. ORTEP drawing of the ruthenium complex **11**. For clarity, aryl groups of the triphenylphosphine ligands on Ru except the ipso carbons are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)−C(1), 2.087(3); C(1)−C(2), 1.316(4); C(2)−C(3), 1.509(4); Ru(1)−C(2)−C(3), 126.9(2); C(1)−C(2)−C(3), 126.6(3).

δ 15.24 with $^3J_{HH} = 12.95$ Hz and $^3J_{PH} = 9.10$ Hz is assigned to Cα−H and a triplet resonance at δ 7.84 with $^3J_{HH} = 12.95$ Hz is assigned to Cβ−H. For **11**, because of the stereogenic center at Cγ, the ^{31}P NMR spectrum shows two doublet resonances at δ 49.06 and 47.29 with $^2J_{PP} = 37.51$ Hz. Resonance of Cα−H appears as multiplet resonance at δ 7.82 in the ^{1}H NMR spectrum.

Single crystals of complexes **9** and **11** are obtained from acetone/methanol/diethylether and acetone, respectively. ORTEP-type views of the cationic complex **9** and the neutral complex **11** are shown in Figures 3 and 4, respectively, and their selected bond distances and angles are collected. For **9**, the butadiene ligand bonds to the Ru atom via C(1), C(2), C(6), and C(7) adopting an *exo* configuration. A bond formation between C(2) and C(6) with a distance of 1.416(5) Å had occurred between the two alkyne and alkene internal carbon atoms of the 1,6-enyne ligand, forming a coordinated butadiene system with the four Ru−C distances being approximately equal. For **11**, the addition of a methoxy group at Cγ forming the neutral vinyl complex is clearly seen. The bond length of Ru−C(1) of **11** is significantly longer than the Ru−C(1) double bond of the

(15) (a) Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7232–7238. (b) Miller, D. C.; Angelici, R. J. *Organometallics* **1991**, *10*, 79–89. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137–2147. (d) Cadierno, V.; García-Garrido, S. E.; Gimeno, J. *Adv. Synth. Catal.* **2006**, *348*, 101–110. (e) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2007**, *26*, 4300–4309. (f) Pino-Chamorro, J. A.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2009**, *28*, 1546–1557.

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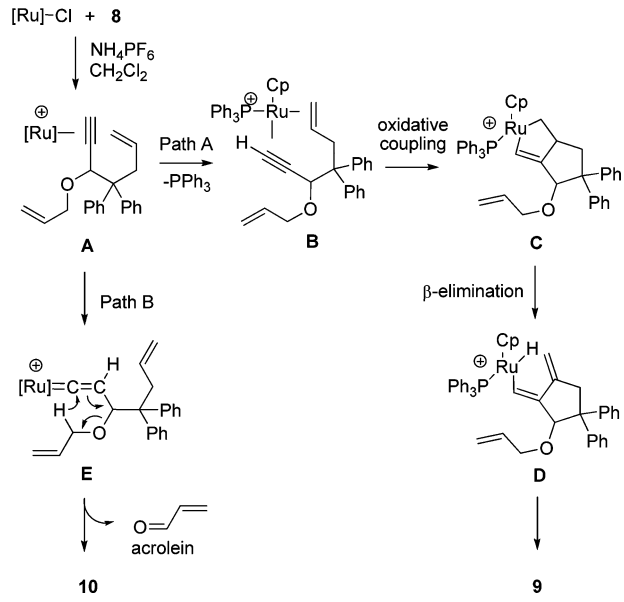
Scheme 4

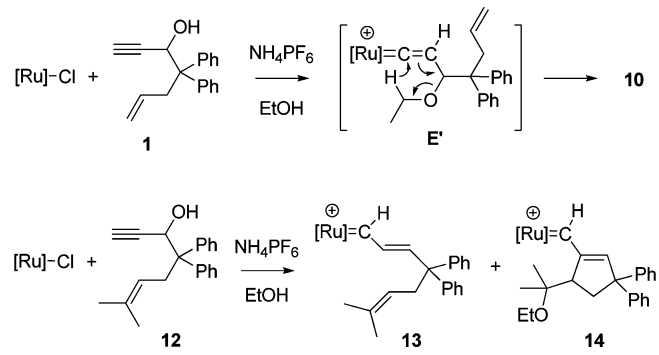


vinylidene complex **7a**, and the C(1)−C(2) distance of 1.316(4) Å reveals a double bond.

A rational mechanism for the formation of **9** and **10** is proposed in Scheme 4. From the initially formed π-coordinated species **A**, there are two pathways to form two different products. Pathway A proceeds by coordination of the triple bond followed by dissociation of a PPh_3 ligand accompanied with filling in the vacant site by the allylic group to form **B**. A C−C bond formation via an oxidative coupling then gave a ruthenacyclopentene intermediate **C**. Subsequent β-hydrogen elimination giving **D** is followed by successive migration of hydride to afford **9**.[17] Alternatively, a cyclization with a C−C bond formation accompanied with a direct 1,3-hydrogen shift also forms **9**. Pathway B to yield the alkenylcarbene[18] complex **10** may involve a pericyclic retro-ene cleavage[19] of the vinylidene species **E** formed from the initially π-coordinated species generating **10** and acrolein. In the ^{1}H NMR spectra of the reaction mixture, three multiplets at δ 9.50, 6.23, and 6.09 attributed to acrolein were observed. It has been shown that thermolysis of propargylic ethers at 350−450 °C leads to allenes and carbonyl compounds by a retro-ene transformation.[20] In our case we believe that mediation of a transition metal reduces the activation energy for the metalloretro-ene reaction[21] thus allows the reaction to occur at lower temperature.

Reactions of Enynes with Methyl Substituents. To prove that the vinylcarbene complex is generated by a retro-ene reaction which is independent of the enyne substrate used, we carried out the reactions of **1** and **12** with [Ru]Cl in the presence of NH_4PF_6 in EtOH (Scheme 5). As expected, no cycloisomerization to form the η^4-butadiene complex was observed. The reaction of **1** with [Ru]Cl in EtOH indeed forms the same alkenylcarbene complex **10** as that from the reaction of **8** with [Ru]Cl. Interestingly, the reaction of [Ru]Cl with 1,6-enyne **12**, having two methyl groups on the terminal carbon of the tethering allyl group, gave the carbene complex **13**, tethering with an unsaturated linear chain, and the other carbene complex **14** with a substituted cyclopentenyl ring in a ratio of 3.5:1. Because complex **13** is insoluble in EtOH, two complexes **13** and **14** are easily separated. Both complexes **13** and **14** are characterized by NMR data and additionally complex **13** is characterized by a single crystal X-ray diffraction analysis.

Scheme 5



The spectroscopic data of **13**, similar to its analog **10**, consist of a characteristic doublet of a triplet resonance at δ 15.27 with $^3J_{HH}$ = 12.76 Hz and $^3J_{PH}$ = 9.04 Hz assigned to Cα−H and a triplet resonance at δ 7.77 with $^3J_{HH}$ = 12.76 Hz assigned to Cβ−H in the ^{1}H NMR spectrum. In the ^{1}H NMR spectrum of **14**, the relatively downfield triplet resonance at δ 16.58 with $^3J_{PH}$ = 9.04 Hz is assigned to Cα−H, two singlet resonances at δ 1.03 and 0.92 are assigned to the two methyl groups. Single crystals of complex **13** were obtained from acetone/ethanol. An ORTEP type view of the cationic complex is shown in Figure 5 and selected bond distances and angles are collected. The C(1)−C(2) distance of 1.442(6) Å reveals a shorter single bond suggesting a contribution of the zwitterionic resonance form.[22] The torsional angle of 172.95° for the skeletal C(1)−C(2)−C(3)−C(4) suggested the trans configuration of C(2)−C(3) double bond.

The above-mentioned reactions of [Ru]Cl with propargylic ether **8**, propargylic alcohol **1** and **12** in EtOH via vinylidene intermediate species provide a simple and direct method for preparing ruthenium alkenylcarbene complexes involving a metal-assisted retro-ene reaction. Besides, in the reactions of 1,6-enyne **1**−**4** and **8**, with no methyl group on the olefinic part, formation of analogous complex of **14** was not observed. This inspires us to attempt more experiments and investigate the controlling factor in the substrates used in these reactions.

As shown in Scheme 6, the reaction of **12** with [Ru]Cl in the presence of NH_4PF_6 in CH_2Cl_2 yielded the hydroxylvinylidene complex **5f** and the carbene complex **15** with a cyclopentenyl ring in a ratio of 10:1. Besides, when the reaction was carried out in methanol for 1 day, the methoxylvinylidene complex **5g** and **16** in a ratio of 4:1 were obtained. Complex **16** was isolated as the only product if the reaction time was prolonged for 4

(17) (a) Mitsudo, T. A.; Zhang, S. W.; Nagao, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 598–599. (b) Trost, B. M.; Indolese, A. *J. Am. Chem. Soc.* **1993**, *115*, 4361–4362. (c) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc.* **1994**, *116*, 4255–4267. (d) Krafft, M. E.; Wilson, A. M.; Dasse, O. A.; Bonaga, L. V. R.; Cheung, Y. Y.; Fu, Z.; Shao, B.; Scott, I. L. *Tetrahedron Lett.* **1998**, *39*, 5911–5914.

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(20) (a) Viola, A.; Collins, J. J.; Filipp, N. *Tetrahedron* **1981**, *37*, 3765–3811. (b) Várnai, P.; Keserü, G. M. *J. Org. Chem.* **1996**, *61*, 5831–5836.

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(22) Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919–2928.

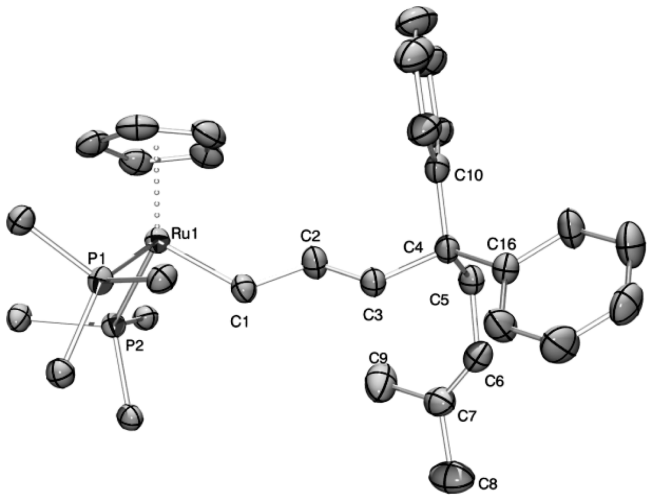
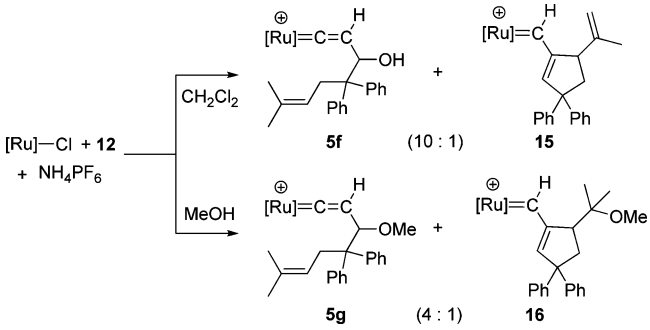


Figure 5. ORTEP drawing of the cationic complex **13**. For clarity, aryl groups of the triphenylphosphine ligands on Ru except the ipso carbons and PF_6^- are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)−C(1), 1.922(5); C(1)−C(2), 1.442(6); C(2)−C(3), 1.315(7); Ru(1)−C(1)−C(2), 124.7(4); C(1)−C(2)−C(3), 123.5(5).

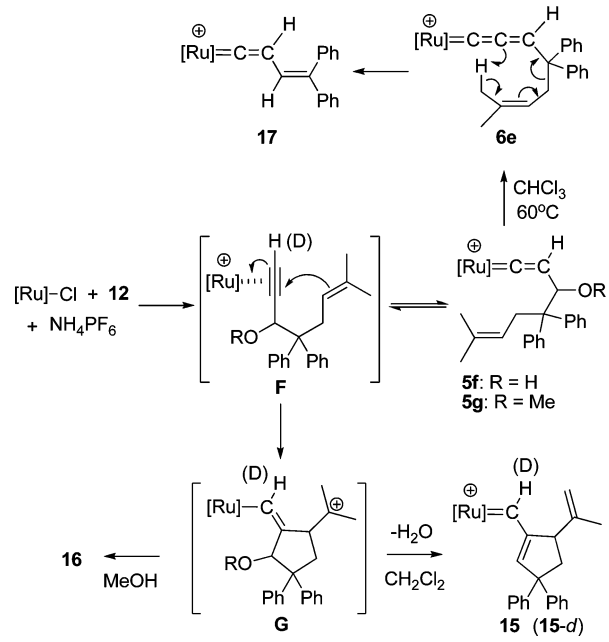
Scheme 6



days in methanol. A series of 2D NMR studies and mass spectroscopy establish the structures of **15** and **16**. In the ^{1}H NMR spectra, the relatively downfield triplet resonances at δ 15.57 for **15** and δ 16.57 for **16** are assigned to Cα−H. The two singlet resonances at δ 4.71 and 4.43 for **15** are assigned to two protons of the terminal olefin and two singlet resonances at δ 1.09 and 0.86 for **16** to two methyl groups.

The lack of carbene products in the reactions of **1**−**4** and **8** leads us to believe that this cycloisomerization of **12** to form carbene complexes **15** and **16** proceeds through an unusual pathway.[5d−f] As shown in Scheme 7, the vinylidene complexes **5f** and **5g** could come from **F** with the triple bond π-coordinated to the metal center. In the other competitive electrophilic pathway, the activation of the triple bond of enynes by a metal center generates species with high electrophilicity and triggers the nucleophilic attack of a double bond to the activated triple bond by an *exo*-dig pathway.[3e,f,4b,d,23] The formation of **15** and **16** may then involve a *5-exo*-dig cyclization of **F** to give the tertiary carbocation **G** stabilized by the presence of two methyl groups, ultimately leading to **15** in CH_2Cl_2 and **16** in

Scheme 7



methanol,[1c,d,5a,24] respectively. To clarify that the formation of **15** and **16** was not via the allenylidene intermediate, the reaction of *d*-labeled enyne **12**, monodeuterted at the terminal alkyne, was explored. The product **15**-*d*, with the deuterium appeared exclusively at Cα, as indicated by the absence of the ^{1}H resonance at δ 15.56, suggests that the Cα−H of **15** is not originated from the terminal methyl group via the allenylidene intermediate. This labeling result confirms that the formation of **15** and **16** is via the π-coordinated species **F**. And the fact that no cyclization was observed for **1**−**4** and **8** strongly suggests the participation of the tertiary carbocationic intermediate **G** in the reaction of **12** with two terminal methyl groups. The formation of the carbene complex **14** described above also conformed with the mechanism in Scheme 7.

Furthermore, dehydration of **5f** and methanol elimination of **5g** in $CHCl_3$ at 60 °C both generated **6e** and subsequently liberated the allyl group leading to the vinylidene complex **17** in good yield. Comparing with the 1,3-allyl shift and the Cope rearrangement of **5a**−**c** and **5e** via allenylidene−ene reaction, further transformation of **5f** and **5g** each with two methyl groups should proceed by a different pathway. On the basis of literature reports on cyclization reactions of similar enynes,[5c,6b,d] the mechanism for the transformation is also proposed as shown in Scheme 7. The vinylidene complexes **5f** and **5g** first form the allenylidene complex **6e**. Then a retro-ene reaction involving the terminal double bond of the allenylidene ligand and the terminal methyl group of the allyl unit results in the conjugated vinylidene complex **17** with elimination of 2-methylbutadiene. Possible reason for **6e** to take a different pathway from that of **6a** might be the steric effect. In **6e**, with two methyl groups, the olefin is away from Cβ thus fails to undergo a Cope rearrangement. An additional point is that the retro-ene reaction cannot take place for **6a**, with no methyl substituent at the olefin portion.

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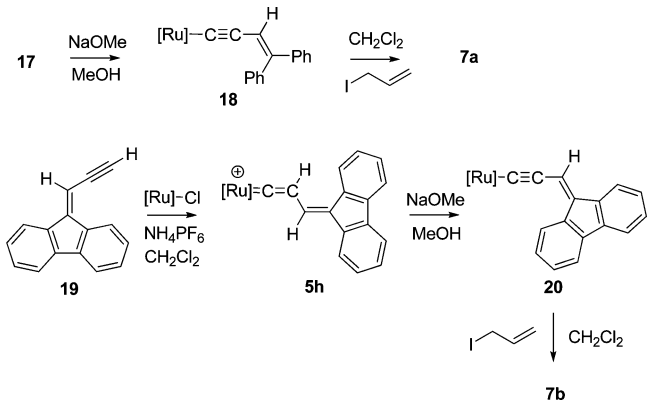
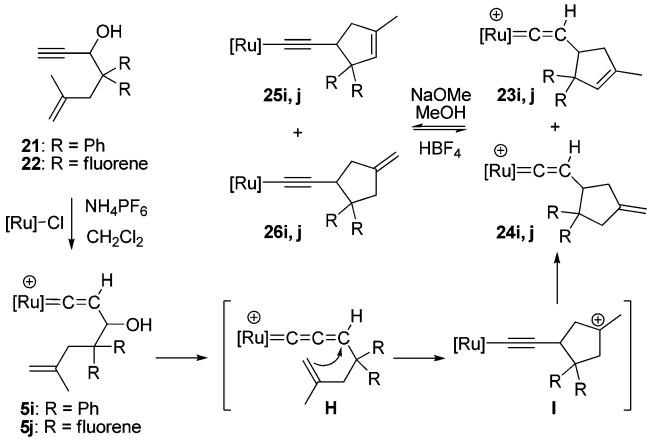
Scheme 8



Scheme 9



Deprotonation of **17** gave the ruthenium acetylide complex **18** as a light yellow powder. Further allylation at Cγ with allyl iodide yielded the vinylidene complex **7a** which is the same product as that obtained from the skeletal rearrangement of **6a** (Scheme 8). We also treated the fluorene enyne **19** with [Ru]Cl in the presence of NH_4PF_6 salt resulting in formation of the vinylidene complex **5h**, analogous to **17** obtained from **6e**. By the same principle, deprotonation of complex **5h** yielded the acetylide complex **20** and then alkylation at Cγ with allyl iodide yielded the vinylidene complex **7b** which is the same product from the rearrangement of **6b** under thermolytic condition.

Furthermore, the reactions of [Ru]Cl with enynes **21** and **22**, with one methyl group added to the internal carbon of the allyl group, afforded the hydroxyvinylidene complexes **5i** and **5j**, respectively. These complexes undergo an intramolecular cyclization via allenylidene intermediate to form different vinylidene complexes each containing a five-membered ring, see Scheme 9. For example, heating a chloroform solution of **5i** to 60 °C afforded the vinylidene complex **23i** together with its isomer **24i** in a ratio of 5:1, as determined by NMR. Both complexes each with a stereogenic center at Cγ display two doublet resonances at δ 43.92 and 43.72 with $^2J_{PP} = 25.75$ Hz for **23i** and at δ 43.48 and 42.84 with $^2J_{PP} = 26.58$ Hz for **24i** in their ^{31}P NMR spectra. The mixture of vinylidene complexes **23i** and **24i**, contaminated with a few unidentifiable side products, was converted to the corresponding acetylide complexes **25i** and **26i** by deprotonation for removal of the side products. Column chromatography yielded a mixture of yellow powder **25i** and **26i**. The pure product **25i** could be obtained by recrystallization of the mixture in acetone at 0 °C. Reprotonation of **25i** at 0 °C yielded the vinylidene complex **23i**. No attempt was made to purify complex **24i** from the mixture. Complex **5j** also shows the same reactivity to yield the corresponding products **23j**−**26j**.

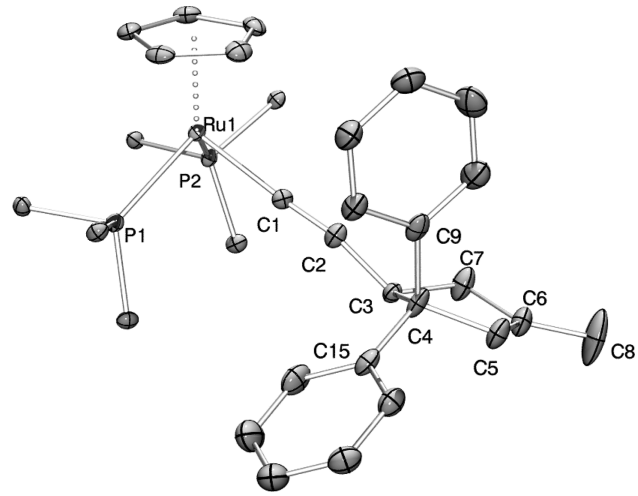


Figure 6. ORTEP drawing of the ruthenium acetylide complex **25i**. For clarity, aryl groups of the triphenylphosphine ligands on Ru except the ipso carbons are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)−C(1), 2.025(2); C(1)−C(2), 1.207(3); C(2)−C(3), 1.521(4); C(3)−C(7), 1.490(5); C(5)−C(6), 1.338(4); C(6)−C(8), 1.451(4); Ru(1)−C(1)−C(2), 175.0(2); C(1)−C(2)−C(3), 169.1(3); C(7)−C(3)−C(4), 104.1(3); C(5)−C(6)−C(7), 109.8(2); C(3)−C(7)−C(6), 106.1(2); C(8)−C(6)−C(7), 123.6(3).

The structures of complexes **23**−**26** are determined by 2D-NMR, and complex **25i** is fully characterized by a single crystal X-ray diffraction analysis. The ^{31}P NMR data exhibit two doublet resonances at δ 51.85 and 51.40 with $^2J_{PP} = 37.58$ Hz for **25i** and at δ 51.66 and 51.30 with $^2J_{PP} = 37.98$ Hz for **26i**. Single crystals of complex **25i** were obtained from CH_2Cl_2/diethyl ether at 5 °C. An ORTEP type view of complex **25i** is shown in Figure 6, and selected bond distances and angles are listed. The complex exhibits the usual acetylide structure in a three-legged piano-stool geometry. Obviously a C−C bond formation had occurred between Cγ and the terminal carbon of the allylic group, forming a five-membered ring. The alkynyl ligand is nearly linear (Ru(1)−C(1)−C(2) angle of 175.0(2)°). The bond lengths of Ru(1)−C(1) of 2.025(2) Å, C(1)−C(2) of 1.207(3) Å and C(2)−C(3) of 1.521(4) Å show a typical acetylide bond skeletal. The bond length of C(3)−C(7) of 1.490(5) Å attests the C−C bond formation and the separations C(5)−C(6) of 1.338(4) Å and C(6)−C(8) of 1.451(4) Å correspond, respectively, to a double and a single bond.

A pathway for the cyclization reaction is proposed as shown in Scheme 9.[6a,c] The allenylidene complex acts as an enophile to afford the vinylidene complexes **23** and **24** via the allenylidene−ene reaction. The dehydration of **5** occurs spontaneously to form the allenylidene complex **H**. A C−C bond formation between the alkene moiety of the methyl allyl group and Cγ of the allenylidene ligand results in the alkynyl complex **I** bearing a cationic charge at the methyl-substituted tertiary carbon of the five-membered ring. Subsequent 1,5-proton shift gives the final products **23i** and **24i**. The driving force for this process seems to be the stability of the tertiary carbocationic species **I**, since for the other types of ruthenium vinylidene complexes **5a**−**e** with no methyl group on the allylic group no cyclization reaction was observed. The fact that the enynes **21** and **22** did not form the cyclic carbene via cyclization through

a π-coordinated species might be due to the lack of a tertiary carbocation intermediate such as **G** described in Scheme 7. On the other hand, the reason that **12** would not proceed the cyclization reaction described in Scheme 9 might be a result of disfavoring the formation of a vinylidene with a four-member ring.

Esteruelas and his co-workers have reported the stoichiometric Diels−Alder-type addition of dienes to the Cβ-Cγ double bond of allenylidene complexes to give the corresponding substituted vinylidene complexes.[25] Uemura and co-workers described the first example of the use of the Cβ−Cγ double bond of allenylidene complexes as an enophile in the catalytic process with a diruthenium complex.[6a] The allenylidene-ene reaction described here is the first example of intramolecular C−C bond forming system by controlling the substituted methyl group of substrates and reaction conditions to lead to allyl migration or cyclization products.

Conclusions

In summary, we report reactions of 1,6-enynes with [Ru]Cl to yield different products by controlling the substituted methyl group of substrates and reaction conditions. The mechanisms via various reaction pathways including skeletal rearrangement, retro-ene cleavage, and cyclization reactions are also proposed. These results can be interpreted by different modes of the coordination of the triple bond of the propargylic alcohol/ether in a π-coordination mode or in the form of vinylidene complex with the oxygen functionality in proximity. For the reactions of enynes **1**−**3**, the interaction between the allylic group and Cβ of the resulting allenylidene ligand causes 1,3-allyl shift and Cope rearrangement simultaneously to yield **7**. This allenylidene-ene reaction described here is the first example of intramolecular C−C bond formation via Cope rearrangement in organometallic system. With a propargylic ether group, the reaction of compound **8** gives **10** as the major product via a pericyclic retro-ene cleavage and the butadiene complex **9** by a cyclization reaction as the minor product. The reaction of enyne **1** in ethanol gives **10** as the only product. For enyne **12**, a C−C bond forming cyclization reaction is observed in the intermediate with π-coordinated triple bond giving the carbene complexes **15** and **16** with a substituted cyclopentenyl ring at Cα via a tertiary carbocationic species. However, the allenylidene complex **6e** derived from the vinylidene intermediate undergoes a retro-ene reaction to bring about cleavage of the dimethyl substituted allyl group giving complex **17**. Deprotonation of **17** and further alkylation at Cγ with allyl iodide yields **7a**. In the reactions of enynes **21** and **22**, unobserved allenylidene complexes act as an enophile to afford the vinylidene complexes **23** and **24** each with a five-membered ring bonded at Cβ via the allenylidene-ene reaction.

Experimental Section

Typical experimental procedures and spectroscopic data of the representative products are described. Further experimental details and spectroscopic data of other products are summarized in the Supporting Information.

General Procedures. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The ruthenium complex $Cp(PPh_3)_2RuCl$[26] and compounds **1**−**4**, **8**, **12**, **19**, **21**, and **22**[27] were prepared by following the method reported in the literature. The C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded using a LCQ Advantage (ESI) and JEOL SX-102A (FAB). X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at the National Taiwan University. NMR spectra were recorded on Bruker Avance-400 and DMX-500 FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvents as a standard.

Reactions of 1−4 with [Ru]Cl: Syntheses of 5a−d. A typical experimental procedure for the reaction of [Ru]Cl with enyne is described below. To a Schlenk flask charged with [Ru]Cl (0.20 g, 0.27 mmol) and NH_4PF_6 (0.09 g, 0.55 mmol) was added 1,6-enyne **1** (0.84 g, 0.32 mmol) and 30 mL of dichloromethane under nitrogen. The resulting solution was stirred at room temperature overnight. After that, the solution was filtered through Celite to remove the insoluble precipitates, then the volatiles were removed under vacuum and the solid residue was extracted with a small volume of dichloromethane followed by reprecipitation by a 60 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as a light-orange powder **5a** (0.27 mg, 89%). The syntheses of **5b**−**j** followed the same procedure. Spectroscopic data of **5a**: ^{1}H NMR (δ, $CDCl_3$): 6.89−7.42 (m, 40H, Ph); 5.45 (m, 1H, C*H*═CH_2); 5.44 (t, $^3J_{HH}$ = 8.15 Hz, 1H, Cγ−H); 5.06 (d, $^3J_{HH}$ = 17.15 Hz, 1H, CH═CH*H*); 4.98 (d, $^3J_{HH}$ = 4.77 Hz, 1H, CH═C*H*H); 4.97 (s, 5H, Cp); 4.45 (d, $^3J_{HH}$ = 8.15 Hz, 1H, Cβ-H); 3.13 (dd, $^2J_{HH}$ = 14.32 Hz, $^3J_{HH}$ = 7.35 Hz, 1H, CH*H*); 2.94 (dd, $^2J_{HH}$ = 14.32 Hz, $^3J_{HH}$ = 6.34 Hz, 1H, C*H*H); 1.92 (d, $^3J_{HH}$ = 8.15 Hz, 1H, OH). ^{13}C NMR (δ, $CDCl_3$, 5 °C): 345.24 (t, $^2J_{CP}$ = 13.70 Hz, Cα); 143.80−127.98 (Ph); 133.94 (*C*H═CH_2); 118.20 (CH═*C*H_2); 115.70 (Cβ); 94.80 (Cp); 70.07 (Cγ); 55.92 (C); 42.19 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.42, 44.35 (2 d, $^2J_{pp}$ = 26.13 Hz). MS (FAB^+) *m*/*z*: 953.3. Anal. Calcd for $C_{60}H_{53}F_6OP_3Ru$: C, 65.63; H, 4.87. Found: C, 65.31; H, 4.56.

Syntheses of 6. A dilute solution of hydroxyvinylidene complex **5a** (0.10 g, 0.09 mmol) in dichloromethane (0.5 mL) was transferred to an Al_2O_3 (Acidic, activity grade I, height of column ca. 5 cm) chromatography column. Elution with dichloromethane collected a green band. The solution was removed under vacuum, and the solid residue was extracted with a small volume of dichloromethane followed by reprecipitation with 60 mL of stirred hexane. Precipitates thus formed were collected in a glass frit, washed with hexane, and dried under vacuum. The final product was obtained as a deep-green powder **6a** (0.04 g, 41%). Complexes **6a**−**c** are too active to be purified for mass spectrum, ^{13}C NMR and elemental analysis. Spectroscopic data of **6a**: ^{1}H NMR (δ, $CDCl_3$): 9.08 (s, 1H, Cγ−H); 6.95−7.40 (m, 40H, Ph); 5.68 (m, 1H, C*H*═CH_2); 5.02−5.07 (m, 2H, CH═CH_2); 4.90 (s, 5H, Cp); 3.28 (d,$^3J_{HH}$ = 6.86 Hz, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): 45.69 (s).

Syntheses of 7. A solution of allenylidene complex **6a** (0.11 g, 0.09 mmol) in chloroform (3 mL) was stirred at 60 °C for 6 h under nitrogen. Then the solution was cooled to room temperature and filtered through Celite to remove the insoluble precipitates. Then the volatiles were removed under vacuum and the solid residue was extracted with a small volume of dichloromethane followed by being reprecipitated with 60 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product was obtained as a pink powder **7a** (0.10 g, 89%). An alternative and more straightforward method to prepare compounds **5a** involves the treatment of the ruthenium vinylidene complexes **5a** in

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chloroform and was followed by further reaction at 60 °C for 6 h to generate the dehydration allenylidene complex **6a** and subsequently the allyl migration product **7a**. The purification was the same with the description above. Spectroscopic data of **7a**: ^{1}H NMR (δ, $CDCl_3$): 6.86−7.70 (m, 40H, Ph); 5.97 (s, 1H, C*H*═C(Ph)$_2$); 5.64 (m, 1H, C*H*═CH$_2$); 5.07 (d, $^3J_{HH}$ = 10.06 Hz, 1H, CH═CH*H*); 4.85 (d, $^3J_{HH}$ = 15.53 Hz, 1H, CH═C*H*H); 4.80 (s, 5H, Cp); 2.70 (d,$^3J_{HH}$ = 6.57 Hz, 2H, CH$_2$). ^{13}C NMR (δ, $CDCl_3$): 354.23 (t, $^2J_{CP}$ = 14.59 Hz, Cα); 144.41 (CPh$_2$); 142.83−128.85 (Ph); 134.76 (*C*H═CH$_2$); 125.21 (Cβ); 117.43 (CH══*C*H$_2$); 114.17 (CH); 94.07 (Cp); 29.35 (CH$_2$). ^{31}P NMR (δ, $CDCl_3$): 41.83 (s). MS (FAB$^+$) *m*/*z*: 935.2. Anal. Calcd for $C_{60.5}H_{53}F_6O_{0.5}P_3Ru$ (crystal containing 0.5 equiv of methanol was used for analysis): C, 66.30; H, 4.87. Found: C, 66.12; H, 5.10.

Reactions of 8 with [Ru[Cl: Syntheses of 9, 10, and 11. The experimental procedure of syntheses complexes **9** and **10** was the same with the synthesis of **5a** described above. The mixture **9** and **10** (0.32 g) was treated with excess NaOMe (0.02 g, 0.36 mmol) in methanol (10 mL), and the light-yellow precipitate formed immediately. Stirring was continued until no further solid was formed. The solvent was removed under vacuum, and the residue was passed through a neutral Al_2O_3 column eluted with ether/CH_2Cl_2. Collecting the yellow band and the second light-yellow band solution separately followed by drying under vacuum resulted in the yellow vinyl product **11** (0.22 g, 76%) and light-yellow diene product **9** (0.04 g, 13%). A solution of complex **11** (0.20 g, 0.21 mmol) with NH_4PF_6 (0.09 g, 0.55 mmol) in $CHCl_3$ was stirred for 3 h at 60 °C under nitrogen atmosphere. After being cooled to room temperature, the solution was filtered through Celite to remove the insoluble precipitates and volume of the filtrate is reduced to 5 mL. The resulting solution was added into a solution of 60 mL vigorously stirred hexane. Brown precipitates thus formed were collected, washed with hexane, and dried under vacuum to afford **10** (0.22 g, 97%). Spectroscopic data of **9**: ^{1}H NMR (δ, $CDCl_3$): 6.98−7.62 (m, 25H, Ph); 5.67 (m, 1H, C*H*═CH$_2$); 5.61 (s, 1H, C*H*OCH$_2$); 4.97 (m, 2H, CH═C*H*$_2$); 4.69 (s, 5H, Cp); 4.46 (dd, $^2J_{HH}$ = 12.39 Hz, $^3J_{HH}$ = 5.48 Hz, 1H,); 4.17 (d, $^2J_{HH}$ = 17.75 Hz, 1H, CH*H*); 4.11 (m, 1H, OC*H*H); 4.10 (s, 1H, OCHC═C*H*H); 3.94 (s, 1H, C═C*H*H); 3.64 (d, $^2J_{HH}$ = 17.75 Hz, 1H, C*H*H); 0.16 (d, $^3J_{HP}$ = 17.03 Hz, 1H, *C*═CH*H*); 0.05 (d, $^3J_{HP}$ = 18.50 Hz, 1H, OCHC═CH*H*). ^{13}C NMR (δ, $CDCl_3$): 146.00−126.28 (Ph); 134.03 (*C*H═CH$_2$); 116.51 (CH══*C*H$_2$); 111.42 (OCH*C*═CH$_2$); 110.08 (*C*═CH$_2$); 90.70 (*C*HOCH$_2$); 72.36 (OCH$_2$); 61.38 (CPh$_2$); 50.96 (CH$_2$); 43.41 (d, $^2J_{CP}$ = 4.65 Hz, OCHC═*C*H$_2$); 42.24 (d, $^2J_{CP}$ = 4.65 Hz, *C*═CH$_2$). ^{31}P NMR (δ, $CDCl_3$): 57.20 (s). MS ESI *m*/*z*: 732.2 (M+1)$^+$. Anal. Calcd For $C_{47}H_{47}F_6O_{1.50}P_2Ru$ (crystal containing 0.5 equiv of diethyl ether was used for analysis): C, 61.84; H, 5.19. Found: C, 61.98; H, 4.99. Spectroscopic data of **10**: ^{1}H NMR (δ, $CDCl_3$): 15.24 (dt, $^3J_{HH}$ = 12.95 Hz, $^3J_{HP}$ = 9.10 Hz, 1H, Cα−H); 7.84 (t, $^3J_{HH}$ = 12.95 Hz, 1H, Cβ−H); 7.16−7.81 (m, 41H, Ph and Cγ−H); 5.52 (m, 1H, C*H* = CH$_2$); 5.21 (d, $^3J_{HH}$ = 17.05 Hz, 1H, CH═C*H*H); 5.09 (d, $^3J_{HH}$ = 10.30 Hz, 1H, CH═CH*H*); 4.90 (s, 5H, Cp); 3.29 (d, $^3J_{HH}$ = 6.85 Hz, 2H, CH$_2$). ^{13}C NMR (δ, $CDCl_3$): 309.29 (t, $^2J_{CP}$ = 9.18 Hz, Cα); 156.65 (Cγ); 153.09 (Cβ); 143.76−127.12 (Ph); 133.93 (*C*H═CH$_2$); 118.83 (CH═*C*H$_2$); 95.00 (Cp); 54.69 (C); 42.73 (CH$_2$). ^{31}P NMR (δ, $CDCl_3$): 46.97 (s). MS ESI *m*/*z*: 938.2 (M+1)$^+$. Anal. Calcd for $C_{60}H_{53}F_6P_3Ru$: C, 66.60; H, 4.94. Found: 66.39; H, 5.10. Spectroscopic data of **11**: ^{1}H NMR (δ, *d*-toluene): 7.82 (m, 1H, Cα−H); 6.88−7.76 (m, 40H, Ph); 5.73 (m, 1H, C*H*═CH$_2$); 5.45 (dd, $^3J_{HH}$ = 16.50 Hz, $^3J_{HH}$ = 8.18 Hz, 1H, Cβ−H); 4.81 (d, $^3J_{HH}$ = 10.26 Hz, 1H, CH═CH*H*); 4.69 (d, $^3J_{HH}$ = 17.15 Hz, 1H, CH═C*H*H); 4.29 (s, 5H, Cp); 4.24 (d, $^3J_{HH}$ = 8.18 Hz, 1H, Cγ−H). 3.08 (s, 3H, OMe); 3.05 (m, 1H, C*H*H), 2.89 (m, 1H, CH*H*). ^{13}C NMR (δ, *d*-toluene, 5 °C): 151.55 (t, $^2J_{CP}$ = 18.36 Hz, Cα); 147.60−124.64 (Ph); 136.34 (Cβ); 136.24 (*C*H═CH$_2$); 117.10 (CH═*C*H$_2$); 91.46 (Cγ); 86.68 (Cp); 56.37 (C); 55.46 (OMe); 44.48 (CH$_2$). ^{31}P NMR (δ, *d*-toluene): 49.06, 47.29 (2 d, $^2J_{pp}$ = 37.51 Hz). MS ESI *m*/*z*: 939.2 (M+1 − OMe)$^+$. Anal. Calcd for $C_{61}H_{56}OP_2Ru$: C, 75.68; H, 5.83. Found: 75.42; H, 5.93. The same procedure was used for the reaction of **19** with [Ru]Cl to synthesize **20**.

Reactions of 12 with [Ru[Cl: Syntheses of 13 and 14. The syntheses of the mixture **13** and **14** followed the standard procedure of synthesis of **5a** in EtOH for 3 days. Extraction of the mixture with EtOH and collected the precipitate to obtain **13**. The filtrates were passed through a neutral Al_2O_3 column eluted CH_2Cl_2. Collecting the green band followed by drying under vacuum resulted in the product **14**. Spectroscopic data of **13** and **14** are given in Supporting Information.

Syntheses of 5f and 15. The syntheses of the mixture **5f** and **15** followed the same procedure of synthesis of **5a** in CH_2Cl_2. Extraction of the mixture with benzene and collected the precipitate to obtain **5f**. The filtrates were passed through a neutral Al_2O_3 column eluted CH_2Cl_2. Collecting the green band followed by drying under vacuum resulted in the product **15**. Spectroscopic data of **15**: Yield: 0.03 g (8%). ^{1}H NMR (δ, $CDCl_3$): 15.57 (t, $^3J_{HP}$ = 11.20 Hz, 1H, Cα−H); 6.83−7.72 (m, 41H, Ph and *C* = CH); 4.83 (s, 5H, Cp); 4.71 (s, 1H, C═C*H*H); 4.43 (s, 1H, *C* = CH*H*); 3.97 (t, $^3J_{HH}$ = 7.90 Hz, 1H, CH); 3.21 (dd, $^3J_{HH}$ = 14.10 Hz,$^3J_{HH}$ = 7.90 Hz, 1H, C*H*H); 2.42 (dd, $^3J_{HH}$ = 14.10 Hz,$^3J_{HH}$ = 7.90 Hz, 1H, CH*H*); 1.30 (s, 3H, CH$_3$). ^{13}C NMR (δ, $CDCl_3$): 308.53 (t, $^2J_{CP}$ = 15.97 Hz, Cα); 163.29 (Cβ); 149.54 (*C*═CH); 147.57−126.81 (Ph); 144.63 (*C*═CH$_2$); 115.12 (*C*═C*H*$_2$); 94.92 (Cp); 62.77 (C); 55.74 (CH); 45.11 (CH$_2$); 18.30 (CH$_3$). ^{31}P NMR (δ, $CDCl_3$): 45.61, 45.28 (2 d, $^2J_{PP}$ = 25.24 Hz). MS ESI *m*/*z*: 964.2 (M+1)$^+$. Anal. Calcd for $C_{62}H_{55}F_6P_3Ru$: C, 67.20; H, 5.00. Found: C, 67.44; H, 5.21.

Syntheses of 5g and 16. Preparation of the mixture **5g** and **16** was carried out in MeOH and followed the same procedure as the syntheses of **5f** and **15**. Spectroscopic data of **16**: Yield: 0.06 g (18%). ^{1}H NMR (δ, $CDCl_3$): 16.57 (t, $^3J_{HP}$ = 9.90 Hz, 1H, Cα-H); 6.84−7.41 (m, 41H, Ph and *C*═CH); 4.68 (s, 5H, Cp); 3.62 (t, $^3J_{HH}$ = 8.40 Hz, 1H, CH); 3.20 (dd, $^3J_{HH}$ = 14.15 Hz,$^3J_{HH}$ = 8.40 Hz, 1H, C*H*H); 2.05 (dd, $^3J_{HH}$ = 14.15 Hz,$^3J_{HH}$ = 8.40, 1H, CH*H*); 1.09 (s, 3H, CH$_3$); 0.86 (s, 3H, CH$_3$). ^{13}C NMR (δ, $CDCl_3$): 318.28 (t, $^2J_{CP}$ = 14.28 Hz, Cα); 165.20 (Cβ); 150.96 (*C*═CH); 148.23−126.74 (Ph); 93.61 (Cp); 78.41 (*C*OMe); 61.50 (C); 56.95 (CH); 48.74 (OMe); 43.67 (CH$_2$); 23.36 (CH$_3$); 19.15 (CH$_3$). ^{31}P NMR (δ, $CDCl_3$): 47.75, 47.48 (2 d, $^2J_{PP}$ = 28.20 Hz). MS ESI *m*/*z*: 996.2 (M+1)$^+$. Anal. Calcd for $C_{63}H_{59}F_6OP_3Ru$: C, 66.37; H, 5.22. Found: C, 66.55; H, 5.31.

Syntheses of 6e, 17 and 18. The syntheses of **6e**, **17**, and **18** followed the same procedure as the syntheses of **6a**, **7a**, and **11**. Complex **6e** is too active to be purified for mass spectrum, ^{13}C NMR and elemental. Spectroscopic data of **17**: Yield: 0.18 g (82%). ^{1}H NMR (δ, $CDCl_3$): 7.02−7.42 (m, 40H, Ph); 6.45 (d, $^3J_{HH}$ = 10.52 Hz, 1H, Cγ−H); 5.54 (dt, $^3J_{HH}$ = 10.52 Hz, $^4J_{HP}$ = 2.38 Hz, Cβ−H); 5.19 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$, 5 °C): 361.99 (t, $^2J_{CP}$ = 15.85 Hz, Cα); 141.35, (Cδ); 138.86−127.30 (Ph); 117.23 (Cβ); 109.49 (Cγ); 95.04 (Cp). ^{31}P NMR (δ, $CDCl_3$): 42.78 (s). MS ESI *m*/*z*: 896.2 (M+1)$^+$. Anal. Calcd for $C_{57}H_{47}F_6P_3Ru$: C, 65.83; H, 4.56. Found: C, 65.92; H, 4.79. Spectroscopic data of **18**: Yield: 0.16 g (84%). ^{1}H NMR (δ, C_6D_6): 6.90−8.18 (m, 40H, Ph); 6.81 (s, 1H, Cγ−H); 4.43 (s, 5H, Cp). ^{13}C NMR (δ, C_6D_6): 144.59 (Cγ); 142.41−126.34 (Ph); 125.97 (t, $^2J_{CP}$ = 24.78 Hz, Cα); 116.38 (Cγ); 115.44 (Cβ) 85.94 (Cp). ^{31}P NMR (δ, C_6D_6): 50.95 (s). MS ESI *m*/*z*: 895.1 (M+1)$^+$. Anal. Calcd for $C_{57}H_{46}P_2Ru$: C, 76.58; H, 5.19. Found: C, 76.74; H, 5.32.

Reactions of 21−22 with [Ru[Cl: Syntheses of 23−26. The syntheses of the crude products **23** and **24** followed the same procedure as the synthesis of **7a**, and the reaction was carried out in $CHCl_3$ at 60 °C for 30 min. The deprotonation of **23i** and **24i** followed the same procedure as the synthesis of **11** giving **25i** and **26i**, respectively. The pure product **25i** as crystals could be obtained by recrystallization of the mixture in acetone at 0 °C (0.07 g, 80%). No attempt was made to purify complex **26i** from the mixture. A diluted solution of HBF_4·Et_2O (48%, 0.02 mL, 0.11 mmol) in diethyl ether was added dropwise at 0 °C to a stirred solution of

25i (0.10 g, 0.10 mmol) in 20 mL of diethyl ether. Immediately, an insoluble solid precipitated, but the addition was continued until no further solid was formed. The solution was then decanted, and the brown solid was washed with diethyl ether (3 × 5 mL) and dried in vacuum to yield **23i** (0.10 g, 92%). Complex **24i** could only be obtained in the mixture by the protonation procedure mentioned above. Spectroscopic data of **23i**: ^{1}H NMR (δ, $CDCl_3$): 6.87−7.43 (m, 40H, Ph); 5.79 (s, 1H, C*H* = CMe); 4.87 (s, 5H, Cp); 4.18 (d, $^{3}J_{HH}$ = 8.62 Hz, 1H, Cβ−H); 4.05 (m, 1H, Cγ−H); 2.48 (dd, $^{2}J_{HH}$ = 15.99 Hz, $^{3}J_{HH}$ = 6.89 Hz, 1H, C*H*H); 2.09 (dd,$^{2}J_{HH}$ = 15.99 Hz,$^{3}J_{HH}$ = 5.00 Hz, 1H, CH*H*); 1.81 (s, 3H, CH_3). ^{13}C NMR (δ, $CDCl_3$): 346.29 (t, $^{2}J_{CP}$ = 15.72 Hz, Cα); 147.46−126.47 (Ph); 139.11 (CMe); 131.01 (*C*H═CMe); 117.41 (Cβ); 94.48 (Cp); 65.20 (CPh_2); 44.87 (CH_2); 43.14 (Cγ); 16.90 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 43.92, 43.72 (2 d, $^{2}J_{pp}$ = 25.75 Hz). MS ESI *m*/*z*: 950.2 $(M+1)^{+}$. Anal. Calcd for $C_{61}H_{53}BF_4P_2Ru$: C, 70.73; H, 5.16. Found: C, 70.97; H, 5.42. Spectroscopic data of **24i**: ^{1}H NMR (δ, $CDCl_3$); 6.87 −7.43 (m, 40H, Ph); 5.05 (s, 1H, C═C*H*H); 4.93 (s, 1H, *C* = CH*H*); 5.01 (s, 5H, Cp); 4.11 (d, $^{3}J_{HH}$ = 7.13 Hz, 1H, Cβ-H); 3.84 (m, 1H, Cγ−H); 3.36 (d, $^{2}J_{HH}$ = 17.04 Hz, 1H, C(Ph)$_2$C*H*H); 2.85 (d, $^{2}J_{HH}$ = 17.04 Hz, 1H, C(Ph)$_2$CH*H*); 2.52 (m, 1H, C*H*H); 2.18 (m, 1H, CH*H*). ^{13}C NMR (δ, $CDCl_3$): The signal of triplet Cα is too weak to be detected. 147.46−126.47 (Ph); 131.79 (*C*═CH_2); 116.35 (Cβ); 107.24 (*C*═*C*H_2); 94.43 (Cp); 57.94 (CPh_2); 46.46 (C(Ph)$_2$*C*H_2) 41.00 (CH_2); 39.73 (Cγ). ^{31}P NMR (δ, $CDCl_3$): 43.48, 42.84 (2 d, $^{2}J_{pp}$ = 26.58 Hz). Anal. Calcd for $C_{61}H_{53}BF_4P_2Ru$: C, 70.73; H, 5.16. No attempt was made to purify complex **24i** from the mixture.

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Supporting Information Available: More characterization data of ruthenium complexes and complete crystallographic data for **7a**, **9**, **11**, **13**, and **25i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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