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Reactions of Aromatic S- and O-Enynes with Two Methyl Substituents on the Olefinic Unit Assisted by a Ruthenium Complex: Tandem Cyclization and Product Selectivity

Yi-Jhen Feng, Ying-Hsuan Lai, Ying-Chih Lin,* Shou-Ling Huang, and Yi-Hung Liu[a]

Abstract: Ruthenium-assisted cyclizations of two enynes, HC≡CCH(OH)-(C_6H_4)X−CH_2CH=CMe_2 (X = S (**1a**), O (**1b**)), each of which contains two terminal methyl substituents on the olefinic parts, are explored. The reaction of **1a** in CH_2Cl_2 gives the vinylidene complex **2a** from the first cyclization and two side products, **3a** and the carbene complex **4a** with a benzothiophene ligand. The same reaction in the presence of HBF_4 affords **4a** exclusively. Air oxidation of **4a** in the presence of Et_3N readily gives an aldehyde product. In MeOH, tandem cyclizations of **1a** generate a mixture of the benzothiochromene compound **10a** and the carbene complex **7a** also with a benzothiochromene ligand. First, cyclization of **1b** likewise proceeds in CH_2Cl_2 to give **2b**. Tandem cyclization of **1b** in MeOH yields comparable products **10b** and **7b** with benzochromene moieties, yet with no other side product. The reaction of [Ru]Cl with HC≡CCH(OH)(C_6H_4)S−CH_2CH=CH_2 (**1c**), which contains no methyl substituent in the olefinic part, in MeOH gives the carbene complex **15c** with an unsubstituted thiochromene by means of a C−S bond formation. Structures of **3a** and **15c** are confirmed by X-ray diffraction analysis. The presence of methyl groups of enynes **1a** and **1b** promotes sequential cyclization reactions that involve C−C bond formation through carbocationic species.

Keywords: cyclization · enynes · oxygenation · ruthenium · vinylidene ligands

Introduction

Heterocyclic sulfur and oxygen-containing compounds such as thiochromane and chromane derivatives attract a great deal of interest because these compounds are commonly found in many natural and biologically active compounds.[1] Thiochromane derivatives are ordinary structural motifs in pharmaceutical molecules for use in antiestrogens,[2] anti-HIV drugs,[3] depression, schizophrenia, and Parkinson's disease.[4] Thus the development of effective strategies for the synthesis of heterocyclic compounds remains a challenge for modern organic synthesis.[5] Transition-metal vinylidene, acetylide, and allenylidene complexes have been among the most prominent catalytic precursors employed in organic synthesis.[6,7] Recently, metal-catalyzed cycloisomerization of enynes has been utilized as an efficient synthetic strategy for a variety of carbo-[8] and heterocycles,[9,10] because of the presence of the metal-stabilized "nonclassical" cationic intermediate. In addition, the metal-catalyzed cycloisomerization of enynes often leads to various skeletal rearrangements.[11] A number of ruthenium allenylidene complexes have been proposed as the key intermediate in intra- and intermolecular carbon−carbon bond-forming reactions between propargylic alcohols and alkenes.[12] Similar C−C bond-forming reactions have been reported in a ruthenium-catalyzed intramolecular cyclization of enynes with a propargylic alcohol containing heteroatoms and with various methyl substituents on the olefinic part.[13]

Previously, we developed ruthenium-mediated skeletal rearrangement of 1,5-enynes, which was proposed to proceed by means of an unusual mechanism that involves a formal metathesis process of the terminal vinyl group with the C=C of the vinylidene group.[14] However, ruthenium-mediated cycloisomerizations of 1,*n*-enynes with a methyl group at the terminal vinyl group produced alkoxycyclohexenes[14] and a vinylidene complex with a cyclic ring that contains an unsaturated vinyl group.[12e] Presumably, this vinylidene ligand might undergo further cyclization, which was not observed. In our previous investigation, we found a ruthenium-mediated tandem cyclization reaction of a phenyl propargylic alcohol, with a methyl-substituted allylic group at the *ortho*-position of the aromatic ring, which afforded a tricyclic compound with two newly formed six-membered rings.[8g] Quite recently, we found that different tandem cyclization reactions took place at similar enynes that contained thioether but with an internal methyl substitutent instead of two terminal methyl substituents in the olefinic group to afford an altered tricyclic compound with a methanobenzothionine skeleton.[9f] The reactions of enynes with various methyl substituents on the olefinic part are significantly different

[a] Y.-J. Feng, Y.-H. Lai, Prof. Dr. Y.-C. Lin, S.-L. Huang, Y.-H. Liu
Department of Chemistry, National Taiwan University
Taipei, 106 (Taiwan)
Fax: (+886) 223636359
E-mail: yclin@ntu.edu.tw

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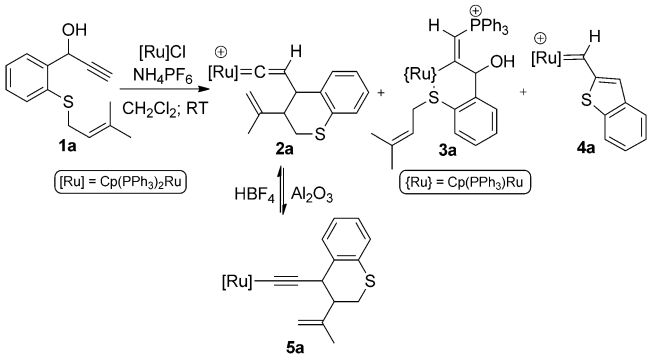
from that of corresponding enynes with no methyl group on the olefinic part.[8g,12e,14] As an extension of our previous study, we explore ruthenium-mediated reactions of an aromatic propargylic alcohol, with a two-terminal methyl-substituent-containing allylic sulfane moiety at the *ortho* position of the aromatic ring. Herein, we report our results on the study of reactions of [Ru]Cl with aromatic sulfur- and oxygen-enynes that contain a propargylic alcohol group.

Results and Discussion

Enyne Cyclization in CH_2Cl_2

Treatment of the aromatic propargyl alcohol **1a**, which contains two terminal methyl groups in the olefinic part, with [Ru]Cl ([Ru]=[Cp(PPh$_3$)$_2$Ru]; Cp=cyclopentadienyl) in the presence of NH_4PF_6 in CH_2Cl_2 at room temperature affords the vinylidene complex **2a** together with the metallacyclic complex **3a** and the carbene complex **4a** in a ratio of 39:55:6 (see Scheme 1). Deprotonation of **2a** takes place when the mixture is passed through an Al_2O_3 column to result in the yellow acetylide complex **5a** and a mixture of **3a** and **4a**. Reprotonation of **5a** with HBF_4 at 0 °C quantitatively yields **2a**. The structure of **2a** with a substituted thiochromane unit at Cβ is revealed by 2D NMR spectra. For example, the COSY NMR spectrum shows correlations of



Scheme 1. Reaction of **1a** with [Ru]Cl in CH_2Cl_2.

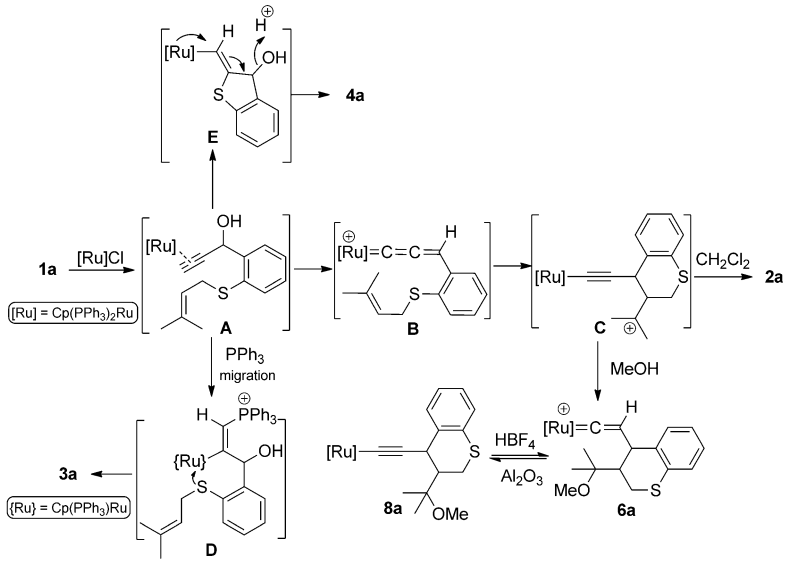
the ^{1}H resonance at $\delta=4.07$ ppm, which is assigned to CγH, with two doublet resonances at $\delta=4.46$ and 2.53 ppm, which are assigned to CβH and the neighboring CH group of the aliphatic ring, respectively, thus indicating formation of the six-membered ring. The 2D HMBC NMR spectrum reveals the correlation between the triplet ^{13}C peak at $\delta=$ 347.84 ppm with ^2J(C,P)=16.1 Hz, which is assigned to Cα, and the CγH resonance at $\delta=4.07$ ppm.

A pathway for the cyclization reaction to yield **2a** might proceed through the formation of an allenylidene **B** followed by either a direct addition of the olefinic group to the electrophilic Cγ,[12d,13b] as shown in Scheme 2. That is to say, an intramolecular attack of the tethering olefinic portion onto Cγ of **B** generates the acetylide intermediate **C**, which bears a cationic charge. Stability of this tertiary carbocationic intermediate could significantly assist this cyclization process. Then transfer of one terminal proton into the acetylide ligand gives **2a**. Alternatively, a concerted allenylidene-ene pathway directly transforms **B** into **2a**.[12a,b]

For the formation of **3a** and **4a**, intermediate **A** with a π-coordinated alkyne might play the key role. Interestingly, at 40 °C in CH_2Cl_2, the C–C bond formation is prohibited; instead, the reaction gives **3a** as the major product in 86% yield with a small amount of **4a**. At higher temperature, formation of **A** is probably favored in CH_2Cl_2, thus leading to **3a**. In the ^{1}H NMR spectrum of **3a**, the characteristic OH proton resonance appears as a doublet at $\delta=3.52$ ppm with ^2J(H,H)=8.4 Hz, which disappears upon addition of D_2O. The ^{31}P NMR spectrum of **3a** shows two broad peaks at $\delta=$ 55.01 and −6.43 ppm at room temperature, which displays two sharp peaks at 233 K. This might be due to the weak coordinating ability of S atom to Ru metal.

Single crystals of **3a** were obtained from CH_2Cl_2/hexanes. The molecular structure was determined by X-ray diffraction analysis. An ORTEP-type view of **3a** is shown in Figure 1, and their selected bond lengths and angles are collected in the legend below. The bond length of Ru1–C1 (2.053(3) Å) is slightly longer than that of a typical Ru–C single bond.[15] The Ru1–S1 bond length of 2.342(1) Å is similar to other Ru–S bond lengths observed for a few arene half-sandwich complexes in which the thioether moiety is part of a metallacycle or a mixed thioether/thiolate

Abstract in Chinese:
含硫原子並有兩個甲基修飾在末端烯基的芳香烯炔化合物 **1a** 與釕金屬化合物 Cp(PPh$_3$)$_2$RuCl 在二氯甲烷下反應，經過一次環化反應，生成釕亞乙烯錯合物 **2a**，反應伴隨著生成 **3a** 和碳烯錯化合物 **4a**。相同反應若加入氟硼酸，或是將金屬化合物改換成(Cp(PPh$_3$)$_2$RuNCCH$_3$)$^+$，則在 NH_4PF_6和二氯甲烷下，只得到單一產物 **4a**。在三乙基胺存在下 **4a** 與氧氣反應，釋出配位基，得到帶有醛基之有機物。相同的反應在以甲醇為溶劑的條件下，則產生連續兩次環化反應，而生成釕金屬碳烯錯化合物 **7a** 和 **10a**，反應並伴隨著 **3a** 的生成。而氧原子取代硫原子的相似芳香烯炔化合物 **1b** 與釕金屬化合物的反應，也可以用溶劑控制，而得到相似的一次環化產物 **2b** 或二次環化的產物 **7b** 以及 **10b**。此反應沒有生成其他副產物。末端烯基上沒有甲基取代基的含硫烯炔化合物 **1c** 與釕金屬化合物在以甲醇為溶劑下作用，產生硫攻擊炔基末端的碳的環化反應，生成含硫六環的金屬碳烯錯合物 **15c**。單晶繞射確定了兩個釕錯合物 **3a** 與 **15c** 的固態結構。



Scheme 2. Formation of **2a**, **3a**, and **4a** in CH_2Cl_2, and **6a** in MeOH.

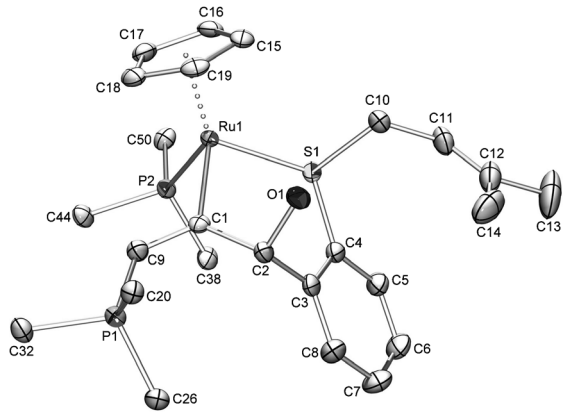


Figure 1. ORTEP drawing of **3a**. For clarity, the aryl group of PPh_3 ligands on Ru except for the *ipso*-carbon atoms are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ru1–C1 2.053(3), Ru1–S1 2.3415(7), C1–C2 1.533(4), C2–C3 1.499(4), C1–C9 1.354(4), C11–C12 1.324(5), C2–O1 1.435(4), S1–C4 1.779(3), S1–C10 1.849(3), P1–C9 1.769(3); C1–Ru1–S1 91.86(8), C2–C1–Ru1 117.31(19), C9–C1–Ru1 123.0(2), C4–S1–Ru1 113.34(10), C3–C2–C1 114.2(2), C1–Ru1–P2 91.87(3), P2–Ru1–S1 87.97(3).

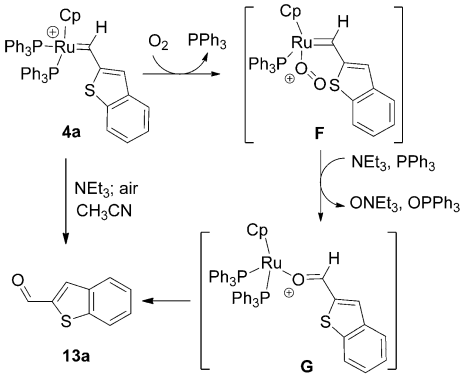
chelating ligand.[16,17] In such complexes Ru–S bond lengths usually range within 2.30–2.34 Å. The C11–C12 and C1–C9 bond lengths of 1.324(5) and 1.354(4) Å are in the range of values for a regular double bond. The addition of a PPh_3 group at C9 is clearly seen. The C2–O1 bond length of 1.435(4) Å is a typical C–O single bond of a hydroxyl group.[12e]

Even though the electrophilic Cα of an allenylidene or a vinylidene ligand is susceptible to attack[18] by a nucleophile such as phosphine,[19] the presence of both the terminal alkynyl hydrogen and the hydroxyl groups on **3a** indicates that nucleophilic attack of PPh_3 should take place while the alkynyl ligand is π-coordinated to the ruthenium center instead of through the allenylidene or vinylidene intermediate.[20] As shown in Scheme 2, direct migration of PPh_3 from metal center onto Cα of the π-alkyne ligand provides a vacant site on the metal. Subsequent sulfur coordination affords **3a**. The high coordination ability of the sulfur atom to transition metals[21,22] is attested by a variety of ruthenium complexes that contain the S,X-chelating ligand (X = N, O, P)[23] reported in the literature. In a recent study, (η^6-*p*-cymene) ruthenium complexes derived from bidentate thiosemicarbazones were evaluated for their biological activity against breast and colorectal carcinoma cells.[24] These complexes exhibited good in vitro cytotoxic activity against all cancer cell lines.

Oxidation of 4a to Aldehyde

Interestingly, the reaction of **1a** is controlled to yield **4a** exclusively. That is to say, the reaction of **1a** with $[Ru]NCCH_3^+$ in the presence of NH_4PF_6 in CH_2Cl_2 gives only **4a** in 83% yield. Alternatively, in the presence of HBF_4 in MeOH at room temperature, the reaction with [Ru]Cl also produces **4a** in 78% yield. The structure of **4a** is determined by spectroscopic methods. In the ^{1}H NMR spectrum of **4a**, the relatively downfield triplet resonance at $\delta = 14.92$ ppm with $^3J(P,H) = 11.2$ Hz is assigned to CαH.[12e,25] As shown in Scheme 2, the reaction that yields **4a** is believed to proceed by means of π coordination of the alkynyl ligand to the metal center to give **A**. Cleavage of the substituted allylic group is accompanied by a nucleophilic attack of the S atom to give **E**.[26] Dehydroxylation of **E** then leads to **4a**. The presence of HBF_4 might assist cleavage of the allylic group and enhances the rate of nucleophilic attack, thus making **4a** the only product.

A recent study by our group revealed that a metal carbene complex with a highly conjugated ring system might be oxidized in the presence of amines in air to yield aldehyde.[25] Also with a highly conjugated ring structure, **4a** undergoes an oxidation reaction in air in the presence of an excess amount of NEt_3 in CH_3CN at ambient temperature to afford 2-benzothiophenecarbaldehyde **13a** in 80% yield (see Scheme 3). In the absence of NEt_3, no aldehyde was obtained even under an oxygen atmosphere. Compound **13a** has been used as a precursor for the synthesis of dihydrofuro[3,4-*c*] pyridinones and shows inhibition of the cytolytic effects of the lymphocyte toxin perforin.[27]

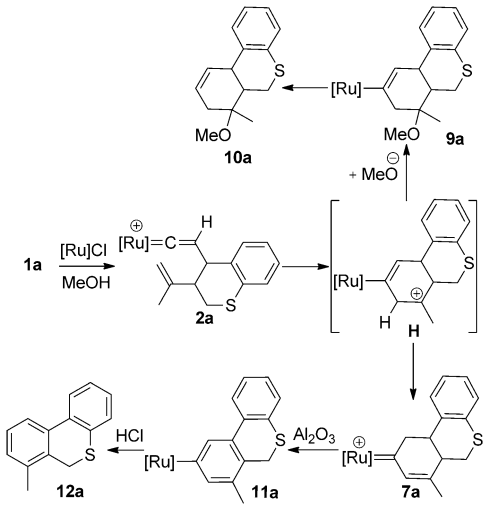


Scheme 3. Oxidation of **4a** to aldehyde.

The proposed pathway for the oxygenation is shown in Scheme 3.[25] Dissociation of a PPh_3 ligand provides a vacant site for coordination of O_2 to give **F**.[28] The promoter NEt_3 or dissociated PPh_3 is then treated with the activated oxygen to give $ONEt_3$ or $OPPh_3$ and a metal oxo/carbene complex.[29] Coupling of two ligands, induced by the incoming PPh_3 yields **G**,[30] which generates aldehyde **13a** in good yield.

Tandem Cyclization in MeOH

Previously, tandem cyclizations of all-carbon-chain aromatic enynes[8g] with methyl groups on the olefinic part in $CHCl_3$/MeOH were found to proceed through vinylidene intermediates that contain unsaturated olefinic groups on the ligand. Complex **2a** also has a tethering olefinic group on the vinylidene ligand, and is expected to show an additional cyclization reaction, which is indeed observed when the reaction is carried out in alcohol. Treatment of **1a** with [Ru]Cl in the presence of KPF_6 in MeOH at 60 °C affords the carbene complexes **7a** and **10a**, in addition to **3a**, in a ratio of 16:63:21 (see Scheme 4). Treatment of **2a** in MeOH at 60 °C also affords **7a** and **10a**. Two products, **7a** and **10a**, which have different tetrahydrobenzothiochromene units, were characterized by spectroscopic methods. For **7a**, the HMBC NMR spectrum shows correlations between the singlet ^1H peak at $\delta = 7.22$ ppm assigned to =CH with three ^{13}C resonances at $\delta = 62.86$, 39.48, and 23.78 ppm assigned to the methylene, bridgehead CH, and methyl carbon atoms, thereby revealing the C–C bond formation. For **10a**, the COSY NMR spectrum shows correlations of the multiplet resonance at $\delta = 5.58$ ppm, which is assigned to one of two olefinic =CH, with that of the next methylene group. Interestingly, aromatization occurs when **7a** is passed through a neutral Al_2O_3 column to give the yellow product **11a** with two aromatic rings (see Scheme 4). Two bridgehead CH resonances of **7a** disappear in the ^1H NMR spectrum of **11a**. When **11a** is treated with HCl, cleavage of the M–C bond gives **12a** in 86% yield. Two singlet peaks at $\delta = 3.84$ and 2.43 ppm in the ^1H NMR spectrum of **12a** are assigned to aliphatic CH_2 and Me groups, respectively.



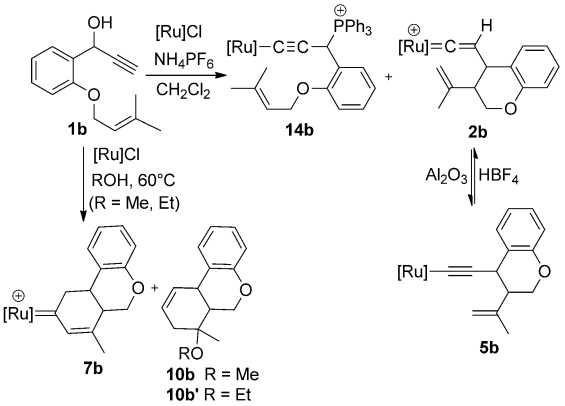
Scheme 4. Tandem cyclization of **1a** in MeOH.

Distribution of products for the reaction of **1a** in MeOH depends on the reaction temperature. The reaction at 0 °C failed to give the desired products. At room temperature, the reaction affords **7a** (31% yield) together with a mixture of **3a**, **4a**, and a new vinylidene complex **6a** in a ratio of 33:28:28:11. The structure of **6a** bears resemblance to **2a**. Presumably, addition of a methanol molecule to **C** generates **6a** in MeOH (see Scheme 2). Deprotonation of **6a** yields the yellow acetylide complex **8a**. The reaction of **1a** in MeOH at 40 °C for 1 day afforded **9a** with benzothiochromene, a precursor for **10a**, in 14% yield, in addition to **3a**, **4a**, and **7a**. The ratio of **9a**/**3a**/**4a**/**7a** is 9:41:28:22. The reaction at 40 °C for 3 days leads to the organic product **10a** by protonation of **9a**, along with **3a**, **4a**, and **7a**. As was mentioned above, the reaction in MeOH at 60 °C for 1 day gave **10a** in 37% yield. Conducting the reaction at a higher temperature in MeOH seems to promote tandem cyclization. Similarly, the reaction of **1a** with [Ru]Cl in EtOH at 60 °C also afforded **3a**, **7a**, and **10a′** with an ethoxy group.

Both **7a** and **9a** are formed through **2a**. As shown in Scheme 4, the second cyclization is believed to proceed by nucleophilic addition of the olefinic moiety to Cα of the vinylidene ligand, thereby affording the intermediate **H**, which contains a cationic charge on the tertiary carbon. Subsequent proton migration generates **7a**. Alternatively, the addition of a methoxide group at the tertiary carbocation of **H** gives **9a**. Experimental results from deuterium-labeling experiments are consistent with this pathway. The reaction of **1a** in MeOD affords **7a**–**d**, with deuteration at the Cβ methylene group, as indicated by the absence of the ^1H signals at $\delta = 3.86/2.20$ ppm. Complexes **7a** and **9a** are not interconvertible, since the attempted reaction of **7a** with MeOH in the presence of NaOMe fails to give **9a**.

Oxygen Analogue of 1a

The ruthenium-induced cyclization reaction of **1b** gives fewer products, which is most likely due to the relatively poor coordinating ability of oxygen. Treatment of the aromatic enyne **1b**, an oxygen analogue of **1a**, with [Ru]Cl in CH_2Cl_2 affords the analogous vinylidene complex **2b** and the phosphonium acetylide complex **14b** in a ratio of 1.5:1 (see Scheme 5). The reaction in the presence of an excess



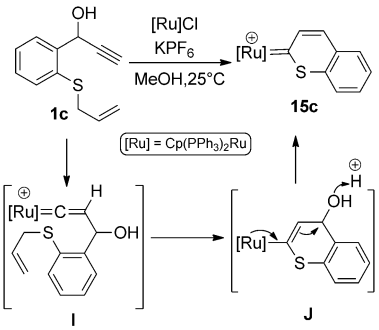
Scheme 5. Reactions of **1b** with [Ru]Cl.

amount of free phosphine gives only **14b** in 94% yield.[31] Deprotonation of **2b** yields the acetylide complex **5b**. The reactions of **1b** with [Ru]Cl in MeOH and EtOH also afford **10b** and **10b′**, respectively, in addition to **7b**. This tandem cyclization of **1b** yields no other side product.

Formation of similar fused cyclic compounds has been reported but in two separate steps.[13] An Ru-catalyzed cyclization by means of an allenylidene-ene process in the first step is followed by a Pt-catalyzed cycloisomerization in the second step. But in our case, tandem cyclizations readily take place in methanol.

Enynes with No Methyl Group

To study the effect of the methyl substituent on the olefinic group, we prepared the aromatic enyne **1c**, which contains an analogous olefinic chain similar to **1a** but has no methyl group. As shown in Scheme 6, treatment of **1c** with [Ru]Cl in the presence of KPF_6 in MeOH at 25°C afforded **15c** as the only isolable product. Nucleophilic attack of S onto Cα was accompanied by cleavage of the *S*-allylic bond. No product with a formed C−C bond was obtained. The structure of **15c** was determined by spectroscopic methods and was fully characterized by X-ray diffraction analysis. In the COSY NMR spectrum, the characteristic doublet resonance at $\delta = 7.87$ ppm assigned to CβH shows correlation with a multiplet resonance at $\delta = 7.05$ ppm assigned to CγH. In the 2D HMBC NMR spectrum, the triplet peak at $\delta =$ 247.10 ppm with $^2J(C,P) = 13.1$ Hz, which is assigned to Cα, shows correlations with the ^{1}H resonances of CβH and CγH.



Scheme 6. Reaction of **1c** with [Ru]Cl.

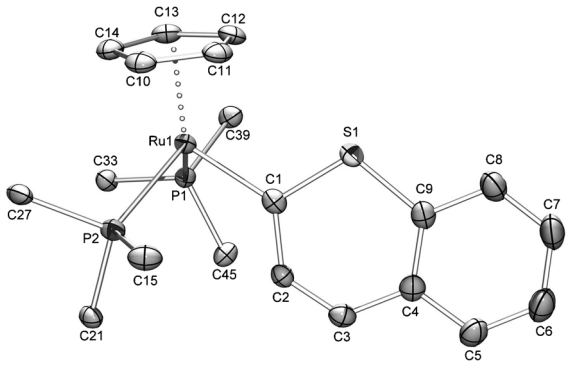


Figure 2. ORTEP drawing of **15c**. For clarity, the aryl group of the PPh_3 ligands on Ru except for the *ipso*-carbon atoms are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ru1−C1 2.015(2), C1−C2 1.425(3), C2−C3 1.354(3), C3−C4 1.426(3), S1−C1 1.719(2), S1−C9 1.745(2); Ru1−C1−C2 128.56(16), Ru1−C1−S1 116.13(12), C2−C1−S1 115.32(16), C1−C2−C3 129.1(2), C1−S1−C9 108.77(11).

Single crystals were obtained by slow evaporation of a solution of **15c** in CH_2Cl_2/hexanes. An ORTEP-type view of **15c** is shown in Figure 2. The Ru1−C1 bond length of 2.015(2) Å is similar to the Ru−C bond length of 2.065(7) Å found for $[Cp^*Ru\{C(SCH_2CH_2{-}CH_3)CH{=}CPh\}(CO)(PMeiPr_2)]^+$,[32] but is longer than that of a six-membered cyclic oxocarbene complex $[CpRu(=C_5H_8O)(dppe)][PF_6]$ (dppe = 1,2-bis(diphenylphosphino)ethane) (1.938 Å).[33]

The C2−C3 bond length of 1.354(3) Å is in the range of a typical double bond,[32] probably due to the conjugated system of the ring structure. Formation of **15c** most likely proceeds by means of the γ-hydroxyvinylidene intermediate **I**, followed by a nucleophilic attack of the sulfur atom to Cα to give **J**, accompanied by the cleavage of the allylic group (see Scheme 6). Dehydroxylation of **J** then leads to **15c**. Unlike **1a**, which shows reactivity of cyclization to result in a C−C bond formation, **1c** displays cyclization that involves a C−S bond formation.

For the cyclization of **1a**, the stability of the tertiary carbocation from the presence of two methyl groups should play the key role in promoting the reaction. The regioselectivities of sulfur attacks on the triple bonds for **1a** and **1c** are quite different. Here the S attack at Cα in **1c** indicates

intermediacy of a vinylidene or allenylidene ligand, whereas the S attack at Cβ in **1a** that leads to **4a** points to the presence of π coordination of the alkynyl ligand. Lack of methyl substituents in **1c** should enhance the rate of formation of the vinylidene ligand, possibly owing to the smaller steric effect. Unlike **4a**, complex **15c** is stable and no air oxidation was observed.

Conclusion

Tandem cyclization of the aromatic O-containing enyne **1b** to cleanly yield **7b** and **10b** with benzochromene groups is induced by [Ru]Cl in MeOH. The reaction proceeds through a first cyclization to give the vinylidene complex **2b**, which is isolated for the reaction in CH_2Cl_2, and in MeOH the second cyclization proceeds to give final products. A similar reaction of S-containing enyne **1a** yields analogous benzothiochromene products **7a**, **10a**, and other side products **3a** and **4a**. The formation of **3a** and **4a** is believed to proceed through a π-coordinated alkyne intermediate instead of the vinylidene species. For **1a**, the reaction conditions can be adjusted to yield exclusively **4a**, which is oxidized by O_2 in the presence of Et_3N to give an aldehyde product. The presence of methyl substituents on the olefinic part of these enynes promotes their cyclization reactions. Therefore the reaction of enyne **1c**, which has no methyl group in the olefinic part, gives nucleophilic addition of S onto Cα accompanied by the cleavage of a C–S bond of the allylic group to yield complex **15c** with a six-membered cyclic thiocarbene ligand.

Experimental Section

General Procedures

The manipulations were performed under an atmosphere of dry nitrogen by using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The ruthenium complexes $[Cp(PPh_3)_2RuCl]$,[34] **1b**,[13] and **1c**[9f] were prepared by following the methods reported in the literature. The C and H analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instruments at National Taiwan University. Mass spectra were recorded with LCQ Advantage (ESI) and Finnigan MAT 95S (EI) mass spectrometers. NMR spectra were recorded with Bruker AvanceIII 400 or DMX-500 FT-NMR spectrometers at room temperature (unless stated otherwise). ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ and CD_2Cl_2 at ambient temperature, and chemical shifts are expressed in parts per million. Proton chemical shifts are referenced to $\delta = 7.26$ ($CDCl_3$), 5.32 (CD_2Cl_2), 7.15 (C_6D_6), and 2.05 ppm ([D_6]acetone). Carbon chemical shifts are referenced to $\delta = 77.1$ ($CDCl_3$), 53.92 (CD_2Cl_2), 127.69 (C_6D_6), and 205.36 and 28.99 ppm ([D_6]acetone). The ^{31}P NMR spectra were measured relative to external 85% phosphoric acid. Both ^{13}C and ^{31}P spectra were proton decoupled spectra.

*Synthesis of **1a***

*n*BuLi (9.9 mL, 25 mmol) was added to a solution of Me_3SiCCH (4.9 mL, 34 mmol) in THF (10 mL) at −78 °C under nitrogen. After 20 min, 2-(3-methylbut-2-enylthio)benzaldehyde[35] (3.2 g, 16 mmol) in dry diethyl ether (10 mL) was added. The mixture was kept at −78 °C for 30 min and was allowed to warm to room temperature. Then the mixture was quenched with saturated aqueous NH_4Cl solution and extracted with diethyl ether (3×10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated to give the crude product, which was purified by flash chromatography on a silica gel column (hexanes/ethyl acetate (EA) 9:1) to give **S1** (4.26 g, 88% yield). ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.69$ (dd, $^3J(H,H) = 7.4$ Hz, $^4J(H,H) = 1.8$ Hz, 1H; Ph), 7.44 (dd, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; Ph), 7.28 (m, 2H; Ph), 5.96 (s, 1H; CH), 5.28 (m, 1H; =CH), 3.52 (d, $^3J(H,H) = 7.9$ Hz, 2H; CH_2), 2.97 (br, 1H; OH), 1.69 (s, 3H; Me), 1.45 (s, 3H; Me), 0.19 ppm (s, 9H; Me_3Si); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 142.06$ (Ph), 137.04 (=$C(Me)_2$), 134.23, 133.54, 128.68, 127.70, 127.66 (Ph), 119.24 (=CH), 105.04 (≡C), 91.55 (≡C), 63.23 (CH), 34.00 (CH_2), 25.65 (Me), 17.55 (Me), −0.14 ppm (Me_3Si).

Bu_4NF (1 M solution in THF, 19.7 mL, 19.7 mmol) was added to a solution of **S1** (3.0 g, 9.9 mmol) in THF (10 mL) at room temperature. After 4 h the reaction was extracted with diethyl ether. The combined organic layer was washed with brine, dried over $MgSO_4$, and subjected to flash column chromatography over silica gel eluting with a mixture of 9:1 hexanes/EA to give **1a** (2.16 g, 94% yield). ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.70$ (m, 1H; Ph), 7.44 (m, 1H; Ph), 7.28 (m, 2H; Ph), 5.96 (s, 1H; CH), 5.28 (m, 1H; =CH), 3.53 (d, $^3J(H,H) = 7.9$ Hz, 2H; CH_2), 2.97 (br, 1H; OH), 2.65 (d, $^3J(H,H) = 2.3$ Hz, 1H; C≡CH), 1.69 (s, 3H; Me), 1.48 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 141.45$ (Ph), 137.21 (=$C(Me)_2$), 134.31, 133.14, 128.90, 127.63, 127.47 (Ph), 119.06 (=CH_2), 83.39 (≡C), 74.94 (≡CH), 62.64 (CH), 33.97 (CH_2), 25.66 (Me), 17.57 ppm (Me).

*Synthesis of **2a** and **5a***

A mixture of [Ru]Cl (300 mg, 0.41 mmol), **1a** (143 mg, 0.62 mmol), and NH_4PF_6 (167.0 mg, 1.03 mmol) in CH_2Cl_2 (40 mL) was stirred at ambient temperature for 1 day. The solvent was removed under vacuum, and CH_2Cl_2 was used to extract the product. The crude mixture was filtered through Celite to remove the insoluble precipitates. The filtrate was concentrated to approximately 5 mL and was added to a stirred diethyl ether (60 mL) to produce olive-colored precipitates. The powder was collected, washed with diethyl ether, and dried under vacuum to give a mixture of **2a**, **3a**, and **4a**. The mixture was dissolved in CH_2Cl_2 and was passed through an acidic Al_2O_3 column eluted with hexanes/diethyl ether/CH_2Cl_2. Collection of the yellow band followed by drying under vacuum resulted in **5a** (278 mg, 75% yield). ^1H NMR (400.1 MHz, C_6D_6): $\delta =$ 7.61–6.88 (m, Ph), 5.12 (s, 1H; =CH), 5.03 (s, 1H; =CH), 4.37 (s, 5H; Cp), 4.29 (s, 1H; CγH), 4.11 (t, $^3J(H,H) = 11.5$ Hz, 1H; CH_2), 2.84 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH_2), 2.57 (d, $^3J(H,H) = 11.4$ Hz, 1H; CH), 1.88 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 147.07$–123.51 (Ph, =C), 110.90 (=CH_2), 108.71 (Cβ), 99.82 (t, $^2J(C,P) = 24.8$ Hz; Cα), 85.45 (Cp), 44.80 (CH), 39.68 (Cγ), 27.22 (CH_2), 22.59 ppm (Me); ^{31}P NMR (162.0 MHz, C_6D_6): $\delta = 51.84$, 51.39 ppm (2d, $^2J(P,P) = 37.4$ Hz; PPh_3); elemental analysis calcd (%) for $C_{55}H_{48}P_2RuS$: C 73.07, H 5.35; found: C 73.36, H 5.47; ESI-MS: m/z: 905.21 $[M+1]^+$.

A solution of $HBF_4{\cdot}Et_2O$ (48%, 0.02 mL, 0.11 mmol) in diethyl ether (20 mL) was added dropwise at 0 °C to a stirred solution of **5a** (300 mg, 0.33 mmol) in diethyl ether (10 mL). Insoluble solid precipitated immediately, but the addition was continued until no further solid was formed. The solution was then decanted, and the pink solid was washed with diethyl ether and dried under vacuum to yield **2a** (225 mg, 75% yield). ^1H NMR (400.1 MHz, CD_2Cl_2): $\delta = 7.43$–6.50 (m; Ph), 5.09 (s, 1H; =CH_2), 5.00 (s, 5H; Cp), 4.84 (s, 1H; =CH_2), 4.43 (d, $^2J(H,H) = 7.0$ Hz, 1H; CβH), 3.99 (d, $^2J(H,H) = 6.6$ Hz, 1H; CγH), 3.28 (t, $^2J(H,H) = 12.1$ Hz, 1H; CH_2), 3.00 (m, 1H; CH_2), 2.51 (d, $^2J(H,H) = 11.8$ Hz, 1H; CH), 1.81 ppm (s, 3H; Me); ^{13}C NMR (125.8 MHz, CD_2Cl_2): $\delta = 347.55$ (t, $^2J(C,P) = 15.3$ Hz; Cα), 145.16–124.49 (Ph, =C), 112.56 (=CH_2), 112.09 (Cβ), 94.59 (Cp), 44.29 (CH), 38.10 (Cγ), 26.58 (CH_2), 23.18 ppm (Me); ^{31}P NMR (162.0 MHz, $CDCl_3$): $\delta = 42.52$, 40.28 ppm (2d, $^2J(P,P) = 26.7$ Hz, PPh_3); elemental analysis calcd (%) for $C_{55}H_{49}BF_4P_2RuS$: C 66.60, H 4.98; found: C 66.03, H 5.28; ESI-MS: m/z: 905.21 $[M]^+$.

*Synthesis of **3a***

A mixture of [Ru]Cl (200 mg, 0.27 mmol), **1a** (94 mg, 0.41 mmol), and NH_4PF_6 (111.7 mg, 1.03 mmol) in CH_2Cl_2 (40 mL) was stirred at 40 °C for 1 day. The solvent was removed under vacuum, and CH_2Cl_2 was used to extract the crude product. The mixture was filtered through Celite to remove the insoluble precipitates. The filtrate was concentrated to approximately 5 mL and added to stirred diethyl ether (60 mL) to produce the olive-colored precipitates. The powder was collected, washed with diethyl ether, and dried under vacuum to give complex **3a** (217 mg, 86% yield). ^{1}H NMR (500.1 MHz, $CDCl_3$, 233 K): δ = 7.79–5.98 (m; Ph), 5.60 (d, ^2J(H,P) = 34.7 Hz, 1H; =CHPPh$_3$), 5.23 (s, 1H; =CH), 5.17 (d, ^3J(H,H) = 7.0 Hz, 1H; Ph), 4.79 (s, 5H; Cp), 4.75 (s, 1H; CH), 3.79 (t, ^2J(H,H) = 11.0 Hz, 1H; CH_2), 3.49 (d, ^2J(H,H) = 8.4 Hz, 1H; OH), 3.34 (br, 1H; CH_2), 1.43 (s, 3H; Me), 0.49 ppm (s, 3H; Me); ^{13}C NMR (125.8 MHz, $CDCl_3$, 233 K): δ = 233.28 (t, ^2J(C,P) = 14.6 Hz; Cα), 141.93–122.50 (Ph), 117.90 (=CH), 101.96 (dd, ^1J(C,P) = 53.9 Hz, ^3J(C,P) = 8.3 Hz; CHPPh$_3$), 80.82 (Cp), 76.72 (CH), 49.15 (CH_2), 26.64 (Me), 16.97 ppm (Me); ^{31}P NMR (202.5 MHz, $CDCl_3$, 233 K): δ = 55.93 (s; PPh$_3$), −5.37 ppm (s; PPh$_3$); single crystals of **3a** were obtained from CH_2Cl_2/hexanes; elemental analysis calcd (%) for $C_{55}H_{51}F_6OP_3RuS$: C 61.85, H 4.81; found: C 61.53, H 4.98; ESI-MS: *m*/*z*: 923.22 $[M]^+$.

*Synthesis of **4a***

Method A: A mixture of [Ru]Cl (100 mg, 0.14 mmol), **1a** (48 mg, 0.21 mmol), and KPF_6 (63.0 mg, 0.34 mmol) in MeOH (20 mL) with 2 drops of HBF_4·Et_2O was stirred at ambient temperature for 1 day. The crude product was processed similarly to that for **3a**. The powder was washed with diethyl ether and dried under vacuum to give **4a** (100 mg, 78% yield). Method B: A mixture of [Ru]NCCH$_3^+$ (200 mg, 0.23 mmol), **1a** (95 mg, 0.41 mmol), and NH_4PF_6 (110 mg, 0.69 mmol) in CH_2Cl_2 (40 mL) was stirred at room temperature for 3 days. The crude mixture was processed similarly to that for **3a**. The filtrate was concentrated to approximately 5 mL and added to a stirred diethyl ether (60 mL) to produce the olive-colored precipitates. The powder was collected, washed with diethyl ether, and dried under vacuum to give complex **4a** (186 mg, 83% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 14.92 (t, ^3J(P,H) = 11.2 Hz, 1H; CαH), 8.12–6.96 (m; Ph), 5.15 ppm (s, 5H; Cp); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 287.18 (Cα), 165.42–123.71 (Ph, =C), 94.68 ppm (Cp); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 46.06 ppm (s; PPh$_3$); elemental analysis calcd (%) for $C_{50}H_{41}F_6P_3RuS$: C 61.16, H 4.21; found: C 61.42, H 4.33; ESI-MS: *m*/*z*: 837.14 $[M]^+$.

*Synthesis of **6a** and **8a***

A mixture of [Ru]Cl (300 mg, 0.41 mmol), **1a** (143 mg, 0.62 mmol), and KPF_6 (189.0 mg, 1.03 mmol) in MeOH (40 mL) was stirred at ambient temperature for 1 day. The crude mixture was obtained similarly to that for **5a**. The mixture was dissolved in CH_2Cl_2 and was passed through an Al_2O_3 column eluted with hexanes/diethyl ethers/CH_2Cl_2. Collection of the first yellow band followed by drying under vacuum resulted in **8a** (49 mg, 83% yield). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.67–6.57 (m; Ph), 4.18 (s, 5H; Cp), 3.91 (s, 1H; CγH), 3.79 (t, ^3J(H,H) = 11.5 Hz, 1H; CH_2), 3.21 (s, 3H; OMe), 2.92 (d, ^3J(H,H) = 11.2 Hz, 1H; CH_2), 2.08 (d, ^3J(H,H) = 11.9 Hz, 1H; CH), 1.57 (s, 3H; Me), 1.40 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 139.82–123.20 (Ph), 109.62 (Cβ), 100.30 (t, ^2J(C,P) = 24.9 Hz; Cα), 84.94 (Cp), 76.96 (C(OMe)(Me)$_2$), 48.23 (OMe), 45.57 (CH), 37.01 (Cγ), 24.65 (CH_2), 23.22 (Me), 23.00 ppm (Me); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 51.95, 50.41 ppm (2d, ^2J(P,P) = 37.0 Hz; PPh$_3$); elemental analysis calcd (%) for $C_{56}H_{52}OP_2RuS$: C 71.85, H 5.06; found: C 71.98, H 5.21; ESI-MS: *m*/*z*: 937.23 $[M+1]^+$.

Synthesis of **6a** (86 mg, 80% yield) was achieved by treating **8a** (98 mg, 0.10 mmol) with HBF_4·Et_2O (48%, 0.02 mL, 0.11 mmol) until no further solid was formed at 0 °C, followed by the same purification procedure as that for the synthesis of **2a**. Data of **6a**: ^{1}H NMR (400.2 MHz, CD_2Cl_2): δ = 7.67–6.80 (m; Ph), 6.10 (d, ^2J(H,H) = 7.6 Hz, 1H; Ph), 5.15 (m, 1H; CβH), 4.96 (s, 5H; Cp), 4.36 (d, ^2J(H,H) = 5.9 Hz, 1H; CγH), 3.28 (t, ^2J(H,H) = 12.1 Hz, 1H; CH_2), 3.20 (s, 3H; OMe), 3.15 (m, 1H; CH_2), 1.85 (m, 1H; CH), 1.35 (s, 3H; Me), 1.32 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 348.79 (br; Cα), 139.32–124.38 (Ph), 112.14 (Cβ), 93.71 (Cp), 76.44 (C(OMe)(Me)$_2$), 49.03 (OMe), 46.94 (CH), 35.08 (Cγ), 24.07 (CH_2), 23.88 (Me), 23.24 ppm (Me); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 43.06, 40.04 ppm (2d, ^2J(P,P) = 27 Hz; PPh$_3$); elemental analysis calcd (%) for $C_{56}H_{53}BF_4OP_2RuS$: C 65.69, H 5.22; found: C 65.48, H 5.13; ESI-MS: *m*/*z*: 937.23 $[M]^+$.

*Synthesis of **7a***

A mixture of [Ru]Cl (200 mg, 0.27 mmol), **1a** (96 mg, 0.41 mmol), and KPF_6 (126 mg, 0.69 mmol) in MeOH (40 mL) was stirred at 60 °C for 1 day. The crude product was processed similarly to that for **3a**. The mixture was collected, washed with diethyl ether, and dried under vacuum to give a mixture of **3a** (34% yield) and **7a** (29% NMR spectroscopic yield). Data of **7a**: ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 7.80–6.62 (m; Ph, =CH), 4.86 (s, 5H; Cp), 3.86 (m, 1H; CβH$_2$), 3.01 (d, ^3J(H,H) = 11.8 Hz, 1H; CγH), 2.63 (d, ^3J(H,H) = 10.2 Hz, 1H; SCH$_2$), 2.49 (t, ^3J(H,H) = 12.1 Hz, 1H; SCH$_2$), 2.30 (m, 1H; CH), 2.20 (m, 1H; CβH$_2$), 1.28 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 313.80 (t, ^2J(C,P) = 9.3 Hz; Cα), 150.61 (=CH), 150.09–124.72 (Ph), 94.97 (Cp), 62.86 (CβH$_2$), 39.48 (CH), 38.96 (CγH), 23.78 (Me), 22.79 ppm (SCH$_2$); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 44.84, 44.37 ppm (2d, ^2J(P,P) = 28.63 Hz; PPh$_3$); ESI-MS: *m*/*z*: 905.21 $[M]^+$. Pure complex **7a** was not obtained.

*Synthesis of **9a***

A mixture of [Ru]Cl (300 mg, 0.41 mmol), **1a** (143 mg, 0.62 mmol), and KPF_6 (189.0 mg, 1.03 mmol) in MeOH (40 mL) was stirred at 40 °C for 1 day. The crude was processed similarly to that for **3a**. The mixture in CH_2Cl_2 (5 mL) was added to stirred hexanes (60 mL) to produce the olive-colored precipitates and yellow filtrate. The yellow filtrate was collected and concentrated to approximately 15 mL at 0 °C to produce the desired yellow precipitates, which were dried under vacuum to give **9a** (131 mg, 14% yield). ^{1}H NMR (400.2 MHz, C_6D_6): δ = 7.44–6.43 (m; Ph), 4.90 (s, 1H; =CH), 4.30 (s, 5H; Cp), 3.19 (br, 1H; CH), 3.12 (s, 3H; OMe), 2.92 (m, 2H; CH_2), 2.85 (m, 2H; CH_2), 2.27 (m, H; CH), 1.20 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 142.94 (t, ^2J(C,P) = 16.6 Hz; Cα), 140.10–122.92 (Ph, =C), 85.09 (Cp), 76.30 (C(OMe)), 54.33 (CH_2), 47.41 (OMe), 43.63 (CH), 39.24 (CH), 23.25 (SCH$_2$), 21.75 ppm (Me); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 53.83, 49.74 ppm (2d, ^2J(P,P) = 37.1 Hz, PPh$_3$); elemental analysis calcd (%) for $C_{56}H_{52}OP_2RuS$: C 71.85, H 5.60; found: C 72.23, H 5.86; ESI-MS: *m*/*z*: 937.23 $[M+1]^+$.

*Synthesis of **10a***

A mixture of [Ru]Cl (200 mg, 0.27 mmol), **1a** (96 mg, 0.41 mmol), and KPF_6 (126 mg, 0.69 mmol) in MeOH (40 mL) was heated to 60 °C for 1 day. The crude product was processed similarly to that for **9a**. The yellow solution was purified by flash chromatography on a silica gel column (hexanes/diethyl ether 9:1) to give **10a** (24.7 mg, 37% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.13–7.03 (m, 4H; Ph), 5.54 (m, 2H; =CH, =CH), 3.53 (br, 1H; CH), 3.24 (s, 3H; OMe), 2.89 (d, ^3J(H,H) = 12.4 Hz, 1H; SCH$_2$), 2.77 (t, ^3J(H,H) = 12.0 Hz, 1H; SCH$_2$), 2.41 (m, 1H; CH), 2.12 (m, 2H; CH_2), 1.33 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 135.68, 133.16, 130.83 (Ph), 130.33 (=CH), 126.57, 126.35, 124.29 (Ph), 123.65 (=CH), 75.01 (C), 48.34 (OMe), 40.48 (CH), 39.59 (CH), 34.33 (CH_2), 22.79 (CH_2), 21.63 ppm (Me); EI-MS: *m*/*z*: 246.1078. Pure compound **10a** was not obtained.

*Synthesis of **10a′***

Compound **10a′** (21 mg, 30% yield) was similarly prepared from a mixture of [Ru]Cl (200 mg, 0.27 mmol), **1a** (96 mg, 0.41 mmol), and KPF_6 (126 mg, 0.69 mmol) in EtOH (40 mL) at 60 °C for 1 day. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.18–7.04 (m, 4H; Ph), 5.55 (m, 2H; =CH, =CH), 3.56 (br, 1H; CH), 3.48 (q, ^3J(H,H) = 7.0 Hz, 2H; OCH$_2$), 2.93 (m, 1H; SCH$_2$), 2.81 (t, ^3J(H,H) = 12.1 Hz, 1H; SCH$_2$), 2.40 (m, 1H; CH), 2.12 (m, 2H; CH_2), 1.33 (s, 3H; Me), 1.21 ppm (t, ^3J(H,H) = 7.0 Hz, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 135.87, 133.22, 130.91 (Ph), 130.33 (=CH), 126.66, 126.41, 124.35 (Ph), 123.85 (=CH), 74.93 (C), 55.69 (OCH$_2$), 40.93 (CH), 39.65 (CH), 34.84 (CH_2), 23.01 (SCH$_2$), 22.46 (Me),

16.07 ppm (Me); elemental analysis calcd (%) for $C_{16}H_{20}OS$: C 73.80, H 7.74; found: C 73.96, H 7.83; EI-MS: *m/z*: 260.1235.

*Synthesis of **11a***

The mixture of **3a** and **7a** was passed through a neutral Al_2O_3 column eluted with diethyl ether/CH_2Cl_2. A yellow band and the second olive-colored band were collected separately followed by drying under vacuum to result in **11a** (71 mg, 46%) and **3a** (90 mg, 49%). Data of **11a**: ^{1}H NMR (400.2 MHz, CD_2Cl_2): δ = 7.72–6.68 (m; Ph), 4.28 (s, 5H; Cp), 3.69 (s, 2H; CH_2), 1.96 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 154.62 (t, ^2J(C,P) = 15.3 Hz; Cα), 149.68, 143.29, 139.92–124.49 (Ph), 85.95 (Cp), 27.24(CH_2), 18.80 ppm (Me); ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 51.11 ppm (s; PPh_3); elemental analysis calcd (%) for $C_{55}H_{46}P_2RuS$: C 73.23, H 5.14; ESI-MS: *m/z*: 903.18 $[M+1]^+$. Pure complex **11a** was not obtained.

*Synthesis of **12a***

HCl (1M, 0.08 mL) was added to a solution of **11a** (72 mg, 0.08 mmol) in $CHCl_3$ (10 mL). The resulting solution was stirred at ambient temperature for 1 day, and CH_3Cl was removed under vacuum. The crude was purified by flash chromatography on a silica gel column (hexanes/EA 4:1) to give **12a** (14.5 mg, 86% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.77 (d, ^3J(H,H) = 7.6 Hz, 1H; Ph), 7.54 (d, ^3J(H,H) = 7.6 Hz, 1H; Ph), 7.44 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.4 Hz, 1H; Ph), 7.23 (m, 4H; Ph), 3.84 (s, 2H; SCH_2), 2.43 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 135.20, 134.68, 134.23, 133.58, 132.66, 129.90, 128.12, 127.42, 127.07, 126.23, 126.06, 124.08 (Ph), 27.32 (SCH_2), 19.90 ppm (Me); elemental analysis calcd (%) for $C_{14}H_{12}S$: C 79.20, H 5.70; found: C 78.78, H 5.84; EI-MS: *m/z*: 212.0660.

*Synthesis of **13a***

NEt_3 (5 mL) and CH_3CN (10 mL) in air were added to a flask that contained **4a** (300 mg, 0.36 mmol). The flask was opened to air, and the mixture was stirred at room temperature for 1 day. The originally brown solution turned into a dark solution. Then solvent was removed under vacuum. The residue was purified by flash chromatography (silica gel, hexanes/diethyl ether 4:1) to afford **13a** (46.4 mg, 80%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 10.12 (s, 1H; CHO), 8.04 (s, 1H; =CH), 7.95 (d, ^3J(H,H) = 7.9 Hz, 1H; Ph), 7.91 (m, 1H; Ph), 7.51 (m, 1H; Ph), 7.44 ppm (m, 1H; Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 184.65 (CH=O), 134.40 (=CH), 128.17, 126.27, 125.27, 123.34 ppm (Ph); elemental analysis calcd (%) for C_9H_6OS: C 66.64, H 3.73; found: C 66.50, H 3.79; EI-MS: *m/z*: 162.0139.

*Synthesis of **14b***

A mixture of [Ru]Cl (200 mg, 0.28 mmol), **1b** (119 mg, 0.55 mmol), KPF_6 (76 mg, 0.41 mmol), and PPh_3 (217 mg, 0.83 mmol) in MeOH (25 mL) was stirred at ambient temperature for 1 day. The resulting yellow solvent was removed under vacuum, and CH_2Cl_2 was used to extract the crude product. The mixture was filtered through Celite to remove insoluble precipitates. The filtrate was concentrated to approximately 5 mL and added to a stirred diethyl ether (60 mL) to produce the yellow precipitates, which were filtered and dried under vacuum to give complex **14b** (298 mg, 94% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.32–6.72 (m, 49H; Ph), 5.32 (dd, ^4J(H,H) = 17.7 Hz, ^4J(H,H) = 2.0 Hz, 1H; Cγ H), 4.93 (t, ^3J(H,H) = 7 Hz, 1H;=CH), 4.30 (dd, ^3J(H,H) = 11.3 Hz, ^2J(H,H) = 8.1 Hz, 1H; OCH_2), 4.22 (s, 5H; Cp), 3.72 (dd, ^3J(H,H) = 11.3 Hz, ^2J-(H,H) = 8.1 Hz, 1H; OCH_2), 1.78 (s, 1H; Me), 1.63 ppm (s, 1H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 155.44 (Ph), 138.22 (=$C(Me)_2$), 137.81–120.25 (Ph), 118.86 (=CH), 118.06 (Cβ), 111.24 (Ph), 97.66 (d, ^2J-(C,P) = 9.2 Hz; Cα), 84.58 (Cp), 64.71 (OCH_2), 33.33 (d, ^1J(C,P) = 47.1 Hz; Cγ), 25.81 (Me), 18.16 ppm (Me); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 50.66, 48.79 (dd, ^2J(P,P) = 35.2 Hz; PPh_3), 14.82 ppm (s; $CPPh_3$); elemental analysis calcd (%) for $C_{73}H_{64}F_6OP_4Ru$: C 67.64, H 4.98; found: C 67.55, H 5.06; ESI-MS: *m/z*: 1151.32 $[M]^+$.

*Synthesis of **2b** and **5b***

Complex **14b** (300 mg, 0.26 mmol) in CH_2Cl_2 was passed through a column packed with neutral Al_2O_3 eluted with diethyl ether and EA. Collection of the yellow band followed by drying under vacuum resulted in a crude mixture. The crude mixture was dissolved in diethyl ether and was passed through a neutral Al_2O_3 column eluted with hexanes/diethyl ether. Collection of the yellow band followed by drying under vacuum resulted in the product **5b** (140 mg, 80% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.79–7.38 (m; Ph), 5.01 (s, 1H; =CH), 4.80 (s, 1H; =CH), 4.64 (d, ^3J(H,H) = 10.9 Hz, 1H; OCH_2), 4.62 (t, ^3J(H,H) = 9.45 Hz, 1H; OCH_2), 4.18 (s, 5H; Cp), 4.12 (s, 1H; Cγ H), 2.60 (d, ^3J(H,H) = 9.3 Hz, 1H; CH), 2.01 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 153.09–116.22 (Ph, =C), 109.88 (=CH_2), 108.74 (Cβ), 98.14 (t, ^2J(C,P) = 26.9 Hz; Cα), 85.15 (Cp), 66.16 (OCH_2), 43.27 (CH), 36.05 (Cγ), 22.71 ppm (Me); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 51.45, 50.75 ppm (2d, ^2J(P,P) = 37.5 Hz, PPh_3); elemental analysis calcd (%) for $C_{55}H_{48}OP_2Ru$: C 74.39, H 5.45; found: C 74.60, H 5.54; ESI-MS: *m/z*: 889.23 $[M+1]^+$.

A solution of HBF_4·Et_2O (48%, 0.02 mL, 0.11 mmol) in dry diethyl ether (20 mL) was added dropwise at 0°C to a stirred solution of **5b** (140 mg, 0.16 mmol) in diethyl ether (10 mL). Insoluble solid precipitates formed immediately, but the addition was continued until no further solid was formed. The solution was then decanted, and the slightly orange solid was washed with diethyl ether and dried under vacuum to yield **2b** (116 mg, 82% yield). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 7.27–6.76 (m; Ph), 5.09 (s, 1H; =CH_2), 5.03 (s, 5H; Cp), 4.86 (s, 1H; =CH_2), 4.66 (s, 1H; OCH_2), 4.48 (d, ^3J(H,H) = 8.0 Hz, 1H; Cβ H), 4.20 (s, 1H; OCH_2), 4.05 (dd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 4.9 Hz, 1H; Cγ H), 2.53 (m, 1H; CH), 1.79 ppm (s, 3H; Me); ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 347.16 (t, ^2J(C,P) = 15.2 Hz; Cα), 154.10–117.13 (Ph, =C), 116.08 (=CH_2), 112.92 (Cβ), 94.84 (Cp), 66.20 (OCH_2), 43.78 (CH), 33.75 (Cγ), 23.47 ppm (Me); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 42.52, 40.28 ppm (2d, ^2J(P,P) = 26.7 Hz; PPh_3); ESI-MS: *m/z*: 889.23 $[M]^+$. Pure complex **2b** was not obtained.

*Synthesis of **7b***

A mixture of [Ru]Cl (400 mg, 0.55 mmol), **1b** (239 mg, 1.10 mmol), and KPF_6 (203 mg, 1.10 mmol) in MeOH (30 mL) was stirred at 60°C for 1 day. The crude mixture was obtained similarly to that for **14b**. The filtrate was concentrated to approximately 5 mL and added to stirred diethyl ether (60 mL) to produce the olive-colored precipitates. The powder was collected, washed with diethyl ether, and dried under vacuum to give **7b** (125 mg, 52% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.66–6.78 (m; Ph, =CH), 4.90 (s, 5H; Cp), 4.07 (d, ^3J(H,H) = 10.3 Hz, 1H; OCH_2), 4.04 (m, 1H; Cβ H_2), 3.57 (t, ^3J(H,H) = 10.3 Hz, 1H; OCH_2), 2.48 (m, 1H; Cβ H_2), 2.88 (d, ^3J(H,H) = 9.4 Hz, 1H; Cγ H), 2.29 (m, 1H; CH), 1.21 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 314.50 (t, ^2J(C,P) = Hz; Cα), 153.73–116.90 (Ph), 151.98 (=CH), 94.90 (Cp), 62.68 (Cβ H_2), 61.50 (OCH_2), 39.21 (CH), 34.53 (Cγ H), 23.68 ppm (Me); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 45.08, 44.33 ppm (2d, ^2J(P,P) = 28.74 Hz; PPh_3); ESI-MS: *m/z*: 889.23 $[M]^+$. Pure complex **7b** was not obtained.

*Synthesis of **10b***

A mixture of [Ru]Cl (500 mg, 0.69 mmol), **1b** (298 mg, 1.38 mmol), and KPF_6 (190 mg, 1.30 mmol) in MeOH (50 mL) was stirred at ambient temperature for 1 day. Solvent of the resulting brownish-black solution was removed under vacuum, and CH_2Cl_2 was used to extract the crude product. The mixture was filtered through Celite to removed insoluble precipitates. The crude mixture was processed similarly to that for **9a**. The yellow solution was purified by flash column chromatography over an Al_2O_3 column by eluting with a mixture of hexanes/diethyl ether (8:1) to give **10b** (192 mg, 61%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.17 (d, ^3J-(H,H) = 7.6 Hz, 1H; Ph), 7.10 (t, ^3J(H,H) = 7.6 Hz, 1H; Ph), 6.90 (t, ^3J-(H,H) = 7.3 Hz, 1H; Ph), 6.83 (d, ^3J(H,H) = 8.2 Hz, 1H; Ph), 5.65 (d, ^3J-(H,H) = 10.0 Hz, 1H; =CH_2), 5.53 (m, 1H; =CH_2), 4.35 (ddd, ^2J(H,H) = 10.6 Hz, ^3J(H,H) = 3.4 Hz, ^5J(H,H) = 1.3 Hz, 1H; OCH_2), 3.69 (t, ^2J-(H,H) = 10.8 Hz, 1H; OCH_2), 3.38 (s, 1H; CH), 3.30 (s, 3H; OMe), 2.42 (m, 1H; CH), 2.07(m, 2H; CH_2), 1.32 ppm (s, 3H; Me); ^{13}C NMR

(100.6 MHz, $CDCl_3$): $\delta = 154.82$ (OPh), 129.63, 127.45, 124.56, 120.52, 116.78 (Ph), 129.38 (=CH_2), 123.30 (=CH_2), 73.76 (C), 63.58 (OCH_2), 48.30 (OMe), 38.20 (CH), 36.44 (CH), 34.35 (CH_2), 21.76 ppm (Me); elemental analysis calcd (%) for $C_{15}H_{18}O_2$: C 78.23, H 7.88; found: C 77.86, H 8.14; EI-MS: m/z: 230.1307.

Synthesis of ***10b′***

Compound **10b′** (160 mg, 47% yield) was similarly prepared from a mixture of [Ru]Cl (500 mg, 0.69 mmol), **1b** (298 mg, 1.38 mmol), and KPF_6 (190 mg, 1.30 mmol) in EtOH (50 mL) at 60°C for 1 day. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.15$ (t, ^3J(H,H) = 7.6 Hz, 1H; Ph), 7.08 (d, ^3J(H,H) = 7.6 Hz, 1H; Ph), 6.89 (t, ^3J(H,H) = 7.4 Hz, 1H; Ph), 6.81 (d, ^3J(H,H) = 8.2, 1H; Ph), 5.64 (d, ^3J(H,H) = 10.1 Hz, 1H; =CH), 5.54 (m, 1H; =CH), 4.36 (m, 1H; OCH_2), 3.70 (t, ^2J(H,H) = 10.9 Hz, 1H; OCH_2), 3.51 (m, 2H; OCH_2), 3.37 (s, 1H; CH), 2.42 (m, 1H; CH), 2.08 (m, 2H; CH_2), 1.32 (s, 3H; Me), 1.98 ppm (t, ^3J(H,H) = 7.0 Hz, 3H; OCH_2Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 154.89$ (OPh), 129.63, 127.47, 124.73, 120.54, 116.81 (Ph), 129.36 (=CH_2), 123.47 (=CH_2), 73.60 (C), 63.83 (OCH_2), 55.64 (OCH_2Me), 38.61 (CH), 36.49 (CH), 34.96 (CH_2), 22.55 (Me), 16.00 ppm (OCH_2Me); elemental analysis calcd (%) for $C_{16}H_{20}O_2$: C 78.65, H 8.25; found: C 78.34, H 8.41; EI-MS: m/z: 244.1463.

Synthesis of ***15c***

A mixture of [Ru]Cl (300 mg, 0.41 mmol), **1c** (109 mg, 0.53 mmol), and KPF_6 (189.0 mg, 1.03 mmol) in MeOH (40 mL) was stirred at ambient temperature for 2 days. The crude mixture was obtained similarly to that for **3a**. The crude mixture in CH_2Cl_2 (5 mL) was added to stirred hexanes (60 mL) to produce the red precipitates, then filtered. The powder was dried under vacuum to give complex **15c** (348 mg, 86% yield). Spectroscopic data of **15c**: ^{1}H NMR (400.1 MHz, [D]acetone): $\delta = 7.87$ (d, ^3J(H,H) = 9.8 Hz, 1H; CβH), 7.75–7.04 (m, 35H; Ph, CγH), 4.81 ppm (s, 5H; Cp); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 247.10$ (t, ^2J(C,P) = 13.1 Hz; Cα), 148.97 (Ph), 144.43 (Cβ), 135.36–123.06 (Ph, Cγ), 91.32 ppm (Cp); ^{31}P NMR (162.0 MHz, $CDCl_3$): $\delta = 44.25$ ppm (s; PPh_3); elemental analysis calcd (%) for $C_{50}H_{41}F_6P_3RuS$: C 61.16, H 4.21; found: C 60.86, H 4.18; ESI-MS: m/z: 837.14 $[M]^+$.

X-ray Structure Determination of ***3a*** *and* ***15c***

Single crystals of complexes **3a** and **15c** suitable for an X-ray diffraction study were glued to a glass fiber and mounted on a SMART CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube $Mo_{K\alpha}$ radiation ($T = 295$ K). The exposure time was 5 s per frame. Siemens area detector absorption (SADABS)[36] corrections were applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL[37] program. Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogen atoms.

CCDC 947596 (**3a**) and 947597 (**15c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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