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Reactions of Propargyl Compounds Containing a Cyclobutyl Group Induced by a Ruthenium Complex

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Abstract: Reactions of [Ru]Cl ([Ru] = {$Cp(PPh_3)_2Ru$}; Cp = cyclopentadienyl) with three alkynyl compounds, **1**, **5**, and **8**, each containing a cyclobutyl group, are explored. For **1**, the reaction gives the vinylidene complex **2**, with a cyclobutylidene group, through dehydration at $C_\delta H$ and $C_\gamma OH$. With an additional methylene group, compound **5** reacts with [Ru]Cl to afford the cyclic oxacarbene complex **6**. The reaction proceeds via a vinylidene intermediate followed by an intramolecular cyclization reaction through nucleophilic addition of the hydroxy group onto C_α of the vinylidene ligand. Deprotonation of **2** with NaOMe produces the acetylide complex **3** and alkylations of **3** by allyl iodide, methyl iodide, and ethyl iodoacetate generate **4a–c**, respectively, each with a stable cyclobutyl group. Dehydration of **1** is catalyzed by the cationic ruthenium acetonitrile complex at 70 °C to form the 1,3-enyne **7**. The epoxidation reaction of the double bond of **7** yields oxirane **8**. Ring expansion of the cyclobutyl group of **8** is readily induced by the acidic salt NH_4PF_6 to afford the 2-ethynyl-substituted cyclopentanone **9**. The same ring expansion is also seen in the reaction of [Ru]Cl with **8** in CH_2Cl_2, affording the vinylidene complex **10**, which can also be obtained from **9** and [Ru]Cl. However, in MeOH, the same reaction of [Ru]Cl with **8** affords the bicyclic oxacarbene complex **12a** through an additional cyclization reaction. Transformation of **10** into **12a** is readily achieved in MeOH/HBF_4, but, in MeOH alone, acetylide complex **11** is produced from **10**. In the absence of MeOH, cyclization of **10**, induced by HBF_4, is followed by fluorination to afford complex **13**. Crystal structures of **6** and **12a′** were determined by single-crystal diffraction analysis.

Keywords: cyclization · cyclobutanes · fluorine · ring expansion · ruthenium

Introduction

During the past decade, the chemistry of transition-metal vinylidene, acetylide, and allenylidene complexes has attracted a great deal of attention. Reactions, such as alkylation,[1] catalytic C–C bond formation,[2] and ring opening, using these complexes have been extensively explored.[3] The first metal vinylidene complex was reported in 1972.[4] It is now known that activation of a terminal alkyne by a metal center and alkylation of a metal acetylide complex are two major methods for the preparation of metal vinylidene complexes. The formation of the first allenylidene complex was reported by Selegue in 1982 through the reaction of propargyl alcohol and an appropriate precursor complex in the presence of NH_4PF_6.[5] The majority of transition-metal allenylidene complexes are based on ruthenium. However, other metals, such as osmium,[6a] molybdenum,[6b] and tungsten,[6c] have also been reported to give similar complexes. The formation of the allenylidene complex generally proceeds by dehydration of a γ-hydroxyvinylidene intermediate. However, if C_δ of such an intermediate has one hydrogen atom, subsequent dehydration may proceed to give a vinylvinylidene complex.[7] In our previous study on the reaction of a ruthenium complex with propargyl alcohol containing a cyclopropyl ring, even with $C_\delta H$, an allenylidene complex with a three-membered ring was isolated. Ring expansion of this allenylidene complex was found to be mildly induced by a halide anion and other reagents. The development of ring expansion of various cycloalkyl groups is an important methodology for organic synthesis.[8] Reactions of functional groups with three-membered rings, such as cyclopropanes,[9a] vinylcyclopropanes,[9b] cyclopropenes,[9a] and methylenecyclopropanes (MCPs),[9c] have been developed. Particularly, owing to high ring strain and the electron-rich double bond, MCPs display a rich range of reactivities, including [3+2] cycloaddition,[10a] rearrangement,[10b] and substitution reactions.[10c] Methylenecyclobutane was first discovered by Gustavson.[11] Because of the presence of the cyclobutyl ring and olefinic double bond, the chemistry and applications of this compound have been exploited,[12] for example, cycloaddition,[13] ring-opening reactions,[14] and polymerization.[15] To further enhance the chemical reactivity, the olefinic functional group bonded to cycloalkyl has been modified by epoxidation or aziridination. For example, ring-opening reactions of highly strained oxiranes easily proceed under both acidic and basic conditions. Propargyl heterocyclopropanes, when

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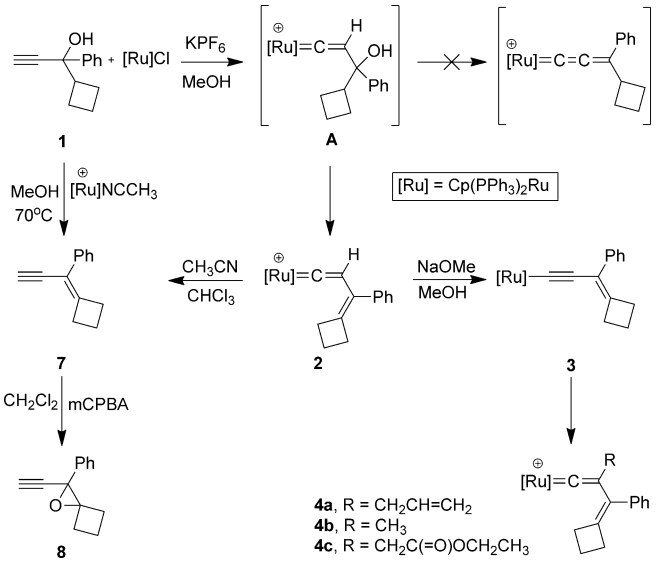
treated with transition-metal complexes, undergo cascade cyclization.[16] Namely, a catalytic amount of silver or gold complexes converts alkynyl oxiranes or aziridines into furans or pyrroles in the presence of external nucleophiles.[16b]

Herein, we report reactions of [Ru]Cl ([Ru]={Cp-(PPh_3)$_2$Ru}; Cp=cyclopentadienyl) with alkynyl compounds containing a cyclobutyl group. Ring expansion of the cyclobutyl group is achieved when epoxidation is introduced near the four-membered ring. Furthermore, participation of the triple bond results in the formation of bicyclic oxacarbene complex, the structure of which was confirmed by single-crystal diffraction analysis. A fluorine derivative of this bicyclic oxacarbene complex was also prepared.

Results and Discussion

Catalytic Dehydration of 1

Propargyl alcohol **1** with a cyclobutyl ring was prepared in high yield from the reaction of cyclobutylphenyl ketone with ethynylmagnesium bromide in tetrahydrofuran (THF). Treatment of [Ru]Cl with **1** in the presence of KPF_6 in MeOH at room temperature afforded the vinylidene complex **2** containing a cyclobutylidene group. Presumably the reaction proceeds through the formation of vinylidene intermediate **A** shown in Scheme 1. The dehydration of **A** then takes place between $C_\delta H$ and $C_\gamma OH$ to afford **2**.[7] No allenylidene complex was observed. Previously, we reported the reaction of the cyclopropyl analogue of **1** with [Ru]Cl, affording a allenylidene complex containing the cyclopropyl group. However, in the reaction of **1**, the dehydration process of the intermediate **A** to form **2** is favored. Theoretical calculations on a simple model with no cycloalkyl group show that the vinylidene complex is 2.1 kcal mol^{-1} more stable than the allenylidene complex.[17] Thus, the presence of the cyclopropyl group may affect the relative stability, whereas the four-membered ring has a less influential role. The ^{31}P NMR spectrum of **2** displays a singlet resonance at $\delta=41.26$ ppm. In the ^{1}H NMR spectrum, no coupling is observed between the broad signal at $\delta=4.90$ ppm, assigned to $C_\beta H$, and resonances in the range of $\delta=2.77$–1.99 ppm, assigned to the cyclobutyl group, revealing the structure of **2**. The triplet ^{13}C resonance at $\delta=357.76$ ppm with $^2J(C,P)=16.3$ Hz is assigned to C_α bound to ruthenium. This chemical shift is within the range of C_α resonances of many other ruthenium vinylidene complexes.[18]



Scheme 1. Reactions of [Ru]Cl with propargyl alcohol **1** with a cyclobutyl ring. mCPBA=*m*-chloroperbenzoic acid.

Treatment of **2** with NaOMe in MeOH afforded the light yellow acetylide complex **3**, the structure of which was determined by NMR spectroscopy. The ^{1}H resonance of $C_\beta H$ at $\delta=4.90$ ppm of **2** disappeared in the ^{1}H NMR spectrum of **3**. Treatment of **3** with allyl iodide, methyl iodide, and ethyl iodoacetate separately in the presence of KPF6 afforded the corresponding cationic vinylidene complexes **4a**, **4b**, and **4c**.[1] In the ^{1}H NMR spectrum of **4c**, the singlet resonance at $\delta=2.87$ ppm is assigned to $C_\gamma H_2$. The C_α resonance in the ^{13}C NMR spectrum appears as a triplet at $\delta=350.77$ ppm with $^2J(C,P)=15.1$ Hz and the C=O resonance appears at $\delta=172.33$ ppm. Previously, we reported the deprotonation reaction of an ester-containing vinylidene complex by nBu$_4$NOH at $C_\gamma H$, followed by a cyclization reaction to afford a cyclopropenyl complex as well as a furyl complex.[19] Unfortunately, treatment of **4c** with nBu$_4$NOH failed to yield the expected product and **4c** decomposed. The vinylidene complexes **4a–4c** are relatively stable. Attempts at ring expansion of the cyclobutylidene group of **4a–4c** by using various transition-metal complexes failed.

The reaction of **2** with a small amount of acetonitrile in $CHCl_3$ at reflux afforded the 1,3-enyne **7** containing the cyclobutylidene group and [Ru]NCMe$^+$ (Scheme 1). Transformation of **2** to **7** proceeds via a π-coordinated alkyne species followed by substitution with acetonitrile.[20] However, the yield of **7** from **1** by this indirect route is low. Interestingly, direct treatment of **1** with 30 mol% of [Ru]NCMe$^+$ in MeOH at 70°C affords **7** in 90% yield, as determined by NMR spectroscopy. In this reaction, a small amount of **2**, less than 10% yield, is also produced. Furthermore, treat-

Abstract in Chinese:

摘要: 利用釕金屬錯合物[Ru]Cl ([Ru] = Cp(PPh_3)$_2$Ru)與含四環之有機炔類**1**，在甲醇溶液中反應，可得釕亞乙烯錯合物**2**。假若將有機物**1**在參鍵旁邊延伸一個亞甲基形成有機物**5**，在同樣條件下，則與[Ru]Cl進行分子內環化反應生成釕卡賓錯合物**6**。錯合物**2**與乙腈反應，釋放出烯炔有機物**7**。釕乙腈錯合物[Ru]MeCN$^+$也可催化**1**的脫水反應得到**7**。再將**7**作環氧化反應得到含四環並環氧基之有機物**8**。釕錯合物[Ru]Cl與**8**在二氯甲烷溶液中進行四環擴環反應，可得釕錯合物**10**。但是相同反應在甲醇溶液中，則可進行進一步環化反應得到含兩個五環稠環釕錯合物**12a**。此外，**10**在酸性甲醇溶液中也可以經環化反應轉化為**12a**。但是若無酸的存在，**10**在甲醇溶液中會脫氫離子得到**11**。錯合物**10**在二氯甲烷和氟硼酸溶液中反應，可進行氟加成反應得到錯合物**13**。單晶繞射確定了兩個釕錯合物**6**與**12a**的固態結構。

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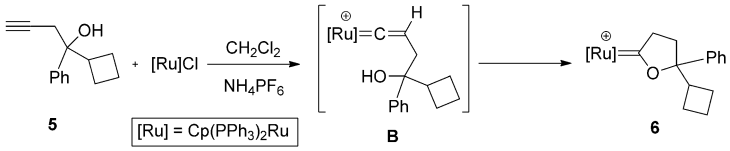
ment of **1** with 30 mol% of [Ru]Cl and MeCN/NH_4PF_6 in MeOH at 70°C also produced **7** after a slightly longer reaction time. If the solvent is changed from MeOH to MeOD, the terminal alkynyl hydrogen of **7** is replaced by deuterium. Deuteration should occur during the formation of vinylidene intermediate **A**. The dehydration of **1** when using P_4O_{10} (from 0°C to RT) also produced **7**, but only in 45% yield with impurities. Catalytic dehydration of analogous compounds, leading to the formation of cyclobutylidene derivatives, has been induced by $FeCl_3$ in toluene, but, the cyclobutylidene compound was formed as a minor product in 38% yield.[21]

Formation of the Cyclic Carbene Complex

Alkynyl alcohol **5**, also with a cyclobutyl group, was prepared in high yield from the reaction of cyclobutylphenyl ketone with prop-2-ynylmagnesium bromide. Treatment of [Ru]Cl with **5** in the presence of NH_4PF_6 in CH_2Cl_2 at room temperature afforded the yellow cyclic oxacarbene complex **6** containing a cyclobutyl group. (Scheme 2)



Scheme 2. Reaction of alkynyl alcohol **5** containing a cyclobutyl ring with [Ru]Cl.

As expected, no dehydration was observed. The reaction presumably proceeds through formation of **B**, followed by an intramolecular cyclization reaction by nucleophilic addition of the hydroxy group to C_α=C_β of the vinylidene ligand of **B** to afford **6**. The structure of **6** was determined by NMR spectroscopy. The ^{31}P NMR spectrum of **6** displays two doublet resonances at $\delta = 46.29$ and 43.60 ppm with $^2J(P,P) = 30.7$ Hz, owing to the stereogenic sp^3 carbon. Two multiplet resonances in the ^1H NMR spectrum at $\delta = 3.78$ and 3.37 ppm were assigned to the diastereotopic $C_\beta H_2$ group. The HMBC spectrum shows correlation of one resonance of $C_\beta H_2$ with the triplet ^{13}C resonance at $\delta =$ 299.82 ppm with $^2J(C,P) = 13.3$ Hz assigned to C_α.

Single crystals of **6** were obtained from a solution of **6** in CH_2Cl_2 layered with diethyl ether. The structure of **6** was confirmed by a single-crystal X-ray diffraction study (Figure 1). Complex **6** has distorted three-legged piano-stool coordination geometry around the ruthenium center, which bonds to a Cp, two PPh_3, and the cyclic carbene ligand. The bond length of Ru1–C1 of 1.943(2) Å shows a typical ruthenium–carbene bond. The twisted four-membered ring is bonded to the tetrahydrofuryl ring.

Ring Expansion Using Epoxides

The ring opening of the methylenecycloalkyl group by epoxidation has been previously reported in the literature.[22] For

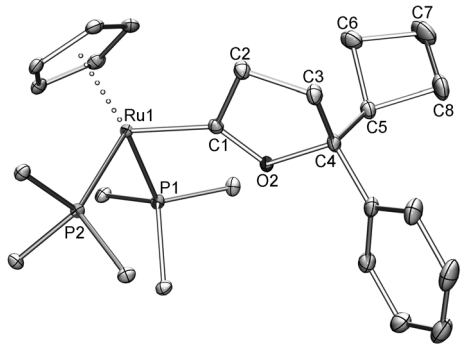
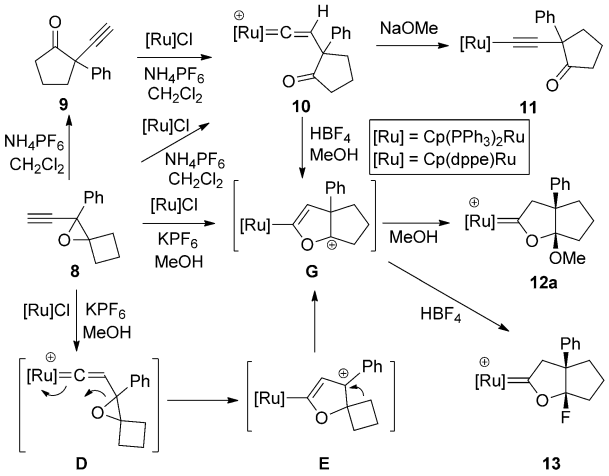


Figure 1. An ORTEP drawing of the cationic complex **6**. For clarity, phenyl groups of the triphenylphosphine ligands on ruthenium, except the ipso carbon atoms, and PF_6^- are omitted (thermal ellipsoids are set at the 30% probability level). Selected bond lengths [Å] and angles [°]: Ru1–P1 2.3262(5), Ru1–P2 2.3631(5), Ru1–C1 1.9430(18), O2–C1 1.318(2), O2–C4 1.512(2), C4–C5 1.519(3), C5–C6 1.549(3), C6–C7 1.545(3), C7–C8 1.542(4), C5–C8 1.540(3); O2-C1-Ru1 127.10(13), C1-O2-C4 113.96(13), C4-C5-C8 118.09(19), C8-C7-C6 88.20(18), C8-C5-C6 88.13(17), C5-C6-C7 87.40(18), C5-C8-C7 87.81(19).

example, the ring expansion of alkylidene epoxide cyclobutane was reported to give cyclopentanone.[22a–c] To achieve ring expansion of the cyclobutyl group in **7**, a new epoxide group was introduced. Compound **7** was treated with mCPBA to afford cyclobutyloxirane **8**. Two olefinic ^{13}C resonances of **7** at $\delta = 154.98$ and 114.61 ppm disappeared in the ^{13}C NMR spectrum of **8**. The reaction of **8** with [Ru]Cl in CH_2Cl_2/NH_4PF_6 produced the vinylidene complex **10** containing a cyclopentanone ring (Scheme 3). Ring expansion



Scheme 3. Proposed mechanism for the formation of **12a** and **13**.

of **8** to generate cyclopentanone compound **9**, induced by the acidic salt NH_4PF_6, was also achieved in the absence of [Ru]Cl.

The reaction of **9** with [Ru]Cl/NH_4PF_6 also yielded **10**. Deprotonation of **10** by NaOMe in MeOH afforded the acetylide complex **11**. The structures of complexes **10** and **11** were determined by various spectroscopic methods. In the

2D HMBC NMR spectrum of **10**, the resonance at $\delta =$ 216.33 ppm, assigned to the carbonyl carbon, correlates with resonances of all methylene hydrogen atoms in the five-membered ring because of ^2J(C,H) and ^3J(C,H) coupling; this revealed the cyclic structure.

Additional cyclization takes place for **10** in MeOH/HBF_4, thereby yielding bicyclic oxacarbene complex **12a**, the structure of which was determined by NMR spectroscopy. In the 2D HSQC NMR spectrum of **12a**, three ^{13}C resonances at $\delta = 39.89$, 32.98, and 21.71 ppm each correlate with the corresponding hydrogen atoms of three methylene groups of the cyclopentyl ring. The ^{13}C resonance at $\delta = 56.25$ ppm is assigned to the bridgehead carbon with the phenyl group. The resonance of the bridgehead acetal carbon of **12a** is expected to appear within the range of $\delta = 130$–140 ppm. In the 2D HMBC NMR spectrum, the ^{13}C resonance at $\delta =$ 137.00 ppm correlates with all methylene hydrogen atoms of the two rings and is assigned to the bridgehead acetal carbon of **12a**. In the ^{1}H NMR spectrum, the two doublet resonances at $\delta = 4.36$ and 4.26 ppm with ^2J(H,H) = 19.3 Hz are assigned to two hydrogen atoms of $C_\beta H_2$ because of the nearby stereogenic sp^3 carbon. In the ^{31}P NMR spectrum, two doublets appear at $\delta = 45.86$ and 44.41 ppm with ^2J(P,P) = 30.8 Hz.[23] However, in the absence of MeOH, the reaction of **10** with HBF_4 in CH_2Cl_2 affords the fluorine-substituted bicyclic oxacarbene complex **13**. Namely, fluorine is added to the carbocationic site to yield **13**. In the ^{13}C NMR spectrum of **13**, a doublet at $\delta = 137.62$ ppm with ^1J(C,F) = 248.8 Hz is assigned to the CF group. All other ^{13}C resonances of the five-membered cyclopentyl ring in the ^{13}C NMR spectrum display doublet signals owing to coupling with the fluorine atom. All coupling constants, including ^1J(C,F), ^2J(C,F) and ^3J(C,F), are comparable to previously reported data.[24] Other main features of the 2D NMR spectra are similar to those of **12a**. Remarkably, the direct reaction of **8** with [Ru]Cl in the presence of KPF_6 in MeOH at room temperature also affords **12a**. This ring-expansion/cyclization reaction occurs only in alcohols, that is, no reaction was observed in $CHCl_3$. However, the reactions in ethanol and *n*-propanol, producing the corresponding products **12b** and **12c** (Table 1), require longer reaction times.

Moreover, treatment of **8** with [Ru′]Cl ([Ru′] = Cp-(dppe)Ru; dppe = 1,2-bis(diphenylphosphino)ethane)) causes similar ring expansion and cyclization to afford the analogous bicyclic oxacarbene complex **12a′**. Single crystals of **12a′** were obtained from a solution of **12a′** in CH_2Cl_2 layered with diethyl ether. The structure of **12a′** was determined by a single-crystal X-ray diffraction study (Figure 2). Complex **12a′** has a distorted three-legged piano-stool coordination geometry around the ruthenium center, which bonds to Cp, dppe, and the bicyclic oxacarbene ligand. The bond length of Ru1–C1 in **12a′** of 1.949(3) Å shows a typical ruthenium–carbene bond. The bond length of C3–C7 in **12a′** of 1.592(7) Å attests to C–C bond formation. Two dihedral angles, C2-C3-C4-C5 and O1-C4-C3-C7, of 123.08 and 89.34°, respectively, indicate twisting of the all-carbon five-membered ring.

Table 1. Cascade cyclization and ring expansion of **8** on [Ru]Cl in different solvents.

Entry	Solvent	*t* [h]	Product (Yield [%])
1	CH_2Cl_2	12	**10** (95)
2	$CHCl_3$	12	–[a]
3	MeOH	12	**12a** (90)
4	EtOH	16	**12b** (85)
5	PrOH	30	**12c** (82)
6	NH_3/MeOH	12	**12a** (88)

[a] No formation of ruthenium complex.

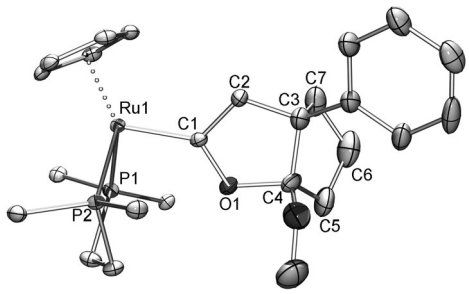


Figure 2. An ORTEP drawing of the cationic complex **12a′**. For clarity, phenyl groups of the dppe ligands on ruthenium, except the ipso carbon atoms, and PF_6^- are omitted (thermal ellipsoids are set at the 30% probability level). Selected bond lengths [Å] and angles [°]: Ru1–P1 2.2796(8), Ru1–P2 2.2823(9), Ru1–C1 1.949(3), C1–C2 1.5025, C1–O1 1.320(4), C2–C3 1.508(5), O1–C4 1.509(5), C3–C4 1.520(6), C4–C5 1.492(7), C3–C7 1.592(7), C6–C7 1.505(9); C1-O1-C4 113.8(3), C4-C3-C7 100.1(4), O1-C1-Ru1 128.1(2).

Oxabicycles are fundamental structural fragments of many natural products.[25] For example, hexahydro-2*H*-cyclopenta[*b*]furans are important heterobicycles because they are a component of HIV-1 protease inhibitors.[26] The formation of oxabicycles has been previously introduced by the oxy-Favorskii rearrangement of α-halolactones.[25] However, the structure of α-halolactones substrates and steric hindrance between the incoming nucleophiles and the substrates can greatly affect the oxy-Favorskii rearrangement process. Herein, we present an efficient way to synthesize hexahydro-2*H*-cyclopenta[*b*]furans. Organofluorides are widely used as pharmaceuticals[27] and agrochemicals.[28] Compounds containing fluorine can increase lipophilicity to enhance bioavailability[29] or increase metabolic stability.[29b] Consequently, synthetic methodologies for carbon–fluorine bond formation have been significantly investigated.[30] Fluorinations including electrophilic[31a] and nucleophilic fluorination,[31b] the use of fluorinated synthons,[31c] and electrochemical methods[31d] have been reported. For example, ring-opening hydrofluorination of substituted aryl epoxides with HBF_4 afforded fluorohydrins.[32] Herein, we describe an easy method to prepare a fluorooxabicyclic product.

The proposed mechanism for the formation of **12a** and **13** is illustrated in Scheme 3. Ring expansion of **8**, induced by the acidic salt NH_4PF_6, generates compound **9**. Then, the terminal alkyne of **9** reacts with [Ru]Cl to give **10**. In

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$MeOH/HBF_4$, intramolecular nucleophilic attack of oxygen of the carbonyl group of **10** takes place in the presence of an acidic proton to afford intermediate **G** with a tertiary carbocation. The role of the acid is believed to prevent deprotonation, thus making the nucleophilic addition of carbonyl oxygen to the cationic vinylidene C_α feasible. Finally, addition of a methoxide from MeOH to **G** forms **12a**. However, in the absence of MeOH, the addition of a fluorine atom from HBF_4 to **G** forms complex **13**. Our attempts to prepare **12a** from **10** in MeOH in the presence of KPF_6 resulted in the formation of **11**. Deprotonation of **10** readily occurs, even in mostly neutral or weakly basic conditions. No cyclization was observed for **11** possibly as a result of a lack of cationic charge to induce nucleophilic addition. Therefore, speculatively, as shown in the lower left part of Scheme 3, direct reaction of **8** with [Ru]Cl may proceed alternatively by cyclization of the vinylidene intermediate **D**, giving **E**, instead of **10**, followed by ring expansion to yield **G**.

Previously, a cascade cyclization/ring-expansion process for 2-alkynyl-1-azaspiro[2,3]hexanes catalyzed by 10 mol% of $PtCl_2$ in dioxane/H_2O (2:1) at 100°C was reported to yield cyclopenta[*b*]pyrroles.[16a] In our case, similar cascade cyclization/ring expansion of **8** is induced by [Ru]Cl at room temperature. The cyclized product remains bonded to the metal as a carbene ligand.

Conclusion

Dehydration of propargyl alcohol **1**, containing a cyclobutyl group, was catalyzed by the cationic complex $[Ru](MeCN)^+$, generating 1,3-enyne **7**, which contained a cyclobutylidene group. Treatment of [Ru]Cl with **1** in MeOH in the presence of KPF_6 afforded vinylidene complex **2**, also with a cyclobutylidene group. With an additional methylene group, propargyl compound **5** reacted with [Ru]Cl to give cyclic oxacarbene complex **6**. Epoxidation of **7** yielded cyclobutyl oxirane **8**, which underwent cascade cyclization/ring expansion with [Ru]Cl in alcohols at room temperature to afford bicyclic oxacarbene complex **12**. Alternatively, the ring-expansion reaction of **8** in CH_2Cl_2 induced by $[Ru]Cl/NH_4PF_6$, afforded vinylidene complex **10**, containing a cyclopentanone group. Cyclization of **10**, induced by HBF_4 in CH_2Cl_2, was followed by fluorination in the absence of MeOH, thus generating the monofluorinated bicyclic oxacarbene complex **13**.

Experimental Section

General Procedures

The manipulations were performed under an atmosphere of dry nitrogen by using vacuum-line and standard Schlenk techniques, unless mentioned otherwise. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and were used without further purification. NMR spectra were recorded on Bruker AC-300, DPX-400, and AVIII-400 FT-NMR spectrometers at room temperature and are reported in units of δ with residual protons in the solvents as a standard. Electrospray ionization mass spectrometry, elemental analysis, and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University. Complex [Ru]Cl[33] was prepared from $RuCl_3{\cdot}xH_2O$, which was purchased from Steam Chemicals, according to a literature method. Complex [Ru′]Cl[34] was prepared from [Ru]Cl, according to a procedure reported in the literature.

*Synthesis of **1***

Ethynylmagnesium bromide (0.50 M, 75.1 mL, 38 mmol) was added to a solution of cyclobutyl phenyl ketone (3.01 g, 18.8 mmol) in THF (40 mL) under nitrogen. The mixture was stirred at 40°C for 24 h. Then the reaction was quenched with a saturated aqueous solution of NH_4Cl (30 mL), and diethyl ether (3×20 mL) was used to extract the crude product. The combined organic layers were dried under vacuum and the residue was purified by column chromatography using ethyl acetate (EA)/hexane (1:7) as the eluent to give **1** (2.91 g, 83%). ^{1}H NMR ($CDCl_3$): δ = 7.62–7.28 (m, 5H; Ph), 2.82–2.75 (m, 1H; CH), 2.73 (s, 1H; ≡CH), 2.38 (s, 1H; OH), 2.29–2.19 (m, 1H; CH_2), 2.14–2.03 (m, 1H; CH_2), 1.94–1.75 ppm (m, 6H; CH_2); ^{13}C NMR ($CDCl_3$): δ = 142.82, 128.06, 127.66, 125.32 (Ph), 85.07 (C≡), 74.91 (≡CH), 74.48 (C), 46.80 (CH), 23.68 (CH_2), 22.95 (CH_2) 16.53 ppm (CH_2); MS: *m*/*z*: 186.10 [M^+]; elemental analysis calcd (%) for $C_{13}H_{14}O$: C 83.83, H 7.58; found: C 83.79, H 7.51.

*Synthesis of Complex **2***

MeOH (20 mL) was added to a Schlenk flask charged with [Ru]Cl (62 mg, 0.085 mmol), **1** (20 mg, 0.10 mmol), and KPF_6 (50 mg, 0.27 mmol) under nitrogen. The resulting solution was stirred at room temperature overnight. Then the solution was filtered through a bed of Celite to remove the insoluble salts and the solvent of the filtrate was removed under vacuum. The solid residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation through the addition of diethyl ether (50 mL) with stirring. Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexanes (1:1), and dried under vacuum. Compound **2** was obtained as a yellow powder (0.078 g, 90%). ^{1}H NMR ($CDCl_3$): δ = 7.52–6.75 (m, 50H; Ph), 5.06 (s, 5H; Cp), 4.90 (s, 1H; = CH), 2.77 (t, ^3J(H,H) = 8.0 Hz, 2H; CH_2), 2.61 (t, ^3J(H,H) = 8.0 Hz, 2H; CH_2), 1.99 ppm (m, 2H; CH_2); ^{13}C NMR ($CDCl_3$): δ = 357.76 (t, ^2J(C,P) = 16.3 Hz, C_α), 139.54–116.08 (C_β, Ph, =CPh, =C(CH_2)$_2$), 94.69 (Cp), 31.14 (CH_2), 30.94 (CH_2), 16.86 ppm (CH_2); ^{31}P NMR ($CDCl_3$): δ = 41.26 ppm (s, PPh_3); MS: *m*/*z*: 859.22 [M^+]; elemental analysis calcd (%) for $C_{54}H_{47}F_6P_3Ru$: C 64.60, H 4.72; found: C 64.42, H 4.58.

*Synthesis of Complex **3***

A mixture of **2** (0.16 g, 0.16 mmol) and NaOMe (8.6 mg, 0.16 mmol) in MeOH (30 mL) was stirred for 3 min at room temperature. Then the solvent was removed under vacuum and diethyl ether (20 mL) was added. The mixture was stirred by using an ultrasonic cleaner. The solution was filtered through neutral Al_2O_3 to remove insoluble salts, then the solvent was removed under vacuum. Compound **3** was obtained as a yellow powder (0.081 g, 95%). ^{1}H NMR ($CDCl_3$): δ = 7.64–700 (m, 42H; Ph), 4.31 (s, 5H; Cp), 3.01 (m, 2H; CH_2), 2.91 (m, 2H; CH_2), 1.95 ppm (m, 2H; CH_2); ^{13}C NMR ($CDCl_3$): δ = 114.34 (t, ^2J(C,P) = 24.6 Hz, C_α), 142.12–111.42 (Ph, C_β, =CPh, =C(CH_2)$_2$), 85.28 (Cp), 33.10 (CH_2), 33.10 (CH_2), 17.59 ppm (CH_2); ^{31}P NMR ($CDCl_3$): δ = 50.49 ppm (s, PPh_3); MS: *m*/*z*: 859.22 [M^+]; elemental analysis calcd (%) for $C_{54}H_{46}P_2Ru$: C 75.60, H 5.40; found: C 75.52, H 5.35.

*Synthesis of Complex **4a***

Allyl iodide (0.10 g, 0.58 mmol) was added to a solution of **3** (0.13 g, 0.15 mmol), KPF_6 (0.02 g, 0.3 mmol), and CH_2Cl_2 (20 mL) in a Schlenk flask under nitrogen. The solution was stirred for 8 h at 40°C. Then the solution was filtered through Celite to remove insoluble salts and the solvent was removed under vacuum, the solid residue was extracted with a small volume of CH_2Cl_2, followed by reprecipitation with diethyl ether (50 mL). Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexanes (1:1) and dried under vacuum. Compound **4a** was obtained as a yellow powder (0.11 g, 90%). ^{1}H NMR ($CDCl_3$): δ =

7.42–6.94 (m, 46H; Ph), 5.84–5.82 (m, 1H; =C(C)H), 5.13 (d, ^3J(H,H)= 10.9 Hz, 1H; =CH), 5.03 (d, ^3J(H,H)=16.7 Hz, 1H; =CH), 4.95 (s, 5H; Cp), 2.94 (s, 2H; CH_2), 2.94 (t, ^3J(H,H)=8.2 Hz, 2H; CH_2), 2.71 (t, ^3J-(H,H)=8.2 Hz, 2H; CH_2), 2.00 ppm (m, ^3J(H,H)=8.2 Hz, 2H; CH_2); ^{13}C NMR ($CDCl_3$): δ=351.23 (t, ^2J(C,P)=15.2 Hz, C_α), 146.25–117.70 ($C_{\beta,}$ Ph, =CPh, =$C(CH_2)_2$, =CH_2, =CH), 93.74 (Cp), 34.05 (CH_2), 32.81 (CH_2), 29.62 (CH_2), 17.74 ppm (CH_2); ^{31}P NMR ($CDCl_3$): δ=42.63 ppm (s, PPh_3); MS: *m/z*: 899.25 [M^+]; elemental analysis calcd (%) for $C_{57}H_{51}F_6P_3Ru$: C 65.58, H 4.92; found: C 65.49, H 4.89.

*Synthesis of Complex **4b***

Complex **4b** (0.11 g, 92%) was similarly prepared from **3** (0.10 g, 0.12 mmol), KPF_6 (0.02 g, 0.30 mmol), and methyl iodide (0.08 g, 0.58 mmol). ^{1}H NMR ($CDCl_3$): δ=7.40–6.92 (m, 37H; Ph), 4.92 (s, 5H; Cp), 2.90 (t, ^3J(H,H)=8.1 Hz, 2H; CH_2), 2.68 (t, ^3J(H,H)=8.1 Hz, 2H; CH_2), 2.02 (s, 3H; CH_3), 2.02 ppm (m, ^3J(H,H)=8.1 Hz, 2H; CH_2); ^{13}C NMR ($CDCl_3$): δ=352.62 (t, ^2J(C,P)=15.3 Hz, C_α), 145.84–121.16 ($C_{\beta,}$ Ph, =CPh, =$C(CH_2)_2$), 93.51 (Cp), 33.84 (CH_2), 32.33 (CH_2), 17.65 (CH_2), 12.71 ppm (CH_3); ^{31}P NMR ($CDCl_3$): δ=42.80 ppm (s, PPh_3); MS: *m/z*: 873.23 [M^+]; elemental analysis calcd (%) for $C_{55}H_{49}F_6P_3Ru$: C 64.89, H 4.85; found: C 64.53, H 4.79.

*Synthesis of Complex **4c***

Complex **4c** (0.23 g, 85%) was similarly prepared from **3** (0.20 g, 0.24 mmol), KPF_6 (0.02 g, 0.3 mmol), and ethyl iodoacetate (0.08 g, 0.37 mmol). ^{1}H NMR ($CDCl_3$): δ=7.40–6.89 (m, 39H; Ph), 5.13 (s, 5H; Cp), 4.19 (q, ^3J(H,H)=7.2 Hz, 2H; CH_2), 2.92 (t, ^3J(H,H)=7.3 Hz, 2H; CH_2), 2.87 (s, 2H; CH_2), 2.80 (t, ^3J(H,H)=7.3 Hz, 2H; CH_2), 2.04 (m, ^3J-(H,H)=7.3 Hz, 2H; CH_2), 1.27 ppm (t, ^3J(H,H)=7.2 Hz, 3H; CH_3); ^{13}C NMR ($CDCl_3$): δ=350.77 (t, ^2J(C,P)=15.1 Hz, C_α), 172.33 (C=O), 145.87–120.34 ($C_{\beta,}$ Ph, =CPh, =$C(CH_2)_2$), 94.53 (Cp), 61.50 (CH_2), 33.73 (CH_2), 32.57 (CH_2), 31.02 (CH_2), 17.47 (CH_2), 14.27 ppm (CH_3); ^{31}P NMR ($CDCl_3$): δ=41.62 ppm (s; PPh_3); MS: *m/z*: 945.26 [M^+]; elemental analysis calcd (%) for $C_{58}H_{53}O_2F_6P_3Ru$: C 63.91, H 4.90; found: C 63.80, H 4.87.

*Synthesis of **5***

Prop-2-yn-1-ylmagnesium bromide in THF (0.50 M, 73.8 mL, 37 mmol) was added to a solution of cyclobutyl phenyl ketone (2.78 g, 17.3 mmol) in THF (40 mL) under nitrogen. The mixture was stirred at 40°C for 24 h. Then the reaction was quenched with a saturated aqueous solution of NH_4Cl (35 mL), and diethyl ether (3×25 mL) was used to extract the crude product. The combined organic layers were dried under vacuum and the residue was purified by column chromatography by using EA/hexanes (1:5) to give **5** (3.10 g, 88%). ^{1}H NMR ($CDCl_3$): δ=7.47–7.27 (m, 5H; Ph), 2.90–2.81 (m, 1H; CH), 2.76–2.66 (m, 2H; CH_2), 2.46 (s, 1H; ≡CH), 2.22–1.57 ppm (m, 7H; OH, 3 CH_2); ^{13}C NMR ($CDCl_3$): δ= 144.00, 127.97, 126.87, 125.37 (Ph), 80.27 (C≡), 75.33 (≡CH), 71.59 (C), 44.91 (CH), 30.30 (CH_2), 22.55 (CH_2), 22.48 (CH_2), 16.86 ppm (CH_2); MS: *m/z*: 200.12 [M^+]; elemental analysis calcd (%) for $C_{14}H_{16}O$: C 83.96, H 8.05; found: C 83.85, H 8.03.

*Synthesis of Complex **6***

The reaction of **5** (0.07 g, 0.35 mmol) and [Ru]Cl (0.20 g, 0.27 mmol) was carried out in the presence of NH_4PF_6 (45 mg, 0.27 mmol) in CH_2Cl_2 (20 mL) at room temperature for 1 day. The solution was filtered through Celite to remove insoluble salts, then the solvent was removed under vacuum, and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation with diethyl ether (50 mL). Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexanes (1:1), and dried under vacuum. Compound **6** was obtained as a yellow carbene complex (0.24 g 85%). ^{1}H NMR (CD_2Cl_2): δ=7.41–6.80 (m, 37H; Ph), 4.81 (s, 5H; Cp), 3.79–3.77 (m, 1H; CH_2), 3.38–3.36 (m, 1H; CH_2), 2.31–2.13 (m, 3H; CH_2, CH), 1.80–1.12 ppm (m, 6H; 3 CH_2); ^{13}C NMR (CD_2Cl_2): δ=299.82 (t, ^2J(C,P)=13.3 Hz, C_α), 138.96–126.02 (Ph), 110.27 (C(O)Ph), 90.62 (Cp), 62.32 (CH_2), 44.23 (CH), 28.86 (CH_2), 25.07 (CH_2), 24.79 (CH_2), 17.01 ppm (CH_2); ^{31}P NMR (CD_2Cl_2): δ=46.29, 43.60 ppm (2d, ^2J(P,P)=30.7, PPh_3); MS: *m/z*: 891.25 [M^+]; elemental analysis calcd (%) for $C_{55}H_{51}OP_3F_6Ru$: C 63.76, H 4.96; found: C 63.60, H 4.90.

*Synthesis of **7***

[Ru]NCMePF_6 (30 mol%, 0.28 g, 0.32 mmol) in MeOH (20 mL) was added to a Schlenk flask charged with **1** (0.20 g, 1.07 mmol) under nitrogen. The resulting solution was stirred at 60°C overnight. Then the solution was filtered through Celite to remove insoluble salts and the solvent was removed under vacuum, the solid residue was extracted with a small volume of CH_2Cl_2, followed by reprecipitation with diethyl ether (50 mL). After filtration, the precipitate was dried under vacuum and the residue was purified by column chromatography using hexanes as the eluent to give **7** (0.13 g, 70%).

Dehydration was also induced by P_4O_{10}. MeOH (20 mL) was added to a Schlenk flask charged with **1** (0.20 g, 1.07 mmol) and P_4O_{10} (0.30 g, 1.07 mmol). The solution was stirred at 0°C and over 4 h the temperature was raised to room temperature under nitrogen to yield **7** (0.08 g 45%). ^{1}H NMR ($CDCl_3$): δ=7.55–7.25 (m, 5H; Ph), 3.24 (s, 1H; ≡CH), 3.14–3.06 (m, 4H; 2 CH_2), 2.16 ppm (m, 2H; CH_2). ^{13}C NMR ($CDCl_3$): δ= 154.98 (=C), 136.41, 128.10, 126.64, (Ph), 114.61, (=C), 81.05 (C≡), 80.47 (≡CH), 33.29 (CH_2), 33.03 (CH_2), 17.27 ppm (CH_2); MS: *m/z*: 168.09 [M^+]; elemental analysis calcd (%) for $C_{13}H_{12}$: C 92.81, H 7.19; found: C 92.70, H 7.15.

*Synthesis of **8***

mCPBA (47 mg, 0.27 mol) dissolved in CH_2Cl_2 (2 mL) was added to a solution of **7** (23 mg, 0.14 mmol) in CH_2Cl_2 (10 mL) under nitrogen at 0°C. The mixture was stirred at room temperature for 24 h. Then the reaction was quenched with a saturated aqueous solution of NH_4Cl (20 mL), and diethyl ether (3×10 mL) was used to extract the crude product. The combined organic layers were dried under vacuum and the residue was purified by column chromatography using EA/hexanes (1:8) as the eluent to give **8** (17 mg, 80%). ^{1}H NMR ($CDCl_3$): δ=7.40–7.24 (m, 5H; Ph), 2.63–2.54 (m, 2H; CH_2), 2.57 (s, 1H; ≡CH), 2.48–2.39 (m, 1H; CH_2), 1.91–1.80 (m, 2H; CH_2), 1.74–1.64 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$): δ= 135.32, 127.99, 126.18, (Ph), 80.78 (C≡), 74.00 (≡CH), 72.06 (C), 58.71 (C), 30.17 (CH_2), 28.41 (CH_2), 11.86 ppm (CH_2); MS: *m/z*: 184.09 [M^+]; elemental analysis calcd (%) for $C_{13}H_{12}O$: C 84.75, H 6.57; found: C 84.68, H 6.52.

*Synthesis of Complex **9***

NH_4PF_6 (20 mg, 0.13 mol) was added to a solution of **8** (23 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) under nitrogen at room temperature. The mixture was stirred for 24 h. Then the reaction was quenched with a saturated aqueous solution of NH_4Cl (20 mL) and diethyl ether (3×10 mL) was used to extract the crude product. The combined organic layers were dried under vacuum and the residue was purified by column chromatography using EA/hexanes (1:8) as the eluent to give **9** (21.8 mg, 95%). ^{1}H NMR (CD_2Cl_2): δ=7.48–7.31 (m, 5H; Ph), 2.56 (s, 1H; C≡), 2.63–2.07 ppm (m, 6H; 3 CH_2); ^{13}C NMR (CD_2Cl_2): δ=212.52 (C=O), 139.00, 128.44, 127.40, 127.10 (Ph), 83.13, 73.53 (C≡, HC≡), 40.07, 37.06, 19.42 ppm (3CH_2); MS: *m/z*: 184.09 (M^+); elemental analysis calcd (%) for $C_{13}H_{12}O$: C 84.75, H 6.57; found: C 84.57, H 6.47.

*Synthesis of Complex **10***

CH_2Cl_2 (20 mL) was added to a Schlenk flask charged with [Ru]Cl (82 mg, 0.11 mmol), **8** (26 mg, 0.14 mmol), and NH_4PF_6 (46 mg, 0.28 mmol) under nitrogen. The resulting solution was stirred at room temperature overnight. Then the solution was filtered through Celite to remove insoluble salts, the solvent was removed under vacuum, and the solid residue was extracted with a small volume of CH_2Cl_2, followed by reprecipitation with diethyl ether (20 mL). Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexanes (1:1), and dried under vacuum. Compound **10** was obtained as a light orange powder (0.11 g, 92%).

Complex **10** can also be prepared from [Ru]Cl and **9**. CH_2Cl_2 (20 mL) was added to a Schlenk flask charged with [Ru]Cl (82 mg, 0.11 mmol), **9** (26 mg, 0.14 mmol), and NH_4PF_6 (46 mg, 0.28 mmol). Product **10** was

similarly isolated in 90% yield. ^{1}H NMR ($CDCl_3$): δ = 7.55–6.88 (m, 46H; Ph), 5.06 (s, 5H; Cp), 4.42 (br, 1H; =CH), 2.48–1.77 ppm (m, 6H; 3 CH_2); ^{13}C NMR ($CDCl_3$): δ = 348.88 (t, ^2J(C,P) = 15.5 Hz, C_α), 216.33 (C=O), 140.65–126.95 (Ph, PPh_3), 118.91 (C_β), 94.52 (Cp), 55.45 (CPh), 38.17 (CH_2), 36.32 (CH_2), 18.94 ppm (CH_2); ^{31}P NMR ($CDCl_3$): δ = 41.18, 40.79 ppm (2d, ^2J(P,P) = 26.3 Hz, 2PPh_3); MS: *m/z*: 875.21 [M^+]; elemental analysis calcd (%) for $C_{54}H_{47}F_6OP_3Ru$: C 63.59, H 4.64; found: C 63.33, H 4.57.

Synthesis of Complex ***11***

A mixture of **10** (0.18 g, 0.18 mmol) and NaOMe (11 mg, 0.21 mmol) in MeOH (30 mL) was stirred at room temperature. Then the solvent was removed under vacuum and then diethyl ether (20 mL) was added. The mixture was stirred in an ultrasonic cleaner. The solution was filtered through neutral Al_2O_3 to remove insoluble salts, then the solvent was removed under vacuum. The final product can be obtained as a yellow powder identified as **11** (0.16 g, 98%). Also, a solution of **10** (0.18 g, 0.18 mmol) in MeOH (30 mL) in the presence of KPF_6 was stirred at room temperature to yield **11** in 90% yield. ^{1}H NMR ($CDCl_3$): δ = 7.68–7.08 (m, 37H; Ph), 4.29 (s, 5H; Cp), 2.24–0.86 ppm (m, 6H; 3 CH_2); ^{13}C NMR ($CDCl_3$): δ = 213.78 (C=O), 142.12–106.55 (Ph, C_β), 105.43 (C_α) 85.30 (Cp), 57.94 (CPh), 42.28 (CH_2), 37.20 (CH_2), 19.48 ppm (CH_2); ^{31}P NMR ($CDCl_3$): δ = 51.18, 50.88 ppm (2d, ^2J(P,P) = 37.8 Hz, 2 PPh_3); MS: *m/z*: 875.21 [M^+]; elemental analysis calcd (%) for $C_{54}H_{46}OP_2Ru$: C 74.21, H 5.31; found: C 74.11, H 5.30.

Synthesis of Complex ***12a***

MeOH (20 mL) was added to a Schlenk flask charged with [Ru]Cl (0.12 g, 0.16 mmol), **8** (36 mg, 0.20 mmol), and KPF_6 (50 mg, 0.27 mmol) under nitrogen. The resulting solution was stirred at room temperature overnight. Then the solution was filtered through Celite to remove insoluble salts, the solvent was removed under vacuum, and the solid residue was extracted with a small volume of CH_2Cl_2, followed by reprecipitation with diethyl ether (30 mL). Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexanes (1:2), and dried under vacuum. Compound **12a** was obtained as a light yellow powder (0.16 g, 90%). The reaction of **10** in HBF_4/MeOH for 30 min also yielded **12a**. ^{1}H NMR (CH_2Cl_2): δ = 7.69–6.86 (m, 42H; Ph), 4.92 (s, 5H; Cp), 4.36, 4.26 (2d, 2H; ^2J(H,H) = 19.3 Hz, CH_2), 3.20 (s, 3H; OCH_3), 2.21–1.18 ppm (m, 6H; 3CH_2); ^{13}C NMR (CH_2Cl_2): δ = 297.61 (br, C_α), 140.05–126.98 (Ph, C(OCH_3)), 91.10 (Cp), 76.35 (CH_2), 56.25 (CPh), 54.40 (OCH_3), 39.89 (CH_2), 32.98 (CH_2), 21.71 ppm (CH_2); ^{31}P NMR (CH_2Cl_2): δ = 45.86, 44.41 ppm (2d, ^2J(P,P) = 30.8 Hz, 2 PPh_3); MS: *m/z*: 907.24 [M^+]; elemental analysis calcd (%) for $C_{55}H_{51}O_2P_3F_6Ru$: C 62.80, H 4.89; found: C 62.69, H 4.82.

Synthesis of Complex ***12a′***

Complex **12a′** (0.14 g, 92%) was similarly prepared from **8** (33 mg, 0.18 mmol), [Ru′]Cl (0.11 g, 0.17 mmol), and KPF_6 (0.02 g, 0.3 mmol). ^{1}H NMR ($CDCl_3$): δ = 7.82–6.49 (m, 46H; Ph), 5.21 (s, 5H; Cp), 3.68, 3.54 (2d, 2H; ^2J(H,H) = 19.4 Hz, CH_2), 3.28–2.80 (m, 4H; CH_2CH_2), 2.55 (s, 3H; OCH_3), 1.79–0.36 ppm (m, 6H; 3CH_2); ^{13}C NMR ($CDCl_3$): δ = 292.73 (t, ^2J(C,P) = 12.3 Hz, C_α), 140.45–126.46 (Ph, C(OCH_3)), 91.02 (Cp), 74.42 (CH_2), 55.21 (CPh), 53.04 (OCH_3), 39.41 (CH_2), 32.99 (CH_2), 27.39 (m, CH_2CH_2), 20.68 ppm (CH_2); ^{31}P NMR ($CDCl_3$): δ = 89.89, 89.06 ppm (2d, ^2J(P,P) = 19.7 Hz, 2 PPh_3); MS: *m/z*: 781.19 [M^+]; elemental analysis calcd (%) for $C_{45}H_{45}O_2P_3F_6Ru$: C 58.38, H 4.90; found: C 58.20, H 4.85.

Synthesis of Complex ***12b***

Complex **12b** (0.24 g, 85%) was similarly prepared from **8** (61 mg, 0.33 mmol), [Ru]Cl (0.22 g, 0.30 mmol), and KPF_6 (0.07 g, 0.4 mmol) in EtOH. ^{1}H NMR ($CDCl_3$): δ = 7.96–6.81 (m, 42H; Ph), 4.94 (s, 5H; Cp), 4.49, 4.32 (2d, ^2J(H,H) = 19.9 Hz, 2H; CH_2), 3.36, 3.16 (m, 2H; CH_2), 2.11–1.11 (m, 6H; 3CH_2), 0.88 ppm (t, ^3J(H,H) = 7.3 Hz, 3H; CH_3); ^{13}C NMR ($CDCl_3$): δ = 296.86 (t, ^2J(C,P) = 12.5 Hz, C_α), 140.31–126.58 (Ph, C(OCH_2CH_3)), 91.10 (Cp), 75.80 (CH_2), 62.25 (OCH_2), 55.67 (CPh), 41.24 (CH_2), 34.54 (CH_2), 21.74 (CH_2), 14.87 ppm (CH_3); ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 46.59, 44.80 ppm (2d, ^2J(P,P) = 30.3 Hz, 2 PPh_3); MS: *m/z*: 921.26 [M^+]; elemental analysis calcd (%) for $C_{56}H_{53}O_2P_3F_6Ru$: C 63.10, H 5.01; found: C 62.89, H 4.89.

Synthesis of Complex ***12c***

Complex **12c** (0.23 g, 82%) was similarly prepared from **8** (78 mg, 0.42 mmol), [Ru]Cl (0.28 g, 0.38 mmol), and KPF_6 (0.07 g, 0.4 mmol) in propanol. ^{1}H NMR ($CDCl_3$): δ = 7.90–6.76 (m, 42H; Ph), 4.87 (s, 5H; Cp), 4.48, 4.23 (2d, ^2J(H,H) = 20.1 Hz, 2H; CH_2), 3.18, 3.04 (m, 2H; CH_2), 2.07–1.16 (m, 8H; 4CH_2), 0.59 ppm (t, 3H; ^3J(H,H) = 7.3 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ = 296.85 (t, ^2J(C,P) = 12.5 Hz, C_α), 140.09–126.60 (Ph, C(OCH_2CH_3)), 91.05 (Cp), 75.62 (CH_2), 68.13 (OCH_2), 55.82 (CPh), 41.10 (CH_2), 34.54 (CH_2), 22.61 (CH_2), 21.78 (CH_2), 10.11 ppm (CH_3); ^{31}P NMR ($CDCl_3$): δ = 46.25, 44.63 ppm (2d, ^2J(P,P) = 30.3 Hz, 2PPh_3); MS: *m/z*: 935.27 [M^+]; elemental analysis calcd (%) for $C_{57}H_{55}O_2P_3F_6Ru$: C 63.39, H 5.31; found: C 63.11, H 5.27.

Synthesis of Complex ***13***

HBF_4 (0.1 mL) and CH_2Cl_2 (20 mL) were added to a Schlenk flask charged with **10** (0.12 g, 0.12 mmol) under nitrogen. The resulting solution was stirred at room temperature for 1 h. The color of solution changed from deep red to light yellow. Then the solution was filtered through Celite to remove insoluble salts, the solvent was removed under vacuum, and the solid residue was extracted with a small volume of CH_2Cl_2, followed by reprecipitation with diethyl ether (40 mL). Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexanes (1:1), and dried under vacuum. Compound **13** was obtained as a light yellow powder (0.12 g, 96%). ^{1}H NMR ($CDCl_3$): δ = 7.41–6.88 (m, 42H; Ph), 5.04 (s, 5H; Cp), 4.60, 4.16 (2d, ^2J(H,H) = 20.34, 2H; CH_2), 2.29–1.17 ppm (m, 6H; 3CH_2); ^{13}C NMR ($CDCl_3$): δ = 300.79 (t, ^2J(C,P) = 13.2 Hz, C_α), 139.65–126.96 (Ph, 2 PPh_3), 137.62 (d, J(C,F) = 248.8 Hz, CF), 92.33 (Cp), 74.00 (CH_2), 56.07 (d, ^2J(C,F) = 16.7 Hz, CPh), 38.97 (d, ^3J(C,F) = 3.0 Hz, CH_2), 34.62 (d, ^2J(C,F) = 25.6 Hz, CH_2), 21.02 ppm (d, ^3J(C,F) = 6.6 Hz CH_2); ^{31}P NMR ($CDCl_3$): δ = 46.06, 42.78 ppm (2d, ^2J(P,P) = 30.5 Hz, 2 PPh_3); MS: *m/z*: 895.22 [M^+]; elemental analysis calcd (%) for $C_{54}H_{48}OP_3F_7Ru$: C 62.37, H 4.65; found: C 62.03, H 4.58.

Single-Crystal X-ray Diffraction Analyses

Single crystals of complexes **6** and **12a′** suitable for X-ray diffraction were grown as mentioned above. A single crystal of **6** and **12a′** was glued to a glass fiber and mounted on a SMART CCD diffractometer. The diffraction data were both collected by using 3 kW sealed-tube $Mo_{K\alpha}$ radiation (T = 150 K). The exposure time was 5 s per frame. SADABS[35] (Siemens area detector absorption) absorption correction was applied and decay was negligible. Data were processed and the structure was solved and refined by the SHELXTL[36] program. Brief crystal data and related parameters of complexes **6** and **12a′** are listed below:

Crystal data for **6**·CH_2Cl_2: $C_{56}H_{53}Cl_2F_6OP_3Ru$; M_r = 1120.86; 0.25 × 0.20 × 0.15 mm; orthorhombic space group *Pbca*; a = 22.2228(2), b = 17.9118(2), c = 24.9796(2) Å; α = 90, β = 90, γ = 90°; V = 9943.14(16) Å^3; Z = 8; ρ_{calcd} = 1.498 mg m^{-3}; μ = 0.583 mm^{-1}; $F(000)$ = 4592; T = 150(2) K; R_1 = 0.0376; wR_2 = 0.0828; 11402 independent reflections.

Crystal data for **12a′**: $C_{45}H_{45}F_6O_2P_3Ru$; M_r = 925.79; 0.20 × 0.15 × 0.10 mm; monoclinic space group $P2_1/n$; a = 13.7867(3), b = 15.0755(2), c = 19.6565(4) Å; α = 90, β = 98.804(2), γ = 90°; V = 4037.30(13) Å^3; Z = 4; ρ_{calcd} = 1.523 mg m^{-3}; μ = 0.574 mm^{-1}; $F(000)$ = 1896; T = 150(2) K; R_1 = 0.0455; wR_2 = 0.1156; 9194 independent reflections.

CCDC 892285 (**6**) and 892286 (**12a′**) 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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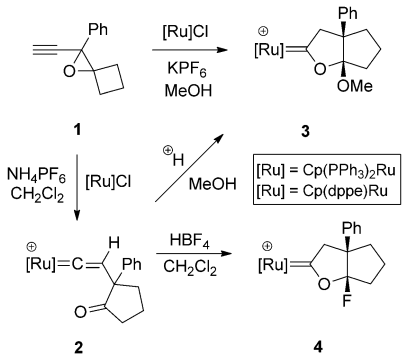
Complex matters: Ring expansion of cyclobutyloxirane **1**, induced by [Ru]Cl in CH_2Cl_2, affords the vinylidene complex **2** with a substituted cyclopentanone. In MeOH, the same reaction gives the bicyclic oxacarbene complex **3** through an additional cyclization reaction. In the absence of MeOH, cyclization of **2**, induced by HBF_4, is followed by a fluorination to afford complex **4**.



Cyclization

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Reactions of Propargyl Compounds Containing a Cyclobutyl Group Induced by a Ruthenium Complex

