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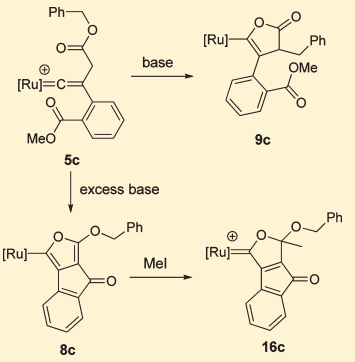
Tandem Cyclization in Ruthenium Vinylidene Complexes with Two Ester Groups

Wei-Chen Chang, Cheng-Wei Cheng, Hao-Wei Ma, Ying-Chih Lin,* and Yi-Hong Liu

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

Supporting Information

ABSTRACT: The reaction of [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$) with *o*-ethynyl-substituted methyl benzoate, followed by a sequential deprotonation and electrophilic alkylation reactions by further reacting with base and various alkyl haloacetates, respectively, generated several disubstituted ruthenium vinylidene complexes. In the deprotonation reactions of these disubstituted vinylidene complexes containing two ester groups, tandem cyclizations of the ligand is accompanied with a methanol elimination to generate a new organometallic product containing a three-ring indenofuranone ligand, which structure has been confirmed by a single-crystal X-ray diffraction analysis. Facile protonation and methylation are observed in these indenofuranone complexes. Additionally, for the simple furyl complex containing an *O*-benzyl group, a 1,3-migration of the benzyl group is observed to yield a lactone product and a Claisen rearrangement is also observed in analogous complexes with *O*-allyl or *O*-propargyl groups.



INTRODUCTION

Tandem reactions are known to rapidly and efficiently assemble complex structures from simple starting materials with minimal production of waste. This type of reaction has been steadily developed with the goal to provide synthetic efficiency and atom economy in modern synthetic research.[1] Owing to the ubiquitous presence of heterocyclic rings in innumerable bioactive natural products,[2] the synthesis of polycyclic compounds containing these heterocyclic rings using tandem techniques is an extensive area of organic chemistry. Derivatives of the furan ring, which are well-known to exhibit a broad range of biological activities including anticancer[3] and antioxidative activity,[4] have shown significant pharmacological potential.[5] The importance of these heterocyclic products has thus encouraged the development of synthesis of new five-membered oxygen heterocycles embedded in a polycyclic system. Transition-metal-catalyzed cyclization of alkynes bearing proximate C, O, N nucleophiles has proven to be a powerful synthetic route to a wide variety of carbo- and/or heterocycles.[6] In particular, the cyclization of alkynyl and allenyl ketones under various reaction conditions for furan synthesis have been pursued.[7] Significant progress in gold and platinum catalysis has led to new synthetic methods as well as versatile applications in the total synthesis of natural products.[8] Hashmi and co-workers reported gold-catalyzed intramolecular alkyne/furan cyclization.[9] Recently, a great deal of attention has been focused on the synthesis of polycyclic products containing furan and furan derivatives to be used as a precursor for natural product synthesis, and highly substituted esters have been considered as useful starting materials for the synthesis of such natural products.[10] The facile conversion of a ruthenium vinylidene complex containing an ester group to a furyl complex had been previously reported by us.[11] As an extension of our study, herein we report the synthesis of a series of disubstituted vinylidene complexes, each containing two ester groups in proximity from *o*-ethynyl-substituted methyl benzoate and various alkyl haloacetates. Deprotonation of this vinylidene complex was found to induce tandem cyclizations involving two ester groups, leading to the synthesis of indeno[1,2-*b*]furanone. Synthesis of derivatives of various indenofuranones have been reported.[12] The intermediate of the tandem cyclization could also be clearly observed by ^{31}P NMR studies. In addition, in the simple ruthenium furyl complex with a $-OCH_2Ph$ group, 1,3-benzyl migration under mild conditions led to the formation of a lactone complex. In a similar ruthenium furyl complex with an *O*-allyl or an *O*-propargyl group, Claisen rearrangement involving C−C bond formation between C_γ and the unsaturated group also generated the lactone product.

RESULTS AND DISCUSSION

Disubstituted Vinylidene Complexes and Cyclization. Three vinylidene complexes, **5a**−**c**, each containing two ester groups, were prepared from [Ru]-Cl (**1**, $Cp(PPh_3)_2Ru$), *o*-ethynyl-substituted methyl benzoate **2**, and various alkyl haloacetates following the procedures described previously, as shown in Scheme 1.[11] Treatment of [Ru]-Cl with **2** in the presence of KPF_6 in CH_2Cl_2 or MeOH for 1 day afforded the cationic monosubstituted vinylidene complex **3** in high yield. Subsequent deprotonation of **3** with base in solution generated the neutral acetylide complex **4**, and the mixture changed from orange to yellow within 15 min. Then, treatment of **4** with three alkyl

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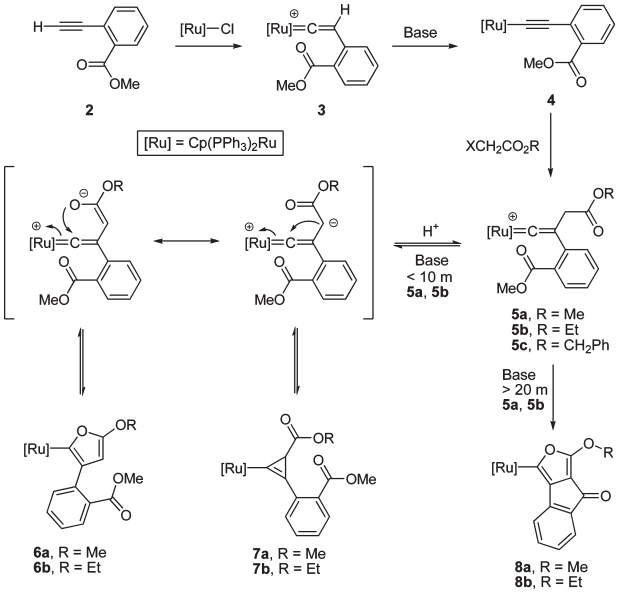
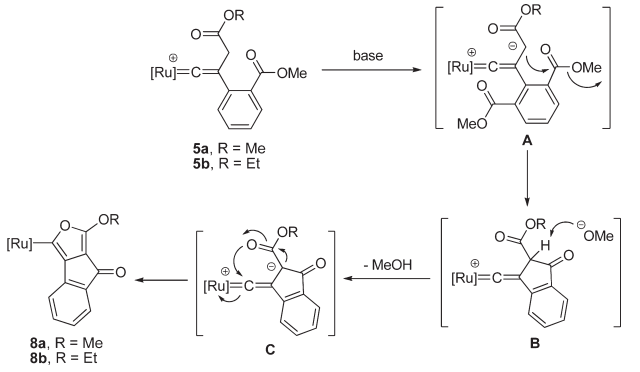
Scheme 1



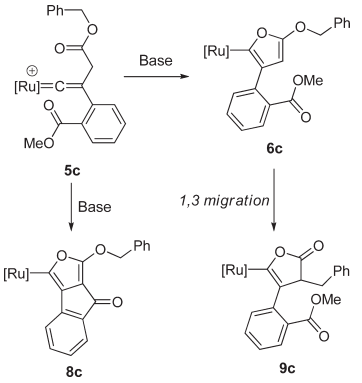
haloacetates XCH_2CO_2R (R = Me, Et, CH_2Ph) as alkylating reagents afforded the cationic disubstituted vinylidene complexes **5a**−**c**, respectively. These alkylation reactions could be speeded up upon heating the reaction mixture to 40 °C, but at higher temperature, side reactions leading to unidentifiable products took place. In the ^{1}H NMR spectrum of **5c**, the relatively downfield singlet peak at δ 5.07 is assigned to CH_2 bonded to C_β and the singlet resonance at δ 3.28 is assigned to CH_2Ph. The vinylidene C_α resonance in the ^{13}C NMR spectrum appears as a triplet at δ 345.05 with $^2J_{CP}$ = 14.5 Hz for **5c**. Complexes **5a**,**b** show similar characteristic NMR data.

Deprotonation of **5a** by *n*-Bu_4NOH in 10 min in acetone induced a cyclization reaction and yielded the neutral furyl complex **6a**. In 20 min, the reaction proceeded further to yield complex **8a**. As shown in Scheme 1, for the first 10 min, the reaction is expected to yield both the cyclopropenyl complex **7** and the furyl complex **6**, as reported previously.[11] The deprotonation presumably yielded a zwitterionic transition state with two resonance forms: i.e., keto and enol forms. The formation of complex **6** from **5** via the cyclopropenyl complex **7** was observed clearly in the ^{31}P NMR spectra. Using **5b** as an example, in the beginning of the reaction, exclusive formation of complex **7b** from **5b** was revealed by the presence of two doublet resonances at δ 52.70 and 45.80 with $^2J_{PP}$ = 36.3 Hz. Within 10 min a broad resonance at δ 49.96 assigned to **6b** appeared, and the peaks attributed to **7b** disappeared completely. The absence of a cyclopropenyl product at this time of the reaction could be reasonably interpreted in terms of comparatively higher strain energy of the cyclopropenyl ring relative to the five-membered furyl ring.[11] The structures of complexes **6a**,**b** have beendetermined by NMR spectroscopy. The ^{1}H NMR spectrum of **6a** consists of one characteristic singlet resonance at δ 4.31 assigned to the methyl unit of the methyl benzoate group and a singlet peak at δ 3.97 assigned to the OMe group in the furyl ligand. The proton resonance at δ 5.32 is assigned to the unique proton on the furyl ring. Transformation of **5** to **6** is reversible; namely, upon addition of excess acid, complexes **6a**,**b** were both reprotonated, converting back to the vinylidene complexes **5a**,**b**, respectively.[13]

Scheme 2



Scheme 3



Complex **6c** could be similarly prepared; however, **6c** is also unstable in solution and is observed only in the ^{31}P NMR spectrum. Further transformation of **6c** will be described below.

Direct deprotonation of **5a**,**b** for longer than 20 min and complexes **6a**,**b** in solution all lead to formation of complexes **8a**,**b**, respectively. Excess bases speed up the formation of **8**. The two new complexes **8a**,**b** display a distinctive light orange color. Crystalline precipitates formed directly from the reaction mixture, and the desired product could be obtained in analytically pure form by simple filtration. In the methoxy region of the ^{1}H NMR spectrum of **8a**, there is only one singlet peak at δ 3.98 assigned to the OMe group on the furyl ring. In the ^{13}C NMR spectrum of **8a** the characteristic C_α resonance appears as a triplet at δ 170.85 with $^2J_{CP}$ = 20.9 Hz, and the carbonyl peak resonance appears at δ 181.07.

Formation of complexes **8a**,**b** is believed to proceed via a formal methanol elimination reaction accompanied by formation of one C−C bond of two sp^2 carbons. As shown in Scheme 2, deprotonation of complex **5a** or **5b** first affords the keto form intermediate **A**, which is followed by an intramolecular C-acylation reaction to afford the intermediate **B**.[14] The remaining hydrogen at C_γ of **B**, which is also between two carbonyl groups, is expected to be reasonably acidic and thus easily deprotonated, in the presence of excess base, resulting in a formal methanol elimination, giving **C**. The enol form of **C** then induced a second intramolecular cyclization, i.e. via a nucleophilic addition of the enol oxygen to C_α[15] to yield **8**. Complex **6a** in acetone was

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Table 1. Distribution of Products 8c and 9c from 5c

entry	concn of **5c** (M)	amt of base (equiv)	**8c** (%)	**9c** (%)
1	4.0×10^{-3}	2	100	0
2	4.0×10^{-3}	1.5	83	17
3	4.0×10^{-4}	1.5	5	95
4	4.0×10^{-4}	<1	0	100

converted to complex **8a** within 30 min by a reversible ring-opening process followed by a formal methanol elimination reaction and then the same ring-closing process.

Ruthenium Lactone Complexes. Interestingly, when the deprotonation reaction of the vinylidene complex **5c**, containing a benzyl acetate and a methyl benzoate group, by *n*-Bu_4NOH was carried out in acetone, two products were obtained. As mentioned before, the reaction yielded the indenofuranone complex **8c**, the expected product from tandem cyclization. In addition, complex **9c** with a lactone moiety in the ligand, formed by a 1,3-benzyl migration, was also acquired (see Scheme 3). In order to better control the reaction for the formation of these two products, the concentration of the reactant and the amount of base used in the reaction were modified. Four reaction conditions were explored, and the results are given in Table 1.

An investigation into the effect of concentrations of the reactants indicated that a relatively higher concentration of **5c** and/or base would favor the formation of complex **8c** via the tandem cyclization pathway. When the deprotonation was carried out at two different concentrations of **5c** in acetone at 4×10^{-3} and 4×10^{-4} M, both with 1.5 equiv of base, complexes **8c** and **9c** in ratios of 83:17 and 5:95, respectively (entries 2 and 3), were obtained. Furthermore, when the base quantities were increased from 1.5 equiv to 2.0 equiv, complex **8c** was obtained as the only product (entry 1). At a lower base concentration, complex **9c** was obtained exclusively via a 1,3-migration pathway in good yield (entry 4). Presumably the lower base concentration hindered the second deprotonation step for the formation of **8c**. These two reaction pathways could be revealed when the reaction was monitored by ^{31}P NMR spectra at low temperature. Complex **5c** was dissolved in *d*-acetone along with [Ru]-CO^+, used as an internal standard. Several ^{31}P NMR spectra were recorded at 253 K in a 2 h period after ca. 1.1 equiv of base was added, and then the temperature was raised to 298 K to speed up the reaction. In the beginning of the reaction, exclusive formation of complex **7c** was revealed by the presence of two sharp doublet resonances at δ 53.98 and 44.58 with $^2J_{PP}$ = 35.7 Hz (Figure 1). Then, a broad resonance at δ 48.59 assigned possibly to **B**/**C** (see Scheme 2) and two doublet resonances at δ 51.58 and 49.32 with $^2J_{PP}$ = 38.1 Hz assigned to **6c**, with a ratio of 1:2, were detected. The broad resonance in the ^{31}P NMR spectrum of **6c** at 298 K splits at 253 K into a pair of two doublets. The decoalescence process is believed to be caused by the restricted rotation of the C−C bond between the furyl group and the methyl benzoate group. Complex **7c** was converted to **6c** and **A**, which was then converted to **B**/**C** (see Scheme 2), in a ratio of 1:2. Complex **6c** was then converted to complex **9c**, displaying two sharp doublet resonances at δ 51.80 and 47.85 with $^2J_{PP}$ = 37.3 Hz. A resonance at δ 48.97 attributed to complex **8c** was also observed, most likely formed from the intermediate **B**/**C**.[11] The ratio of the two final products, complexes **8c** and **9c** in a ratio of ca. 1:2, was approximately the same as the ratio of two intermediates **B**/**C** and **6c**. Pure complex **9c**, dissolved in *d*-acetone with excess base for 2 days, did not yield

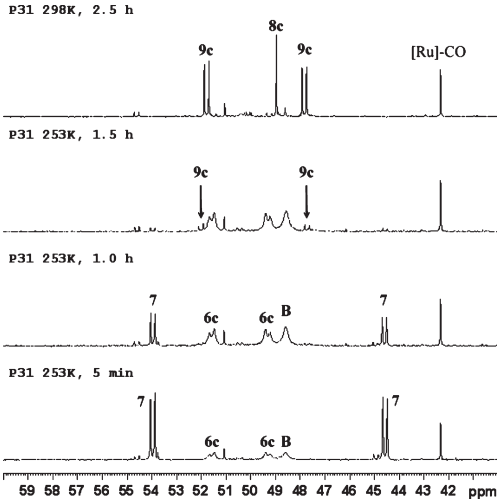

Figure 1. ^{31}P NMR spectra for the deprotonation reaction of **5c** in *d*-acetone. The peak at δ 42.33 is due to the added [Ru]-CO^+. The conversion from **7c** to **8c** and **9c** is shown clearly.

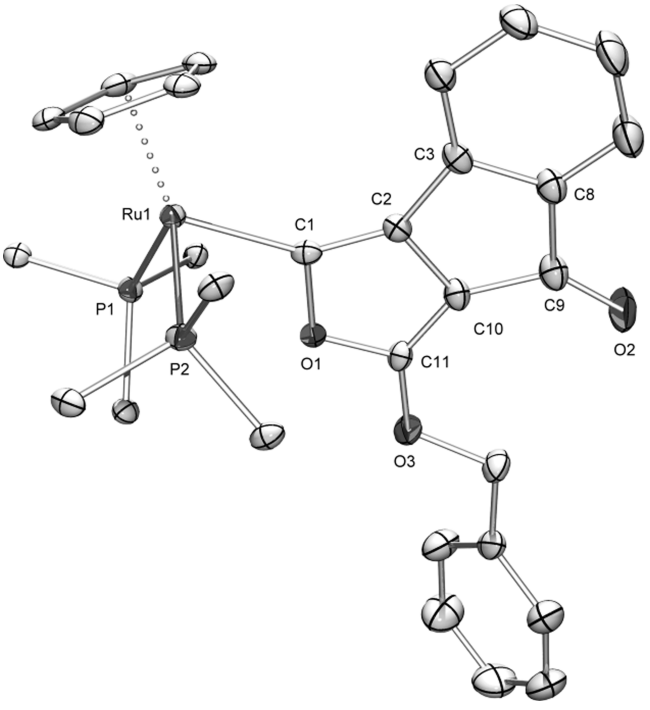

Figure 2. ORTEP drawing of complex **8c**. For clarity, aryl groups of the triphenylphosphine ligands on Ru, except the ipso carbons and PF_6^-, are omitted (thermal ellipsoids are given at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)−C(1), 2.042(2); C(1)−C(2), 1.373(3); C(2)−C(3), 1.467(3); C(1)−O(1), 1.453(3); C(11)−O(1), 1.340(3); C(9)−O(2), 1.224(3); C(11)−O(3), 1.329(3); Ru(1)−C(1)−C(2), 142.6(2); O(1)−C(1)−C(2), 103.5(2); C(2)−C(10)−C(11), 105.1(2); C(1)−O(1)−C(11), 109.8(2); O(1)−C(11)−O(3), 111.9(2); C(10)−C(11)−O(3), 137.1(2).

complex **8c**. Therefore, complexes **8c** and **9c** are not interconvertible and the transformation from **6c** to **9c** is not reversible.

Single crystals of complex **8c** were obtained from acetone. The solid-state structure of **8c** was determined by a single crystal

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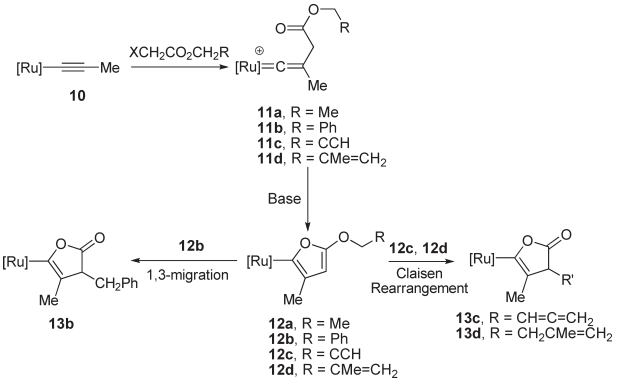
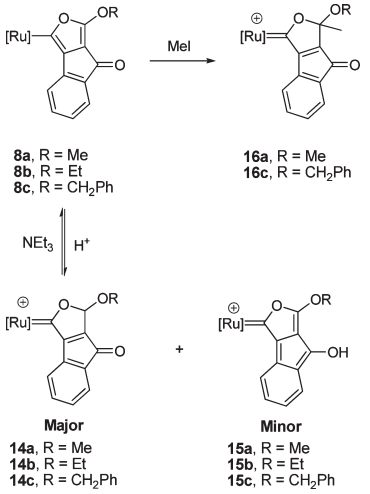
Scheme 4



Scheme 5



X-ray diffraction analysis. An ORTEP type view of the neutral complex is shown in Figure 2. Selected bond distances and angles are given in the figure caption. Bond formation between C(9) and C(10) between the furyl group and the carbonyl carbon atom of the methyl acetate group on the aromatic ring is clearly revealed, with the bond distance of C(9)−C(10) being 1.459(3) Å. The C(9)−O(2) distance of 1.224(3) Å shows a CO double bond. The Ru−C(1) bond length of 2.042(2) Å indicates a Ru−C single bond, and the C(1)−C(2) and C(10)−C(11) bond lengths of 1.373(3) and 1.357(3) Å, respectively, are both typical C═C double bonds.

As for **9c**, the 1,3-benzyl migration in the furyl ring of **6c**, classified as a sigmatropic process, results in the formation of the lactone complex. Similar 1,3-benzyl migration has been described in the literature.[16] Examples of competitive 1,3- and 1,5-migrations have also been noted in the 2-(benzyloxy)-3-(trifluoromethyl)furan series.[17] Complex **9c** was obtained at room temperature, and 1,5-migration was not detected. The regioselectivity may be attributed to the steric effect of the bulky ruthenium fragment.

Since the Claisen rearrangement is a well-known process for an allyl vinyl ether, the same migration is expected to take place in the analogous vinylidene complex with an allyl group substituting the benzyl group. However, treatment of the acetylide complex **4** with allyl 2-bromoacetate did not generate the expected vinylidene complex; instead, the vinylidene complex $[Ru]{=}C{=}C(C_6H_4COOMe)CH_2CH{=}CH_2^+$ from addition of only the allylic group was obtained as the only product. Allylation directly took place at C_β, instead of alkylation of the whole allyl haloacetate group. Therefore, a few other vinylidene complexes were synthesized as precursors in order to further explore this migration process on the furyl ligand. As shown in Scheme 4, the acetylide complex **10** with a terminal methyl group was used as a starting material to synthesize the various disubstituted vinylidene complexes **11a**−**d** via alkylation using four different alkyl haloacetates XCH_2CO_2R (R = Et, CH_2Ph, $CH_2C{\equiv}CH$, $CH_2CMe{=}CH_2$), respectively, in the presence of KPF_6 in CH_2Cl_2 at different temperatures. Complexes **11b**−**d** havevarious unsaturated organic moieties on the ester group for the purpose of investigating the migration process.

Treatment of complex **11a** with excess *n*-Bu_4NOH caused the typical deprotonation-induced cyclization, generating in good yield the furyl complex **12a**, which is stable, and no rearrangement was observed. However, deprotonation of complex **11b** containing the benzyl acetate group at C_β caused a two-step reaction process, the same as that mentioned for complex **5c**. That is, a cyclization is followed by a migration process, to give complex **13b** in moderate yield. The reaction proceeds via the unstable furyl intermediate **12b**, which could only be characterized by ^{31}P and ^1H NMR spectra. The ^1H NMR spectrum of **12b** consists of two singlet resonances at δ 5.35 and δ 4.34, assigned to $C_\gamma H$ and CH_2 of the benzyl group, respectively. In the ^1H NMR spectrum of **13b** a multiplet resonance at δ 2.96 is assigned to $C_\gamma H$ and multiplet resonances with an AB pattern at δ 2.82 and 2.46 with $^2J_{HH}$ = 13.7 Hz are assigned to the CH_2 of the benzyl group at C_γ. Two doublet resonances at δ 53.31 and 48.42 with $^2J_{PP}$ = 37.9 Hz in the ^{31}P NMR spectrum are due to the stereogenic center C_γ in **13b**.

Deprotonations of complexes **11c,d**, containing *O*-propargyl and *O*-methylallyl groups, respectively, were carried out with base in acetonitrile for 20 min at room temperature. Intramolecular cyclization, presumably yielding the furyl intermediate **12**, was quickly followed by a spontaneous Claisen rearrangement at room temperature to give the orange lactone complexes **13c,d**, respectively, in moderate yields. Complexes **13c,d** were characterized by a series of 2D NMR studies and mass spectroscopy. Attempts to monitor the reaction by NMR failed to give the spectroscopic data of the proposed furyl complex **12**. For the two ^1H NMR spectra of **11c** and **13c**, it is clear that the propargylic resonances at δ 4.68 (CH_2) and 2.51 (CH) of **11c** with J = 2.3 Hz are converted to the characteristic allenylic resonances at δ 4.74 (CH_2) and 4.90 (CH) attributed to the $CH{=}C{=}CH_2$ group in **13c** with the ═CH proton showing coupling with the unique lactone ring proton at δ 3.53 with J = 8.0 Hz. For the conversion of **11d** to **13d**, the singlet ^1H resonance of the OCH_2 group at δ 4.48 is converted to a complicated multiplet resonance at δ 1.90, which is also coupled with the unique ring proton at δ 2.69. Therefore, transformations of complexes **11c,d** to **13c,d** were considered to proceed via the Claisen rearrangement, which normally required drastic reaction conditions. The rearrangement leading to complexes **13c,d** was observed at room temperature.[18] The Claisen rearrangement of a fluorinated system[19] has been reported to take place also at room temperature, and the presence of a trifluoromethyl group was considered to result in significant rate enhancement. The rearrangement process, occurring at room temperature in the deprotonation of **11**, should be assisted by the metal fragment.

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Protonation and Methylation. The indenofuranone ligands of complexes **8a**−**c** readily undergo electrophilic addition reactions, generating various stable organometallic benzenoid systems (Scheme 5). Treatment of complex **8a** with HBF_4 in diethyl ether at room temperature afforded the carbene complex **14a** together with its isomer **15a** in a ratio of 2:1, as determined by NMR.[20] Protonation takes place at the carbonyl group as well as the at alkoxy-substituted carbon of the furyl ring.

The ^{31}P NMR spectrum of complex **14a** with a stereogenic center displays two doublet resonances at δ 41.69 and 39.84 with $^2J_{PP}$ = 26.6 Hz. The singlet resonance at δ 39.97 in the ^{31}P NMR spectrum is attributed to complex **15a**. Deprotonation of the mixture of two carbene complexes **14a** and **15a** by triethylamine regenerated complex **8a**. Protonation of complexes **8b,c** similarly yielded **14b**/**15b** and **14c**/**15c** mixtures, respectively, both in a ratio of 2:1. Because indenofuranones are prone to conjugate addition of nucleophiles at the α-position of the furyl ring, treatment of complexes **8a,c** with MeI afforded complexes **16a,c**, respectively (Scheme 5).[21] A series of 2D NMR studies and mass spectroscopy established the structure of **16a**. The triplet resonance at δ 357.35 with $^2J_{CP}$ = 14.0 Hz in the ^{13}C NMR spectrum of **16a** is assigned to the carbene carbon directly bound to the ruthenium. This resonance is shifted rather downfield relative to a regular carbene resonance in other ruthenium carbene complexes. In the ^1H NMR spectrum, two singlet resonances at δ 3.73 and 1.49 are assigned to the methoxyl group and the methyl group on C_δ, respectively. The ^{31}P NMR spectrum of complex **16a** with a stereogenic center displays two doublet resonances at δ 39.71 and 39.36 with $^2J_{PP}$ = 27.5 Hz. Complex **16c** can be prepared similarly and also shows similar characteristic NMR data.

CONCLUSIONS

In conclusion, we have reported reactions of [Ru]Cl with terminal aromatic alkynes containing *o*-substituted ester groups on the phenyl ring, yielding monosubstituted vinylidene products. Deprotonation of these vinylidene complexes followed by an alkylation using various alkyl haloacetates gave the cationic disubstituted vinylidene complexes **5** with two ester groups. For **5**, cyclization was induced by deprotonation using less than a stoichiometric amount of base to yield the furyl complexes **6**. Excess bases bring about tandem cyclizations to yield complexes **8** with the indenofuranone ligand, which has been confirmed by a single-crystal X-ray diffraction analysis. For the deprotonation of **5c** with a benzyl acetate group, in addition to **8c**, the lactone complex **9c** was obtained by a 1,3-benzyl migration process. Presumably the migration process takes place at the stage of the furyl complex **6c** obtainable from the first deprotonation of **5c**. Competitive formation of **8c** and **9c** is controlled by the concentration of the reactant and the amount of base used in the reaction. For deprotonation of vinylidene complexes with analogous ester substituents, Claisen rearrangement of the methylallyloxy or propargyloxy groups on the furyl ring also generates lactone complexes at room temperature.

EXPERIMENTAL SECTION

General Procedures. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and were distilled under nitrogen before use. All reagents were obtained from commercial suppliers and were used without further purification. NMR spectra were recorded on a Bruker AC-300, Avance-400, or DMX-500 FT-NMR spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ at ambient temperature, and chemical shifts are expressed in parts per million (δ, ppm). Proton chemical shifts are referenced to 7.26 ppm - ($CHCl_3$), and carbon chemical shifts are referenced to 77.0 ppm - ($CDCl_3$). ^{31}P (121 MHz) NMR spectra were measured relative to external 85% phosphoric acid. Both ^{13}C and ^{31}P spectra were proton-decoupled spectra. Mass spectra were recorded using LCQ Advantage (ESI) and Finnigan TSQ 700 spectrometers (EI). X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at the National Taiwan University. The complex [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$)[22] was prepared from $RuCl_3 \cdot xH_2O$, which was purchased from Strem Chemicals, according to the literature methods. Compound **10** was also synthesized according to the literature methods.[22]

Synthesis of 3. A solution of [Ru]-Cl (0.50 g, 0.69 mmol), **2** (0.20 g, 1.24 mmol), and KPF_6 (0.25 g, 1.36 mmol) in 10 mL of CH_2Cl_2 was stirred for 2 days under nitrogen at room temperature. Then the solution was filtered through Celite to remove the insoluble precipitates. Subsequently, the volume of the solution was reduced to ca. 2 mL under vacuum and was added to 50 mL of ether to give an orange precipitate, which was filtered and washed with ether and dried under vacuum to give complex **3** (0.61 g, 89% yield). Spectroscopic data for **3** are as follows. ^1H NMR (δ, $CDCl_3$): 8.00−7.01 (m, 34H, Ph); 6.67 (br, CH); 5.28 (s, 5H, Cp); 3.78 (s, 3H, OMe). ^{13}C NMR (δ, $CDCl_3$): 350.7 (t, $^2J_{CP}$ = 15.7 Hz, C_α); 133.9−124.8 (Ph); 117.1 (C_β); 166.1 (C═O); 94.9 (Cp); 52.0 (OMe). ^{31}P NMR (δ, $CDCl_3$): 42.30 (s, 2 PPh_3). Anal. Calcd for $C_{51}H_{43}F_6O_2P_3Ru$: C, 61.51; H, 4.35. Found: C, 61.23; H, 4.21. MS ESI: *m*/*z* 851.2 (M^+).

Deprotonation of 3. Complex **3** (0.49 g, 0.50 mmol) was treated with excess sodium methoxide (0.051 g, 0.93 mmol) in 15 mL of MeOH. The solution was stirred at room temperature for 20 min under nitrogen. Subsequently, the solvent was removed and then the residues were extracted with 4 × 20 mL of diethyl ether and filtered through Celite. The solvent of the filtrate was removed under vacuum to give a yellow precipitate, identified as compound **4** (0.41 g, 96% yield). Spectroscopic data for **4** are as follows. ^1H NMR (δ, C_6D_6): 8.05−6.90 (m, 33H, Ph); 4.64 (s, 5H, Cp); 3.69 (s, 3H, OMe). ^{13}C NMR (δ, C_6D_6): 166.1 (C═O); 95.0 (br, C_α); 133.9−124.8 (Ph); 117.1 (C_β); 94.9 (Cp); 52.0 (OMe). ^{31}P NMR (δ, C_6D_6): 52.04 (s, 2 PPh_3). Anal. Calcd for $C_{51}H_{42}O_2P_2Ru$: C, 72.07; H, 4.98. Found: C, 72.22; H, 4.88. MS ESI: *m*/*z* 851.16 ($M^+ + 1$).

Synthesis of 5a. To a solution of complex **4** (0.31 g, 0.35 mmol) and KPF_6 (0.25 g, 1.36 mmol) in 10 mL of CH_2Cl_2, was added methyl 2-bromoacetate (0.13 g, 0.85 mmol) at room temperature. The mixture was stirred for 5 days under nitrogen at 40 °C. The solution was filtered through Celite to remove insoluble precipitates, and the volume of the filtrate was reduced to ca. 1 mL under vacuum and was added to an ether/hexane mixture (1/1, 50 mL) to cause formation of an orange precipitate, which was filtered and washed with ether and dried under vacuum to give complex **5a** (0.29 g, 77% yield). Spectroscopic data for **5a** are as follows. ^1H NMR (δ, $CDCl_3$): 8.07−6.97 (m, 34H, Ph); 5.23 (s, 5H, Cp); 3.94 (s, 3H, OMe); 3.65 (s, 3H, OMe); 3.28 (s, 2H, CH_2). ^{13}C NMR (δ, $CDCl_3$): 345.4 (t, $^2J_{CP}$ = 14.5 Hz, C_α); 134.1−128.5 (Ph); 126.6 (C_β); 172.2 (C═O); 166.3 (C═O); 95.0 (Cp); 52.1 (OMe); 33.9 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.97 (s, 2 PPh_3). Anal. Calcd for $C_{54}H_{47}F_6O_4P_3Ru$: C, 60.73; H, 4.44. Found: C, 60.62; H, 4.51. MS ESI: *m*/*z* 923.20 (M^+).

Synthesis of 5b. To a solution of complex **4** (0.33 g, 0.39 mmol) in 10 mL of CH_2Cl_2, was added 2.5 equiv of ethyl 2-iodoacetate (0.19 g, 0.89 mmol), and the mixture was stirred under nitrogen at room temperature for 2 days. The solution was filtered through Celite to remove insoluble precipitates, and the volume of the solution was

reduced to ca. 1 mL under vacuum and added to an ether/hexane mixture (1/1, 50 mL) to give an orange precipitates, which was filtered and washed with ether and dried under vacuum to give complex **5b** (0.30 g, 79% yield). Spectroscopic data for **5b** are as follows. ^{1}H NMR (δ, $CDCl_3$): 8.04−6.98 (m, 34H, Ph); 5.26 (s, 5H, Cp); 4.09 (q, 2H, $^3J_{HH}$ = 7.1 Hz, OCH_2); 3.94 (s, 3H, OMe); 3.27 (s, 2H, CH_2); 1.16 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3). ^{13}C NMR (δ, $CDCl_3$): 345.5 (t, $^2J_{CP}$ = 14.6 Hz, C_α); 134.1−128.5 (Ph); 126.8 (C_β); 171.7 (C═O); 166.2 (C═O); 95.0 (Cp); 61.1 (OCH_2); 52.2 (OMe); 34.1 (CH_2); 14.2 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 42.98 (s, 2 PPh_3). Anal. Calcd for $C_{55}H_{49}IO_4P_2Ru$: C, 62.09; H, 4.64. Found: C, 58.93; H, 4.08 (deviations may be due to the presence of both I and I_3 anion; no attempt was made to purify the product) MS ESI: m/z 937.17 (M^+).

Synthesis of 5c. To a solution of complex **4** (0.31 g, 0.36 mmol) and KPF_6 (0.25 g, 1.36 mmol) in 10 mL of CH_2Cl_2, was added benzyl 2-bromoacetate (0.21 g, 0.92 mmol), and the solution was stirred under nitrogen at 40 °C for 7 days. The solution was filtered through Celite to remove insoluble precipitates, and the volume of the filtrate was reduced to ca. 1 mL under vacuum and added to anether/hexane mixture (1/1, 50 mL) to give an orange precipitate, which was filtered and washed with ether and dried under vacuum to give complex **5c** (0.35 g, 85% yield). Spectroscopic data for **5c** are as follows. ^{1}H NMR (δ, $CDCl_3$): 8.01−6.94 (m, 39H, Ph); 5.18 (s, 5H, Cp); 5.08 (s, 2H, OCH_2); 3.91 (s, 3H, OMe); 3.28 (s, 2H, CH_2). ^{13}C NMR (δ, $CDCl_3$): 345.1 (t, $^2J_{CP}$ = 14.5 Hz, C_α); 135.3−128.2 (Ph); 126.7 (C_β); 171.4 (C═O); 166.1 (C═O); 94.9 (Cp); 66.9 (OCH_2); 52.0 (OMe); 34.0 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.97 (s, 2 PPh_3). Anal. Calcd for $C_{60}H_{51}F_6O_4P_3Ru$: C, 62.99; H, 4.49. Found: C, 62.89; H, 4.41. MS ESI: m/z 999.11 (M^+).

Synthesis of 6a and 8a. To a solution of complex **5a** (0.36 g, 0.34 mmol) in 3 mL of acetone was added n-Bu_4NOH (0.83 mL, 1 M in MeOH, 0.83 mmol), and the mixture was stirred under nitrogen for 30 min, giving an orange precipitate which was collected by filtration and washed with cold acetone to remove excess base. The powder was dried under vacuum to give complex **8a** (0.25 g, 85% yield). Spectroscopic data for **8a** are as follows. ^{1}H NMR (δ, C_6D_6): 8.11−6.92 (m, 34H, Ph); 4.42 (s, 5H, Cp); 3.98 (s, 3H, OMe). ^{13}C NMR (δ, C_6D_6): 181.1 (C═O); 170.9 (t, $^2J_{CP}$ = 20.9 Hz, C_α); 162.5 (C_δ); 142.8−121.1 (Ph and C_β); 102.8 (C_γ); 85.2 (Cp); 60.3 (OMe). ^{31}P NMR (δ, C_6D_6): 50.10 (s, 2 PPh_3). Anal. Calcd for $C_{53}H_{42}O_3P_2Ru$: C, 71.53; H, 4.76. Found: C, 71.68; H, 4.88. MS ESI: m/z 891.10 ($M^+ + 1$). Complex **6a** was observed in NMR spectra for the reaction in C_6D_6. Spectroscopic data for **6a** are as follows. ^{1}H NMR (δ, C_6D_6): 8.10−6.91 (m, 34H, Ph); 5.32 (s, 1H, CH); 4.42 (s, 5H, Cp); 4.31 (s, 3H, OMe); 3.97 (s, 3H, OMe). ^{13}C NMR (δ, C_6D_6): 169.4 (C═O); 154.0 (t, $^2J_{CP}$ = 18.90 Hz, C_α); 164.5 (C_δ); 142.9−121.1 (Ph and C_β); 87.9 (C_γ); 84.8 (Cp); 58.0 (OMe); 51.5 (OMe). ^{31}P NMR (δ, C_6D_6): 50.10 (s, 2 PPh_3).

Synthesis of 6b and 8b. To a solution of complex **5b** (0.39 g, 0.36 mmol) in 3 mL of acetone was added n-Bu_4NOH (0.81 mL, 1 M in MeOH, 0.81 mmol), and the mixture was stirred under nitrogen for 30 min. The orange powder that precipitated was collected and washed with 2 × 2 mL of acetone to remove excess base. The powder was dried under vacuum to give complex **8b** (0.29 g, 87% yield). Spectroscopic data for **8b** are as follows. ^{1}H NMR (δ, C_6D_6): 8.09−6.92 (m, 34H, Ph); 4.57 (q, 2H, $^3J_{HH}$ = 7.0 Hz, OCH_2); 4.42 (s, 5H, Cp); 0.95 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3). ^{13}C NMR (δ, C_6D_6): 180.9 (C═O); 170.2 (t, $^2J_{CP}$ = 21.0 Hz, C_α); 161.6 (C_δ); 142.7−121.1 (Ph and C_β); 102.6 (C_γ); 85.2 (Cp); 69.1 (OCH_2); 15.1 (CH_3). ^{31}P NMR (δ, C_6D_6): 50.06 (s, 2 PPh_3). Anal. Calcd for $C_{54}H_{44}O_3P_2Ru$: C, 71.75; H, 4.91. Found: C, 71.83; H, 4.81. MS ESI: m/z 905.14 ($M^+ + 1$). Complex **6b** was observed by NMR spectra in C_6D_6. Spectroscopic data for **6b** are as follows. ^{1}H NMR (δ, C_6D_6): 8.21−7.05 (m, 34H, Ph); 5.40 (s, 1H, CH); 4.43 (s, 5H, Cp); 4.57 (q, 2H, $^3J_{HH}$ = 7.0 Hz, OCH_2); 4.31 (s, 3H, OMe); 0.83 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3). ^{13}C NMR (δ, C_6D_6): 169.5 (C═O); 154.5 (t, $^2J_{CP}$ = 18.9 Hz, C_α); 163.3 (C_δ); 142.9−121.1 (Ph and C_β); 89.7 (C_γ); 85.2 (Cp); 67.0 (OCH_2); 51.5 (OMe); 15.0 (CH_3). ^{31}P NMR (δ, C_6D_6): 50.05 (s, 2 PPh_3).

Synthesis of 8c. To a solution of complex **5c** (0.33 g, 0.29 mmol) in 3 mL of acetone was added n-Bu_4NOH (0.82 mL, 1.0 M in MeOH, 0.82 mmol), and the mixture was stirred under nitrogen for 30 min. The orange powder that precipitated was collected and washed with acetone to remove excess base. Then the powder was dried under vacuum to give **8c** (0.21 g, 75% yield). Spectroscopic data for **8c** are as follows. ^{1}H NMR (δ, C_6D_6): 8.11−6.91 (m, 39H, Ph); 5.73 (s, 2H, CH_2); 4.42 (s, 5H, Cp). ^{13}C NMR (δ, d-acetone): 181.1 (C═O); 174.2 (t, $^2J_{CP}$ = 19.0 Hz, C_α); 161.8 (C_δ); 143.1−121.8 (Ph and C_β); 102.8 (C_γ); 85.7 (Cp); 74.4 (CH_2). ^{31}P NMR (δ, C_6D_6): 50.05 (s, 2 PPh_3). Anal. Calcd for $C_{59}H_{46}O_3P_2Ru$: C, 73.36; H, 4.80. Found: C, 73.47; H, 4.91. MS ESI: m/z 967.41 ($M^+ + 1$).

Synthesis of 9c. To a solution of complex **5c** (0.24 g, 0.21 mmol) in 3 mL of acetone was added n-Bu_4NOH (0.20 mL, 1 M in MeOH, 0.20 mmol), and the mixture was stirred under nitrogen at 40 °C for 2 h. The mixture was cooled to room temperature, and the solvent was removed under vacuum. The residues were extracted with hexane to give a light yellow solution which was then dried under vacuum to give complex **9c** (0.14 g, 69% yield). Spectroscopic data for **9c** are as follows. ^{1}H NMR (C_6D_6): δ 7.97−6.94 (m, 39H, Ph); 4.38 (s, 5H, Cp); 4.20 (m, 1H, $^3J_{HH}$ = 6.2, 7.2 Hz, CH); 3.63 (s, 3H, OMe); 2.84 (dd, 1H, J_{HH} = 14.0, 6.2 Hz, CH_2); 2.59 (dd, 1H, $^2J_{HH}$ = 14.0, 7.2 Hz, CH_2). ^{13}C NMR (δ, C_6D_6): 181.8 (C_δ); 173.2 (t, $^2J_{CP}$ = 14.6 Hz, C_α); 168.0 (C═O); 142.1−125.5 (Ph and C_β); 84.6 (Cp); 51.5 (OMe); 49.6 (C_γ); 37.1 (CH_2). ^{31}P NMR (δ, C_6D_6): 53.06, 48.01 (2 d, $^2J_{PP}$ = 37.0 Hz, 2 PPh_3). Anal. Calcd for $C_{60}H_{50}O_4P_2Ru$: C, 72.20; H, 5.05. Found: C, 72.36; H, 5.16. MS ESI: m/z 999.47 ($M^+ + 1$).

Synthesis of 11a. Complex **11a** (0.25 g, 95%) was prepared from [Ru]-C≡CMe (0.20 g, 0.27 mmol), KPF_6 (0.076 g, 0.41 mmol), and 5.0 equiv of ICH_2CO_2Et (0.16 mL, 1.4 mmol) using the same procedure as that for the synthesis of **5**. Spectroscopic data for **11a** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.40−6.98 (m, 30H, Ph); 5.24 (s, 5H, Cp); 4.11 (q, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2); 2.78 (s, 2H, CH_2); 1.90 (s, 3H, CH_3); 1.16 (t, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3). ^{13}C NMR (δ, $CDCl_3$): 350.4 (t, $^2J_{P-C}$ = 14.9 Hz, C_α); 171.5 (C═O); 135.6−128.4 (Ph); 117.8 (C_β); 94.2 (Cp); 61.0 (OCH_2); 30.8 (CH_2); 14.2 (CH_3); 11.3 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 42.72 (s, 2 PPh_3). Anal. Calcd for $C_{48}H_{45}F_6O_2P_3Ru$: C, 59.94; H, 4.72. Found: C, 60.11; H, 4.69. MS ESI: m/z 817.18 (M^+).

Synthesis of 11b. Complex **11b** (0.25 g, 88%) was similarly prepared from [Ru]-C≡CMe (0.21 g, 0.28 mmol), KPF_6 (0.076 g, 0.410 mmol), and 5.0 equiv of $BrCH_2CO_2CH_2Ph$ (0.31 g, 1.4 mmol). Spectroscopic data for **11b** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.38−6.95 (m, 35H, Ph); 5.13 (s, 5H, Cp); 5.12 (s, 2H, OCH_2); 2.80 (s, 2H, CH_2); 1.90 (s, 3H, CH_3). ^{13}C NMR (δ, $CDCl_3$): 350.4 (t, $^2J_{P-C}$ = 15.4 Hz, C_α); 171.4 (C═O); 135.8−128.5 (Ph); 117.9 (C_β); 94.2 (Cp); 66.9 (OCH_2); 30.9 (CH_2); 11.2 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 42.66 (s, 2 PPh_3). IR (KBr, cm^{-1}): ν 1733 (C═O). Anal. Calcd for $C_{53}H_{47}F_6O_2P_3Ru$: C, 62.17; H, 4.63. Found: C, 62.23; H, 4.58. MS FAB m/z: 879.21 ($M^+ + 1$), 617.1 ($M^+ + 1 - PPh_3$).

Synthesis of 11c. Complex **11c** (0.23 g, 87%) was similarly prepared from [Ru]-C≡CMe (0.20 g, 0.27 mmol), KPF_6 (0.076 g, 0.410 mmol), and 5.0 equiv of $BrCH_2CO_2CH_2C{\equiv}CH$ (0.24 g, 1.4 mmol). Spectroscopic data for **11c** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.40−6.98 (m, 30H, Ph); 5.21 (s, 5H, Cp); 4.68 (d, 2H, $^4J_{HH}$ = 2.3 Hz, OCH_2); 2.79 (s, 2H, CH_2); 2.51 (t, 1H, $^4J_{HH}$ = 2.3 Hz, CH); 1.92 (s, 3H, CH_3). ^{13}C NMR (δ, $CDCl_3$): 350.4 (t, $^2J_{P-C}$ = 14.8 Hz, C_α); 170.8 (s, C═O); 135.5−127.3 (Ph); 123.0 (C_β); 95.6 (Cp); 80.1 (≡C); 77.2 (≡C); 52.4 (OCH_2); 30.7 (CH_2); 11.4 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 42.56 (s, 2 PPh_3). Anal. Calcd for $C_{49}H_{43}F_6O_2P_3Ru$: C, 60.56; H, 4.46. Found: C, 60.43; H, 4.38. MS FAB m/z: 827.5 ($M^+ + 1$), 563.3 ($M^+ + 1 - PPh_3$).

Synthesis of 11d. A mixture (0.21 g) of **11d** and [[Ru]=C=C(Me)CH_2C(Me)=CH_2][PF_6] in a ratio of 9:1 was similarly prepared from [Ru]-C≡CMe (0.26 g, 0.33 mmol), KPF_6 (0.076 g, 0.41 mmol), and $BrCH_2CO_2CH_2C(Me)=CH_2$ (0.16 g, 0.82 mmol). No attempt was made to separate **11d** from the mixture. Spectroscopic data for **11d** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.40−6.98 (m, 30H, Ph); 5.19 (s, 5H, Cp); 4.93 (br s, 2H, =CH_2); 4.48 (s, 2H, OCH_2); 2.84 (s, 2H, CH_2); 1.93 (s, 3H, CH_3); 1.72 (s, 3H, CH_3). ^{31}P NMR (δ, $CDCl_3$): 42.66 (s, PPh_3). MS FAB m/z: 844.21 ($M^+ + 1$), 581.2 ($M^+ + 1 - PPh_3$).

Synthesis of 12a. To a solution of **11a** (0.22 g, 0.23 mmol) in CH_3CN (5 mL) was added a solution of *n*-Bu_4NOH (2.5 mL, 1 M in MeOH). The mixture was stirred for 20 min at room temperature, and a light yellow precipitate formed. The precipitate was filtered, washed with 2 × 5 mL of CH_3CN and 2 × 10 mL of diethyl ether, and dried under vacuum. The product was identified as **12a** (0.15 g, 85%). Spectroscopic data for **12a** are as follows. ^{1}H NMR (δ, C_6D_6): 7.46−6.90 (m, 30H, Ph); 5.33 (s, 1H, CH); 4.47 (s, 5H, Cp); 3.29 (q, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2); 2.26 (s, 3H, CH_3); 0.95 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3). ^{13}C NMR (δ, C_6D_6): 163.2 (C_δ); 149.9 (t, $^2J_{P-C}$ = 19.8 Hz, C_α); 88.3 (C_β); 84.4 (Cp); 80.4 (C_γ); 58.6 (OCH_2); 15.4 (CH_2CH_3). ^{31}P NMR (δ, C_6D_6): 51.53 (s, 2 PPh_3). Anal. Calcd for $C_{48}H_{44}O_2P_2Ru$: C, 70.66; H, 5.44. Found: C, 70.83; H, 5.51. MS FAB: m/z 817.20 ($M^+ + 1$).

Synthesis of 12b. To a solution of **11b** (0.22 g, 0.22 mmol) in 5 mL of CH_3CN was added a solution of *n*-Bu_4NOH (2.2 mL, 1 M in MeOH). The mixture was stirred for 2 min at room temperature, and an orange precipitate formed, which was filtered, washed with 2 × 5 mL of CH_3CN and 2 × 10 mL of diethyl ether, and dried under vacuum. The product was identified as **12b** (0.17 g, 87%). Spectroscopic data for **12b**: ^{1}H NMR (δ, C_6D_6): 7.48−6.90 (m, 35H, Ph); 5.35 (s, 1H, CH); 4.48 (s, 5H, Cp); 4.34 (s, 2H, CH_2); 2.25 (s, 3H, CH_3). ^{31}P NMR (δ, C_6D_6): 51.50 (s, PPh_3). Anal. Calcd for $C_{53}H_{46}O_2P_2Ru$: C, 72.51; H, 5.28. Found: C, 72.73; H, 5.41. MS FAB: m/z 879.23 ($M^+ + 1$).

Synthesis of 13b. Complex **12b** (0.20 g, 0.23 mmol) was dissolved in benzene, and the solution was stirred for 30 min under nitrogen at room temperature. The resulting solution was dried to give complex **13b** (0.20 g) quantitatively. Complex **12b** was also converted to **13b** in 7 days as a solid at room temperature. Spectroscopic data for **13b** are as follows. ^{1}H NMR (δ, C_6D_6): 7.46−7.03 (m, 35H, Ph); 4.33 (s, 5H, Cp); 2.96 (m, 1H, $^3J_{HH}$ = 7.5, 6.0 Hz, CH); 2.82 (dd, 1H, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 6.0 Hz, CH_2); 2.46 (dd, 1H, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 7.5 Hz, CH_2); 1.63 (s, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 181.2 (C=O); 169.9 (t, $^2J_{CP}$ = 19.1 Hz, C_α); 140.6−126.1 (Ph); 123.3 (C_β); 84.4 (Cp); 50.1 (C_γ); 37.6 (CH_2); 15.3 (Me). ^{31}P NMR (δ, C_6D_6): 53.31, 48.42 (2 d, $^2J_{PP}$ = 37.9 Hz, 2 PPh_3). IR (KBr, cm^{-1}): ν 1746 (C=O). Anal. Calcd for $C_{53}H_{46}O_2P_2Ru$: C, 72.51; H, 5.28. Found: C, 72.38; H, 5.19. MS FAB: m/z 879.23 ($M^+ + 1$).

Synthesis of 13c. To a solution of **11c** (0.20 g, 0.21 mmol) in 5 mL of CH_3CN was added a solution of *n*-Bu_4NOH (3.0 mL, 1 M in MeOH). The mixture was stirred for 5 min at room temperature and yielded a yellow precipitate, which was filtered, washed with 2 × 5 mL of CH_3CN and 2 × 10 mL of diethyl ether, and dried under vacuum. The product was then extracted with benzene (5 mL) and dried under vacuum to yield **13c** (0.14 g, 84%). Spectroscopic data for **13c** are as follows. ^{1}H NMR (δ, C_6D_6): 7.55−7.04 (m, 30H, Ph); 4.90 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 6.6 Hz, =CH); 4.77−4.70 (m, 2H, CH_2); 4.48 (s, 5H, Cp); 3.53 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH); 2.05 (s, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 210.2 (=C=); 179.7 (C=O); 171.3 (t, $^2J_{CP}$ = 19.4 Hz, C_α); 140.4−127.4 (Ph); 121.6 (C_β); 89.1 (=CH); 84.4 (Cp); 76.0 (=CH_2); 49.7 (C_γH); 14.6 (Me). ^{31}P NMR (δ, C_6D_6): 50.92, 50.54 (2 d, $^2J_{PP}$ = 37.1 Hz, PPh_3). Anal. Calcd for $C_{49}H_{42}O_2P_2Ru$: C, 71.26; H, 5.13. Found: C, 71.08; H, 5.17. MS FAB: m/z 827.15 ($M^+ + 1$).

Synthesis of 13d. Complex **13d** was similarly prepared from a mixture of **11d** and [[Ru]=C=C(Me)CH_2C(Me)=CH_2][PF_6] (9:1, total weight 0.22 g; estimated weight of **11d** 0.20 g, 0.20 mmol) and *n*-Bu_4NOH (0.25 mL, 1 M in MeOH). Complex **13d** (0.15 g, *ca.* 88%) was purified by column chromatography from the product mixture. Spectroscopic data for **13d** are as follows. ^{1}H NMR (δ, C_6D_6): 7.40−7.21 (m, 30H, Ph); 4.73 (s, 1H, =CH_2); 4.62 (s, 1H, =CH_2); 4.27 (s, 5H, Cp); 2.69 (m, 1H, CH); 1.90 (m, 2H, CH_2); 1.87 (s, 3H, CH_3); 1.69 (s, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 182.5 (C=O); 171.3 (t, $^2J_{CP}$ = 19.1 Hz, C_α); 143.6 (=C); 139.8−127.2 (Ph); 123.5 (C_β); 112.0 (=CH_2); 83.9 (Cp); 46.7 (C_γH); 38.9 (CH_2); 22.4 (CH_3); 14.9 (Me). ^{31}P NMR (δ, C_6D_6): 51.01, 50.32 (2 d, $^2J_{PP}$ = 37.2 Hz, PPh_3). Anal. Calcd for $C_{50}H_{46}O_2P_2Ru$: C, 71.33; H, 5.51. Found: C, 71.55; H, 5.67. MS FAB: m/z 843.20 ($M^+ + 1$).

Reactions of 8a−c with HBF_4. A typical experimental procedure for the reaction of HBF_4 with **8** is described below. Complex **8a** (0.11 g, 0.12 mmol) was treated with excess HBF_4 (48% in diethyl ether, 0.04 mL, 0.22 mmol) in diethyl ether (10 mL), and a brown precipitate formed immediately. The mixture was stirred until no further solid was formed. The precipitates were collected by filtration and washed with diethyl ether to yield a mixture of **14a** and **15a** in a ratio of 2:1 (total yield: 0.082 g, 82%). No attempt was made to separate the two products. Spectroscopic data for **14a** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.75−6.58 (m, 34H, Ph); 5.41 (s, 5H, Cp); 4.27 (s, 1H, CH); 3.76 (s, 3H, OMe). ^{13}C NMR (δ, $CDCl_3$): 351.0 (t, $^2J_{CP}$ = 14.5 Hz, C_α); 192.3 (C=O); 168.5 (C_β); 144.4−121.5 (Ph); 95.5 (Cp); 53.3 (OMe); 49.6 (OCH). ^{31}P NMR (δ, $CDCl_3$): 41.69, 39.84 (2 d, $^2J_{PP}$ = 26.6 Hz, 2 PPh_3). Spectroscopic data for **15a**: are as follows. ^{1}H NMR (δ, $CDCl_3$): 9.93 (OH); 7.68−6.31 (m, 34H, Ph); 5.34 (s, 5H, Cp); 3.66 (s, 3H, OMe). ^{13}C NMR (δ, $CDCl_3$): 365.0 (t, $^2J_{CP}$ = 15.9 Hz, C_α); 144.4−121.5 (Ph); 95.7 (Cp); 53.5 (OMe); 49.6 (OCH). ^{31}P NMR (δ, $CDCl_3$): 39.97 (s, PPh_3). The synthesis of **14b** and **15b** from **8b** (0.11 g, 0.12 mmol) followed the same procedure. The ratio of **14b** to **15b** is also 2:1 (total yield: 0.094 g, 86%). Spectroscopic data for **14b** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.72−6.69 (m, 34H, Ph); 5.40 (s, 5H, Cp); 4.26 (s, 1H, CH); 4.25 (m, 1H, CH_2); 4.15 (m, 1H, CH_2); 1.27 (t, J_{HH} = 6.8 Hz, 3H, CH_3). ^{13}C NMR (δ, $CDCl_3$): 351.5 (t, $^2J_{CP}$ = 16.2 Hz, C_α); 192.1 (C=O); 168.0 (C_β); 144.2−121.5 (Ph); 95.5 (Cp); 62.5 (OCH_2); 53.8 (OCH); 14.0 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 41.52, 39.60 (2 d, $^2J_{PP}$ = 26.2 Hz, 2 PPh_3). Spectroscopic data for **15b** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.65−6.29 (m, 34H, Ph); 5.26 (s, 5H, Cp); 4.34 (q, 2H, $^3J_{HH}$ = 6.8 Hz, CH_2); 1.40 (t, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3). ^{13}C NMR (δ, $CDCl_3$): 365.9 (t, $^2J_{CP}$ = 16.2 Hz, C_α); 144.2−121.5 (Ph and C_β); 95.9 (Cp); 63.0 (OCH_2); 14.7 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 39.44 (s, PPh_3). The synthesis of **14c** and **15c** from **8c** (total yield: 0.090 g, 83%) followed the same procedure (yield: 0.10 g, 0.10 mmol). The ratio of **14c** to **15c** is 2.5:1. Spectroscopic data for **14c** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.72−6.69 (m, 39H, Ph); 5.17 (s, 5H, Cp); 5.31, 5.07 (2d, 2H, $^2J_{HH}$ = 12.3 Hz, CH_2); 4.19 (s, 1H, CH). ^{13}C NMR (δ, $CDCl_3$): 350.8 (t, $^2J_{CP}$ = 14.0 Hz, C_α); 192.4 (C=O); 168.3 (C_β); 144.2−121.6 (Ph); 95.4 (Cp); 62.7 (OCH_2); 53.6 (OCH). ^{31}P NMR (δ, $CDCl_3$): 41.86, 39.45 (2d, $^2J_{PP}$ = 26.1 Hz, 2 PPh_3). MS ESI: m/z 987.2 (M^+). Spectroscopic data for **15c** are as follows. ^{1}H NMR (δ, $CDCl_3$): 9.30 (OH); 7.73−6.38 (m, 39H, Ph); 5.38 (s, 2H, CH_2Ph); 5.23 (s, 5H, Cp). ^{31}P NMR (δ, $CDCl_3$): 39.58 (s, 2 PPh_3).

Reactions of 8a,c with MeI. In a Schlenk flask charged with **8a** (0.10 g, 0.11 mmol) and 15 mL of dichloromethane was added MeI (15.0 μL, 0.24 mmol) under nitrogen. The mixture was stirred at room temperature for 2 days. Then, the solution was filtered through Celite to remove the insoluble precipitates, the volatiles were removed under vacuum, and the solid residue was extracted with dichloromethane followed by reprecipitation by adding the extract to 60 mL of stirred diethyl ether/hexane (1/1). The precipitate thus formed was collected on a glass frit, washed with diethyl ether, and dried under vacuum to give the final product **16a** as a brown powder (0.092 g, 79% yield). Spectroscopic data for **16a** are as follows. ^{1}H NMR (δ, $CDCl_3$): 7.25−6.23 (m,

34H, Ph); 5.35 (s, 5H, Cp); 3.73 (s, 3H, OMe); 1.49 (s, 3H, CH_3). ^{13}C NMR (δ, $CDCl_3$): 357.4 (t, $^2J_{CP}$ = 14.0 Hz, C_α); 197.0 (C═O); 172.0 (C_γ); 143.4−125.7 (Ph and C_β); 95.5 (Cp); 57.7 (OMe); 53.5 (CCH_3); 21.1 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 39.71, 39.36 (2 d, $^2J_{PP}$ = 27.5 Hz, 2 PPh_3). Anal. Calcd for $C_{54}H_{45}IO_3P_2Ru$: C, 62.86; H, 4.40. Found: C, 60.41; H, 3.93 (deviations may be due to the presence of both I and I_3 anion). MS ESI: m/z 905.2 ($M^+ + 1$). The synthesis of **16c** (0.093 g, 81% yield) followed the same procedure from **8c** (0.10 g, 0.10 mmol). Spectroscopic data for **16c** are as follows. ^1H NMR (δ, $CDCl_3$): 7.37−6.25 (m, 39H, Ph); 5.20 (s, 5H, Cp); 5.27, 5.19 (2 d, 2H, $^2J_{HH}$ = 12.6 Hz); 1.47 (s, 3H, CH_3). ^{13}C NMR (δ, $CDCl_3$): 357.1 (t, $^2J_{CP}$ = 12.8 Hz, C_α); 196.9 (C═O); 171.5 (C_γ); 143.3−125.6 (Ph and C_β); 95.3 (Cp); 67.8 (CH_2Ph); 57.7 (CCH_3); 20.7 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 39.77, 39.05 (2 d, $^2J_{PP}$ = 27.0 Hz, 2 PPh_3). Anal. Calcd for $C_{60}H_{49}IO_3P_2Ru$: C, 65.04; H, 4.46. Found: C, 61.42; H, 3.85 (deviations may be due to the presence of both I and I_3 anions). MS ESI: m/z 981.11 (M^+).

■ ASSOCIATED CONTENT

Supporting Information. A CIF file giving crystallographic data for complex **8c**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: yclin@ntu.edu.tw.

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