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FULL PAPER

Intermolecular Dehydrative Coupling and Intramolecular Cyclization of Ruthenium Vinylidene Complexes Formed from Aromatic Propynes Containing Carbonyl Functionalities

Pi-Yeh Chia, [a] Cheng-Chen Kuo,[a] Shou-Ling Huang,[a] Yi-Hong Liu,[a] Ling-Kang Liu,[a] and Ying-Chih Lin,*[a]

Dedication ((optional))

Abstract: A remarkable intermolecular dehydrative coupling reaction with formation of a C-C bond was found for the vinylidene complex **2a**, yielding the dinuclear bisvinylidene complex **4a**. Complex **2a** containing 1-hydroxyindan moiety was first formed from the reaction of *o*-propynyl benzaldehyde **1a** with [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$) by a cyclization process. For analogous aldehyde **1b** containing an additional 1,3-dioxolane group on the aryl ring, similar intermolecular coupling yields the dinuclear bisvinylidene complex **4b**. However, the fluoro group on the aryl ring in aldehyde **1c** inhibits the coupling reaction, thus the reaction gives only the vinylidene complex **2c**. For the reactions of [Ru]-Cl in MeOH with compounds **1f**, **1g** and **1h**, each with a ketone functionality, cyclization gives the vinylidene complexes **2f, 2g** and **2h**, respectively. However, no similar intermolecular coupling was observed, instead, the intramolecular dehydration yields **8f**, **8g** and **8h**, respectively. In $CDCl_3$, catalytic cyclization is observed for the *o*-propynylphenyl ketone **1h** with [Ru]-Cl at 50 °C giving the isochromene products **14h**. Furthermore, treatment of the *o*-propynylaryl α,β-unsaturated ketones **1k-m** and **1n** with [Ru]-Cl in MeOH affords the corresponding vinylidene complexes **10k-m** and **11n** each with 1-benzosuberone moiety in the presence of NH_4PF_6. These intramolecular cyclization products are formed by the addition of Cβ onto the terminal carbon of the alkene moiety. All these reaction products are characterized by spectroscopic methods. In addition, structures of complexes **4a**, and **10l** are confirmed by single crystal X-ray diffraction analysis.

Introduction

The development of effective strategies for the synthesis of cyclic and heterocyclic compounds is an important challenge for modern organic chemistry and natural products synthesis.[1] Various transition metal vinylidene complexes are found to serve as important intermediates in these synthetically important organic transformations employing terminal alkynes.[2a-e] The nucleophilic addition of Cβ of the vinylidene moiety onto a proper functional group[2f] is commonly observed, even though addition of the electrophilic Cα of the vinylidene moiety onto electron-rich atoms is also possible.[2g] Recently, metal complexes of gold, palladium, copper, and tungsten have been shown to induce intramolecular cyclization of alkynes with oxygen-containing functional groups, forming benzofuran rings.[3] Saá and co-workers reported Ru-catalyzed cycloisomerizations of aromatic homo- and bis-homopropargylic alcohols affording benzofurans and isochromenes.[4] We recently described the cyclization of terminal arylalkynes containing aldehyde, ketone or hydroxyl functionality on the aryl ring induced by ruthenium complex giving isochromene carbene, isobenzofuryl carbene and cyclic oxocarbene complexes.[5] The cascade cyclization reactions of several aromatic 1,n-propargylic enynes (n = 7 or 8) catalyzed by ruthenium via allenylidene and vinylidene intermediates forming tricyclic compounds was also reported by us.[6]

In using terminal alkyne for these studies, it is common to see the monosubstituted vinylidene ligand, instead of the disubstituted one. Several methods for preparing disubstituted metal vinylidene complex have been developed recently, for instance, electrophilic attack on Cβ of an acetylide complex by alkyl halide[7], halogen[8] or diazonium salt[9], and deprotonation of carbyne complex.[10] Ishii and his co-workers reported preparation of the disubstituted vinylidene metal complex directly from internal alkyne via 1,2-migration of their carbon substituent.[11] The disubstituted vinylidene with a heteroatom bound to Cβ can also be obtained from heteroatom-substituted internal alkyne.[12] In addition, we reported that the nucleophilic addition of propargyl Grignard reagent to Cγ and subsequent $Au(PR_3)$-catalyzed cyclization of the resulting diyne yielded a vinylidene with the Cβ incorporated into a five-membered ring.[13]

Saá and co-workers reported the intramolecular dehydrative cyclization of vinylidene complexes of iridium, osmium and rhodium obtained from alkynals.[14a] Compared to the well-established intramolecular dehydration, the intermolecular dehydration is relatively rare, while a few catalytic reactions had been reported.[14b, c] In recent years, reaction of inexpensive and abundantly available alcohols (C-OH) with a C-H bond of the other unactivated nucleophilic coupling partners, leading to the construction of a C-C bond, has emerged as one of the vital strategies since it is an atom-economical and environmentally benign approach yielding only water as the by-product. Studies on the transition metal-catalyzed dehydrative coupling have been reported previously.[15] The development of metal-free approach for the direct dehydrative functionalization of the C-OH bond by Brønsted and Lewis acid with various carbon nucleophile has gained significant attention. Coupling of C_{sp3}-OH with C_{sp3}-H leading to a C_{sp3}-C_{sp3} bond formation

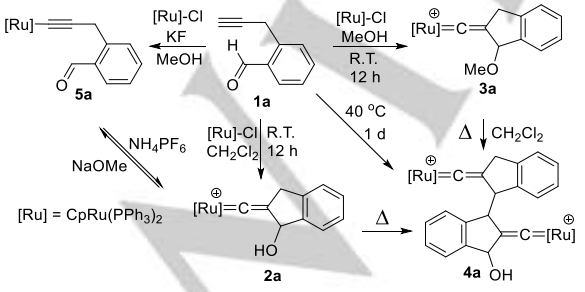
[a] P.-Y. Chia, C.-C. Kuo, Prof. Dr. L.-K. Liu, Prof. Dr. Y.-C. Lin, S.-L. Huang, Y.-H. Liu
Department of Chemistry
National Taiwan University
Taipei, 106 (Taiwan)
E-mail: yclin@ntu.edu.tw

has been explored for the dehydrative reaction of allylic, benzylic and propargylic alcohols with 1,3-dicarbonyls by using Brønsted and Lewis acids.[16] The advantage of these coupling processes is the formation of H_2O as the only by-product. Compared with halide reagents, alcohols are inexpensive and environmentally and friendly coupling reagents. However, it is rare to see an alcohol employed as coupling agent, because of the tendency to undergo energetically more favorable alkoxylation or dehydrogenation reactions over the respective C-O bond cleavage reaction.

Herein, we report the cyclization reactions of benzenefused *o*-propynyl aldehyde or ketone induced by [Ru]-Cl ([Ru] = $CpRu(PPh_3)_2$) yielding organometallic compounds. The cyclization proceeds by formation of a vinylidene ligand followed by intramolecular addition of the carbonyl carbon to Cβ to give the disubstituted vinylidene complexes with a 1-hydroxyindan moiety. Depending on the type of carbonyl substrates, reaction conditions, or solvents used, the vinylidene complexes can undergo further reactions and proceed via inter-molecular dehydrative coupling, intramolecular dehydration, alkoxylation and demetallation reactions.

Results and Discussion

Intermolecular Dehydrative Coupling. The reaction of [Ru]-Cl ([Ru] = $CpRu(PPh_3)_2$) with *o*-propynyl benzaldehyde **1a** in the presence of NH_4PF_6 in MeOH at room temperature for 12 h yields the vinylidene complex **3a** with 1-methoxyindan moiety. The same reaction in CH_2Cl_2 for 12 h, gives a mixture of the cationic vinylidene complex **2a** containing a 1-hydroxyindan moiety and the dinuclear bisvinylidene complex **4a** in a ratio of 14:1, see Scheme 1. When the reaction is carried out at reflux in CH_2Cl_2 for 1 day, only **4a** is obtained in 82% yield. In CH_2Cl_2 complex **3a** is transformed slowly to **4a** at room temperature. The reactions of **2a** and **3a** in $CDCl_3$ both giving **4a** are faster at 40ºC. Nevertheless, treatment of **1a** with [Ru]-Cl and KF in MeOH afforded the stable acetylide complex **5a**, which was also obtained in high yield by treating **2a** with NaOMe. Transformation of **5a** to **2a** is achieved with NH_4PF_6 or with other protic acids such as HBF_4 in CH_2Cl_2. Acetic acid promotes the dehydrative coupling reaction, but base inhibits the reaction. In the presence of 5% of acid at 40 ºC, the transformation of **2a** to **4a** is quantitative in 6 h and treatment of **2a** with sodium methoxide inhibits the dehydrative coupling.



Scheme 1. Reactions of **1a** with [Ru]-Cl and intermolecular dehydrative coupling of **2a**.

Attempted crystallization from a mixture of **2a** and **4a** in CH_2Cl_2 yielded only single crystals of **4a**. Compound **2a** was not observed in the remaining solution, showing spontaneous dehydration of **2a** to give **4a**. The structural assignment of **4a** is based on ^1H, ^{31}P, ^{13}C NMR data and a single crystal X-ray diffraction analysis. The doublet ^1H NMR resonance at δ 3.88 is assigned to the OH group, which disappears upon addition of D_2O. Two sets of two doublet peaks are observed at δ 41.64, 39.56, 41.38 and 39.02 in the ^{31}P NMR spectrum. Two characteristic $^{13}C\alpha$ resonances for the vinylidene ligands appear at δ 341.8 and 338.9 both displaying doublet of doublet pattern. The solid state structure is determined by a single crystal X-ray diffraction analysis confirming formation of the dinuclear bisvinylidene complex. An ORTEP type view of **4a** is shown in Figure 1, with selected bond distances and angles. The bond distance of 1.554(5) Å for the newly formed C10-C61 bond indicates a typical single bond. The Ru1-C1, C1-C2, Ru2-C52 and C52-C53 bond lengths of 1.850(4), 1.307(5), 1.860(4) and 1.301(5) Å, with the Ru1-C1-C2 and Ru2-C52-C53 bond angles of 175.3(0)° and 175.5(3)°, respectively, showing two bonding skeletons of typical vinylidene ligand.

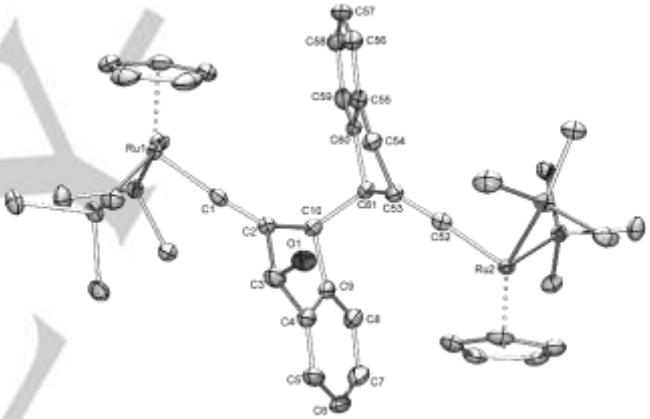


Figure 1. An ORTEP drawing of **4a**. Phenyl groups except C_{ipso} atoms on the phosphine ligands and PF_6^- have been omitted for clarity. Thermal ellipsoid is set at the 35% probability level. Selected bond distances (Å) and bond angles (deg): Ru1-C1, 1.850(4); C1-C2, 1.307(5); Ru2-C52, 1.860(4); C52-C53, 1.301(5); C10-C61, 1.554(5); O1-C3, 1.426(8); C2-C1-Ru1, 175.3(0); C3-C2-C10, 108.8(3); C53-C52-Ru2, 175.53; C54-C53-C61, 108.4(3); C60-C61-C10, 113.4(3); O1-C3-C4, 117.0(4).

Intermolecular dehydrative coupling that involves activation of a C_{sp3}-H bond followed by a C_{sp3}-C_{sp3} bond formation is rare. The coupling reaction of **2a** involves an unfavorable C-O bond cleavage. Metal-free approaches for the direct dehydrative coupling of a C_{sp3}-OH bond, such as allylic, benzylic and propargylic alcohols, with C_{sp3}-H bond of 1,3-dicarbonyls derivatives catalyzed by Brønsted and Lewis acids have been reported.[17] These reactions are confined only to the use of 1,3-dicarbonyl derivatives as carbon nucleophiles. Aminobenzannulation of **1a** with various dialkylamines was reported to afford various 2-aminonaphthalenes under metal-free condition.[19]

To further explore the reactivity of this unusual dimerization, two similar aryl aldehydes **1b** and **1c**, with an electron-donating 1,3-dioxolane group and with an electron-withdrawing fluoro group, respectively, are synthesized. Different from **1a**, both **1b** and **1c** react

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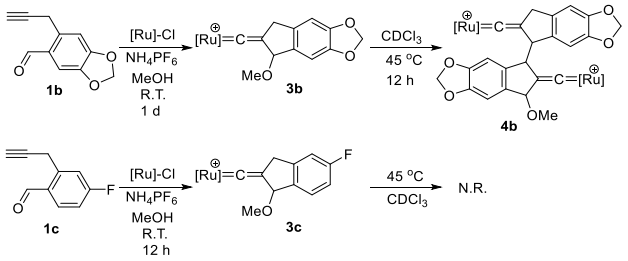
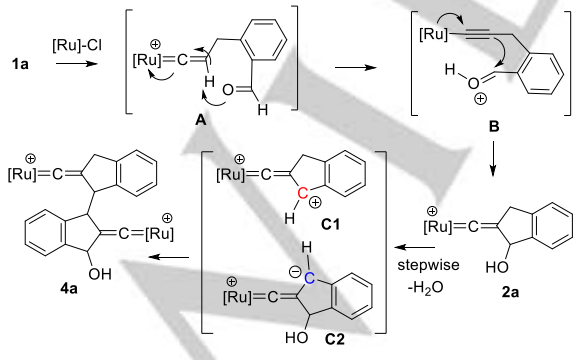
with [Ru]-Cl in CH_2Cl_2 in the presence of NH_4PF_6 giving complicated crude products. Only in MeOH, treatment of **1b** with [Ru]-Cl and NH_4PF_6 affords the vinylidene complex **3b** with a methoxy group, see Scheme 2. Upon heating **3b** in $CDCl_3$ at 45 °C, a similar intermolecular coupling process also yields the dinuclear bisvinylidene complex **4b** in 81% yield. The reaction of **1c** with [Ru]-Cl in MeOH also afforded the vinylidene complex **3c**, however, no further intermolecular coupling reaction occurs, even when the solution of **3c** is heated in CH_2Cl_2 or $CDCl_3$. The electron-withdrawing fluoro substituent on the aromatic ring clearly inhibits the intermolecular dehydration,[20] possibly by hindering the elimination of OH or OR and destabilizing the carbocation intermediate.



Scheme 2. Reactions of two *o*-propynyl aryl aldehydes

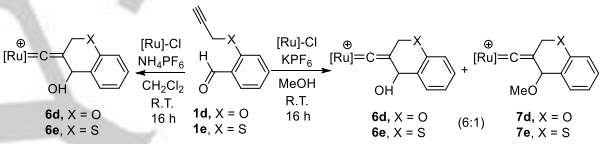
Proposed mechanism for the formation of **4a** from **1a** on the basis the above-mentioned observations is shown in Scheme 3. All reactions of **1a** yielding **2a**, **3a**, **4a** and **5a** are proposed to proceed via activation of the triple bond forming the metal vinylidene complex **A**. In the presence of KF, deprotonation of **A** generates **5a**. For **A** to undergo cyclization in CH_2Cl_2, transfer of a proton from $C_\beta H$ to the carbonyl group forms the oxonium acetylide intermediate **B**. Subsequent intramolecular C-C bond formation via attack of C_β onto the carbonyl carbon gives **2a** with a five-membered ring. Coupling of the aldehyde carbon with Cβ of the vinylidene ligand was previously reported.[14] The cationic character of **2a** along with the presence of two benzylic and allylic carbon atoms in the five-membered ring play crucial role in stimulating the subsequent dehydrative coupling reaction.



Scheme 3. Proposed mechanism for the formation of **2a** and subsequent transformation to **4a.**

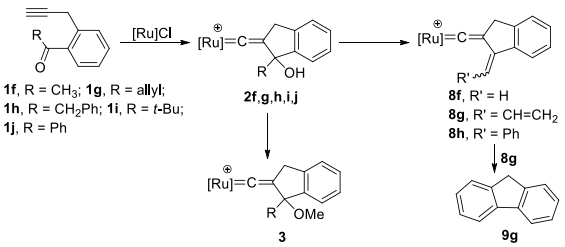
We propose a stepwise pathway for this dehydrative coupling reaction, as shown in Scheme 3. In this process, the benzylic methylene group of **2a** could serve as an acid generating the zwtterionic **C2** by deprotonation, which protonates the hydroxyl group of the other **2a** inducing elimination of H_2O to give intermediate **C1** with a benzylic as well as an allylic carbocation. Subsequent intermolecular C-C bond formation occurs between the electrophilic and the nucleophilic benzylic carbon atoms of **C1** and **C2**, respectively, to yield the coupling product **4a**. A concerted process by moving one **2a** toward the other **2a** via the vinylidene ligand with the acidic proton of one **2a** getting closer to the hydroxyl group of the other **2a**, followed by dehydration and formation of a C-C bond to give **4a**, is less likely. Because, approach of two sp^3 carbon atoms would be difficult.

The reactions of **1d** and **1e** with *o*-oxo- and *o*-thio-propargyl benzaldehydes with [Ru]Cl under the same reaction condition generate the corresponding cyclization products **6d** and **6e** (Scheme 4) each with a six-membered ring in CH_2Cl_2. In MeOH, along with **6d** and **6e**, relating complexes **7d** and **7e** with methoxy groups are observed as a minor product (6:1 in both cases). No intermolecular coupling is observed in both **6** and **7**, possibly because only one electrophilic benzylic carbon exists.



Scheme 4. Reactions of **1d** and **1e** with [Ru]-Cl.

The Reaction of the *o*-Propynylphenyl Ketones. With this unique dehydrative coupling process in mind, we carried out reactions of [Ru]-Cl with five aryl propynes **1f-1j** containing *ortho*-substituted keto derivatives, see Scheme 5. These compounds display different reactions depending on various functional groups on the keto part, see Scheme 5, and the solvents used. The reactions of **1f-1j** with [Ru]Cl in the presence of NH_4PF_6 in CH_2Cl_2 first give corresponding complexes **2f-2j**. Then for **2f-2h** each with a hydrogen near the hydroxyl group, intramolecular dehydration gives **8f-8h**. Interestingly, for the reaction of **1h** in MeOH, a mixture of the MeO-substituted complex **3h** and **8h** (E/Z isomer ratio 3:1) is observed first, which is also converted to **8h** (E/Z isomer ratio 3:1) in CH_2Cl_2. But complexes **2i** and **2j** (R = *t*-Bu and Ph), with no such hydrogen, are stable, as shown in Scheme 5.



Scheme 5. Reactions of *o*-propynyl aryl ketone with no α,β-unsaturated olefin**.**

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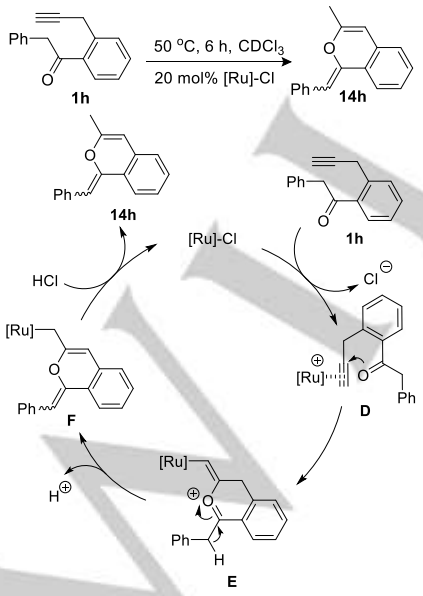
The structures of these complexes are determined by NMR spectroscopy. No further intermolecular coupling was observed for all complexes **2f-2j** derived from these keto derivatives, possibly because of the preferred intramolecular process and the steric effect of the substituted group near the hydroxyl group prohibiting the intermolecular dehydration reaction. Maybe the steric effect inhibits replacement of the OH group by an OMe group.

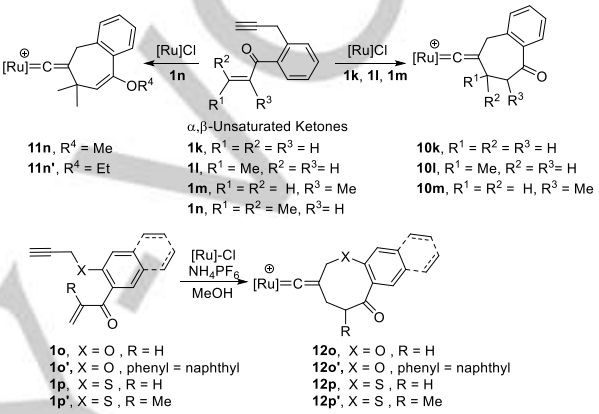
For **2g,** with an allyl group, the dehydration process, giving **8g** containing an 1,4-diene moiety, is followed by an additional C-C bond formation yielding the organic fluorene **9g** at 50°C for 3 day in 27% yield, Scheme 5. The cyclization of **8g** proceeds via intramolecular nucleophilic attack of the terminal unsaturated alkenes onto the electrophilic Cα of the vinylidene moiety followed by demetallation. Previously, we reported several ruthenium-catalyzed cyclizations of aromatic 1,n-propargylic enynes (n = 7 or 8) via allenylidene and vinylidene intermediates, and if the intermediate contains tethering olefinic chain, cascade cyclization via intramolecular nucleophilic addition of the double bond to Cα of the allenylidene or vinylidene ligand would form tricyclic compounds.[5]

Interestingly, **1h** displays solvent dependent reactivity, namely, heating **1h** in $CDCl_3$ at 50°C for 6 h in the presence of 20 mol% of [Ru]-Cl gives the isochromene **14h** in 73% isolated yield. (Scheme 6) The isochromene motif is commonly found in biologically active natural products.[25] Some derivatives of isochromene ring display significant pharmacological potential exhibiting extensive range of biological activities including anticancer and antibacterial activity.[26] The proposed mechanism for the formation of **14h** is shown in Scheme 6. The triple bond of **1h** is activated electrophilically by [Ru]-Cl leading to formation of the η^2-coordinated species **D**. Then the 6-exo-*dig* cyclization via a nucleophilic attack of the carbonyl oxygen to the internal carbon of the η^2-alkyne ligand generates **E**. This is followed by deprotonation and 1,3-hydrogen shift to give **F**. In the presence of HCl, **14h** is produced with regeneration of [Ru]-Cl. On the basis of NMR spectrum only one isomer was obtained.



Scheme 6. Formation of isochromene **14h** and proposed mechanism

Ruthenium-catalyzed cyclizations or cycloisomerizations of terminal alkynes commonly proceed via vinylidene intermediates followed by nucleophilic attack at Cα of the vinylidene ligand.[3,29] But the cyclization of **1h** occurs when the alkyne is π-coordinated to the Ru metal center causing the nucleophilic attack of the carbonyl oxygen to occur at the internal carbon Cβ of the η^2-alkynyl ligand. An asymmetric synthesis of chiral isochromenes catalyzed by Cu(II) phosphate with intramolecular cyclization via 6-endo-*dig* cyclization and asymmetric transfer hydrogenation sequence of *o*-alkynylaceto-phenone derivatives was previously reported.[28] Nevertheless, when **1a** is treated with a catalytic amount of [Ru]-Cl, no organic product other than **1a** is isolated.



Scheme 7. Reactions of *o*-propynyl aryl α,β-unsaturated ketone**.**

Interestingly, for several α,β-unsaturated ketones **1k-1n**, a different mode of cyclization is observed. Namely the C-C bond formation occurs only between the internal carbon of the alkyne and the terminal carbon of olefinic group yielding organometallic vinylidene complexes with sevenycli-membered ring ligand. (Scheme 7) Treatment of **1k-1m** with [Ru]-Cl in the presence of NH_4PF_6 in MeOH affords the vinylidene complexes **10k-10m** respectively, each with 1-benzosuberone moiety containing a seven-membered ring. The structures of **10k-10m** are determined by NMR data. The vinylidene complex with a five-membered ring similar to **2** or **3** is not observed. The C-C bond formation occurs exclusively at the olefinic terminal carbon giving a seven-membered ring, instead of at the carbonyl carbon.

This type of cyclization is also observed in the reactions of **1o, 1o', 1p** and **1p'** with [Ru]-Cl, producing corresponding complexes **12o, 12o' , 12p** and **12p'** containing eight-membered heterocyclic ring. (see lower part of Scheme 7) As also shown in the upper left part of Scheme 7, treatment of **1n** with [Ru]Cl in MeOH affords the vinylidene complex **11n** with an enol ether. In this case, two terminal methyl groups may limit the ring flipping, thus preventing transformation of the enol form to give the keto form. Analogous product **11n'** with an OEt group is obtained in EtOH. The structural assignment of **11n** and **11n'** is based on ^1H, ^{31}P, ^{13}C NMR and other spectroscopic data. In the ^1H NMR spectrum of **11n**, two singlet resonances at δ 3.02 and 5.56 are assigned to the OMe group and to the olefinic hydrogen in the seven-membered ring, respectively.

Single crystals of **10l** are obtained from a mixture of CH_2Cl_2/toluene solution and the structure is determined by single crystal

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X-ray diffraction analysis. An ORTEP type view of **10l** is shown in Figure 2 with selected bond distances and angles. The Ru1-C1 and C1-C2 bond lengths of 1.860(4) and 1.312(5) Å and the linear Ru1-C1-C2 bond angle of 170.1(3)° show a typical Ru=C=C vinylidene bonding skeleton. The bond distance of 1.210(6) Å for O1-C5 indicates a normal C=O bond. Two bond distances of 1.545(7) and 1.510(7) Å for C3-C4 and C4-C5, respectively, indicate typical C-C single bonds.

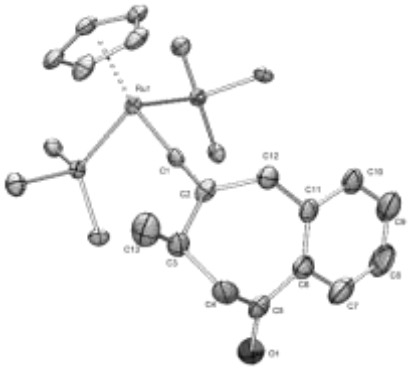
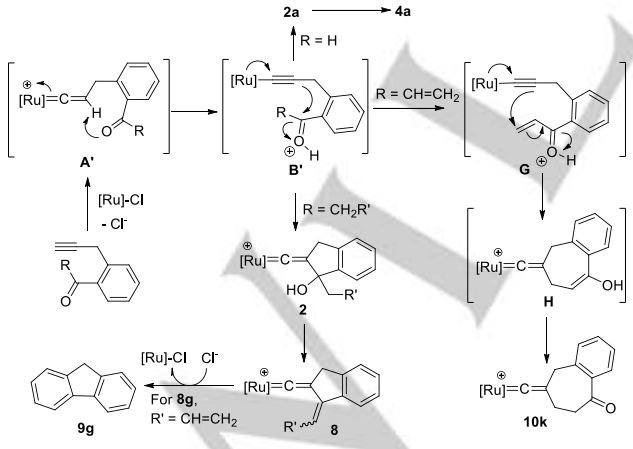


Figure 2. An ORTEP drawing of **10l**. Phenyl groups except the C_{ipso} atoms on the phosphine ligands and PF_6^- have been omitted for clarity. Thermal ellipsoid is set at the 35% probability level. Selected bond distances (Å) and bond angles (deg): Ru1-C1, 1.860(4); C1-C2, 1.312(5); O1-C5, 1.210(6); C3-C13, 1.530(7); C2-C1-Ru1, 170.1(3); C2-C3-C4, 111.1(4); O1-C5-C4, 120.0(5); C13-C3-C4, 108.7(4)

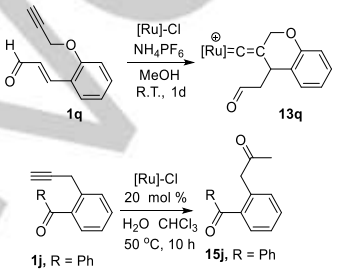
Proposed mechanism for the overall cyclization processes of various *o*-propynyl aryl aldehydes and ketones induced by [Ru]-Cl is shown in Scheme 8. The first step is the formation of the vinylidene intermediate **A'**, see also Scheme 3, followed by a proton transfer of CβH to the carbonyl oxygen forming the acetylide intermediate **B'** for an aldehyde or a ketone with no unsaturated C=C double bond.



Scheme 8. Proposed mechanism for the overall cyclization of *o*-propynyl aryl carbonyl compounds induced by [Ru]-Cl.

In these cases, a C-C bond formation then takes place between Cβ and the carbonyl carbon in **B'** yielding **2**. For aldehydes **1a** and **1b**, further intermolecular coupling would generate dinuclear complexes **4a** and **4b**. But for a ketone with no α,β-unsaturated group, intramolecular dehydration generates **8** containing an exo alkene. In the case of α,β-unsaturated ketones, the Micheal-addition of **G** leads to a C-C bond formation between Cβ and the terminal carbon, as shown in Scheme 8, yielding the di-substituted vinylidene enol intermediate **H**. Tautomerization then gives the cyclic ketone complex **10k**.

The favored C-C bond formation of the olefinic carbon over the carbonyl group is also shown in the cyclization reaction of the aryl alkyne **1q** with an *ortho*-substituted α,β-unsaturated ketone but containing internal alkene and terminal aldehyde, Scheme 9.



Scheme 9. Michael addition reaction of α,β-unsaturated aldehyde **1q** with [Ru]Cl and addition of water to **1j** catalyzed by [Ru]Cl.

The reaction of **1q** with [Ru]-Cl in MeOH yields **13q** keeping the aldehyde group. These results show that the Michael type addition is a favored pathway. The C-C bond formation takes place between Cβ of the alkyne and the internal alkene group. Attempted cyclization reactions of ketones **1j** in the presence of water cause addition of water to the terminal alkyne yielding the diketone compounds **15j**. (Scheme 9) These reactions are made catalytic by the use of 20 mole percent of [Ru]Cl.

Conclusions

A new intermolecular dehydrative coupling reaction is observed in our systematic studies on the ruthenium complex mediated cyclization reactions of aryl propynes with *ortho*-substituted aldehyde or ketone groups. This dehydrative coupling reaction of the two specific vinylidene complexes **2a** and **2b** involves unfavorable C-O bond cleavage and activation of a C_{sp3}-H bond. The cyclizations of aryl propynes with aldehyde or with simple ketone on the aryl ring would proceed by formation of vinylidene ligand. Then transfer of the vinylidene hydrogen to the oxygen atom assists formation of an acetylide complex with oxonium group. Subsequent coupling of the carbonyl carbon with Cβ atom gives the disubstituted vinylidene complexes with a 1-hydroxyindan moiety. The subsequent intermolecular dehydrative coupling reaction, giving the dinuclear bis-vinylidene complexes, occurs only for two starting substrates **1a** and **1b** with aldehyde group, and the coupling is promoted by heat or weak protic acid such as acetic acid. Conversely, in the reaction of aryl alkynes with ketone groups, the intramolecular dehydration takes place if nearby

hydrogen is available. For the α,β-unsaturated ketone, the intramolecular attack of Cβ onto the alkene moiety gives vinylidene complexes with a 1-benzosuberone moiety. Furthermore, demetallation of disubstituted vinylidene complex is achieved in the reaction of *o*-propynylphenyl β,γ-unsaturated ketone. Subsequent intramolecular nucleophilic addition of the terminal double bond to Cα of the vinylidene ligand gives fluorene as the unique organic product. In addition, we demonstrated the cyclization via nucleophilic attack of the carbonyl oxygen to the alkyne moiety in the presence of ruthenium catalyst to afford the corresponding isochromene derivatives. For aryl propynes with *ortho*-substituted aldehyde or ketone with either terminal or internal α,β-unsaturated olefinic groups, the C-C bond formation favorably takes place on the olefinic, instead of the carbonyl group.

Experimental Section

General procedures: Manipulations were performed under an atmosphere of dry nitrogen by using vacuum-line and standard Schlenk techniques unless mentioned otherwise. All reagents were obtained from commercial suppliers and were used without further purification. Solvents were dried by standard methods and were distilled under nitrogen before use. NMR spectra were recorded on Brucker AVIII-400, DMX-500 or on AVIII-800 FT-NMR spectrometer at room temperature and were reported in units of δ with residual protons in the solvents as a standard. Electrospray ionization mass spectrometry, elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at National Taiwan University. The ruthenium complex $Cp(PPh_3)_2RuCl$[30] and compound **1a-1q**[19] were prepared by following the method reported in the literature.

Synthesis of 2a and Conversion to 4a. A mixture of [Ru]-Cl (0.30 g, 0.41 mmol), **1a** (0.066 g, 0.46 mmol), and NH_4PF_6 (0.074 g, 0.45 mmol), in CH_2Cl_2 (40 mL) was stirred at ambient temperature under nitrogen for 12 h. The resulting red solution was filtered through Celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation by adding to a stirring mixture of 50/50 diethyl ether/hexane (100 mL). Precipitates thus formed were collected in a glass frit, washed with diethyl ether and dried under vacuum. The final product can be obtained as a pink powder containing a mixture of **2a** and **4a** (0.33 g) in a ratio of 14:1 determined by NMR. Spectroscopic data of **2a**: ^{1}H NMR (δ, acetone-d_6): 7.69-7.17 (m, 34H, Ph); 6.29 (d, 1H, $^3J_{HH}$ = 10.5 Hz, CH); 5.42 (s, 5H, Cp); 5.16 (d, 1H, $^3J_{HH}$ = 10.5 Hz, OH); 4.52, 4.10 (2d, 2H, $^2J_{HH}$ = 18.6 Hz, CH_2); ^{13}C NMR (δ, $CDCl_3$): 349.1 (t, $^3J_{CP}$ = 15.6 Hz, Cα); 134.8-124.3 (Ph and Cβ); 94.4 (Cp); 76.9 (CH); 31.4 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 44.25, 42.71 (2d, $^2J_{PP}$ = 27.1 Hz, PPh_3). MS (ESI$^+$) m/z: 835.1833 (M)$^+$. When the reaction time of [Ru]-Cl (0.31 g, 0.43 mmol) with **1a** (0.066 g, 0.46 mmol), was extended for 1 day at 40 °C, the final product can be obtained as a pink powder identified as **4a** (0.34 g, 82%). Spectroscopic data of **4a**: ^{1}H NMR (δ, CD_2Cl_2): 7.73-7.33 (m, 68H, Ph); 5.78 (d, 1H, $^3J_{HH}$ = 9.8 Hz, CH); 4.73 (d, 1H, $^3J_{HH}$ = 17.3 Hz, CH); 4.62 (s, 1H, CH); 4.61 (s, 5H, Cp); 4.45 (s, 5H, Cp); 4.40 (d, 1H, CH); 3.88 (d, 1H, $^3J_{HH}$ = 9.8 Hz, OH); 3.50 (d, 1H, $^2J_{HH}$ = 17.3 Hz, CH), ^{13}C NMR (δ, CD_2Cl_2): 341.8 (dd, $^3J_{CP}$=12.2 Hz, Cα^1); 338.9 (dd, $^3J_{CP}$=12.6 Hz, Cα^2); 144.7-125.5 (Ph, Cβ^1 and Cβ^2); 94.8 (Cp); 94.5 (Cp); 74.1 (CH); 54.9 (CH); 54.7 (CH); 33.5 (CH_2); ^{31}P NMR (δ, CD_2Cl_2): 41.64, 39.56 (2d, $^2J_{PP}$ = 26.9 Hz, PPh_3) 41.38, 39.02 (2d, $^2J_{PP}$ = 27.4 Hz, PPh_3). MS (ESI$^+$) m/z: 826.1781 (M)$^{+2}$. Elemental analysis calcd (%) for $C_{102}H_{84}F_{12}OP_6Ru_2$: C, 63.09; H, 4.36; found: C, 63.36; H, 4.61.

Reaction of 1f with [Ru]-Cl giving mixture of 2f/8f. The reaction of **1f** (0.063 g, 0.40 mmol) with [Ru]-Cl (0.28 g, 0.39 mmol), for 16 h in CH_2Cl_2 giving mixture of **2f/8f** (0.30 g) followed the same procedure as the synthesis of **2a/4a**. The final product can be obtained as a pale pink powder identified as a mixture of **2f** and **8f** in a ratio of 2:1 as determined by NMR. Spectroscopic data of **2f**: ^{1}H NMR (δ, $CDCl_3$): 7.57-7.02 (m, 34H, Ph); 5.14 (s, 5H, Cp); 4.06 (s, 2H, CH_2); 2.40 (s, 1H, OH); 1.55 (s, 3H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 352.03 (t, $^3J_{CP}$ = 15.5 Hz, Cα); 147.17-127.21 (Ph and Cβ); 94.26 (Cp); 84.50 (CCH_3); 30.76 (CH_3); 30.56 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 42.22, 42.02 (2d, $^2J_{PP}$ = 27.5 Hz, PPh_3). MS (ESI$^+$) m/z: 849.1981 (M)$^+$. Spectroscopic data of **8f**: ^{1}H NMR (δ, $CDCl_3$): 7.52-7.04 (m, 34H, Ph); 5.70, 4.93 (s, 1H, =CH_2); 5.32 (s, 5H, Cp); 3.88 (s, 2H, CH_2); ^{13}C NMR (δ, $CDCl_3$): 359.6 (t, $^3J_{CP}$ = 15.3 Hz, Cα); 140.6-120.3 (Ph and Cβ); 139.4 (=C); 105.2 (=CH_2); 94.4 (Cp); 30.8 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 41.82 (s, PPh_3). MS (ESI$^+$) m/z: 831.1911 (M)$^+$. No analysis data were obtained.

Synthesis of 2i. The synthesis of **2i** from **1i** (0.106 g, 0.53 mmol) and [Ru]-Cl (0.36 g 0.50 mmol) for 20 h followed the standard procedure as the synthesis of **2a**. The final product can be obtained as a pink powder identified as **2i** (0.40 g, 77%). Spectroscopic data of **2i**: ^{1}H NMR (δ, $CDCl_3$): 7.44-6.80 (m, 34H, Ph); 5.05 (s, 5H, Cp); 3.95, 3.43 (2d, 2H, CH_2); 1.06 (s, 9H, $C(CH_3)_3$); 0.47 (s, 1H, OH); ^{13}C NMR (δ, $CDCl_3$): 345.58, 345.39 (dd, $^3J_{CP}$ = 12.5 Hz, Cα); 144.16-124.55 (Ph and Cβ); 94.80 (Cp); 92.94 ($CC(CH_3)_3$); 40.73 ($C(CH_3)_3$); 32.2 (CH_2); 25.40 (($CH_3)_3C$); ^{31}P NMR (δ, $CDCl_3$): 41.61, 41.05 (2d, $^2J_{PP}$ = 26.1 Hz, PPh_3). MS (ESI$^+$) m/z: 891.2458 (M)$^+$. Elemental analysis calcd (%) for $C_{55}H_{51}F_6OP_3Ru$: C, 63.76; H, 4.96; found: C, 63.60; H, 4.89.

Synthesis of 2j. The synthesis of complex **2j** (0.33 g, 81%) from **1j** (0.086 g, 0.39 mmol) and [Ru]-Cl (0.28 g 0.39 mmol) for 20 h followed the standard procedure as the synthesis of **2i**. The final product can be obtained as a pink powder. Spectroscopic data of **2j**: ^{1}H NMR (δ, $CDCl_3$): 7.55-6.85 (m, 39H, Ph); 4.73 (s, 5H, Cp); 4.31, 4.21 (2d, 2H, CH_2); 2.02 (s, 1H, OH); ^{13}C NMR (δ, $CDCl_3$): 355.63 (t, $^3J_{CP}$ = 15.9 Hz, Cα); 147.49-124.07 (Ph and Cβ); 93.78 (Cp); 88.33 (CPh); 31.80 (CH_2); 25.40 (($CH_3)_3C$); ^{31}P NMR (δ, $CDCl_3$): 41.11, 40.98 (2d, $^2J_{PP}$ = 27.5 Hz, PPh_3). MS (ESI$^+$) m/z: 911.2145(M)$^+$. Elemental analysis calcd (%) for $C_{57}H_{47}F_6OP_3Ru$: C, 64.83; H, 4.49; found: C, 64.67; H, 4.68.

Synthesis of 3a. A mixture of [Ru]-Cl (0.32 g, 0.44 mmol), **1a** (0.065 g, 0.45 mmol), and NH_4PF_6 (0.075 g, 0.46 mmol), in MeOH (40 mL) was stirred at ambient temperature for 12 h. Then the solvent was removed under vacuum and 3 mL of CH_2Cl_2 was used to extract the crude product. The solution was filtered through celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation by adding to a stirring solution (50 mL) of diethyl ether hexane (1:1). Precipitates thus formed were collected in a glass frit, washed with diethyl ether and dried under vacuum. The final product can be obtained as a pink powder identified as **3a** (0.35 g, 75%). Spectroscopic data of **3a**: ^{1}H NMR (δ, $CDCl_3$): 7.30-6.97 (m, 34H, Ph); 6.01 (s, 1H, CH); 5.15 (s, 5H, Cp); 4.47, 3.80 (2d, 2H,$^2J_{HH}$ = 18.7 Hz, CH_2); 3.18 (s, 3H, OCH_3); ^{13}C NMR (δ, $CDCl_3$): 344.43 (t, $^3J_{CP}$ = 15.7 Hz, Cα); 140.42-123.87 (Ph and Cβ); 94.32 (Cp); 83.79 (CH); 51.99 (OCH_3); 32.33 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 43.54, 42.41 (2d, $^2J_{PP}$ = 26.4 Hz, PPh_3). MS (ESI$^+$) m/z: 849.1989 (M)$^+$. Elemental analysis calcd (%) for $C_{52}H_{45}F_6OP_3Ru$: C, 62.84; H, 4.56; found: C, 62.69; H, 4.64.

Synthesis of 3b. The synthesis of **3b** from [Ru]-Cl (0.46 g, 0.63 mmol) and **1b** (0.124 g, 0.66 mmol) followed the standard procedure as the synthesis of **3a** for 1 day. The final product can be obtained as a pale pink powder identified as **3b** (0.57g, 87%). Spectroscopic data of **3b**: ^{1}H NMR (δ, $CDCl_3$): 7.43-6.57 (m, 32H, Ph); 5.96 (s, 1H, CH); 5.95 (s, 2H, CH_2); 5.18 (s, 5H, Cp); 4.43, 3.72 (2d, 2H, $^2J_{HH}$ = 18.3 Hz, CH_2); 3.23 (s, 3H, OCH_3); ^{13}C NMR (δ, $CDCl_3$): 344.09 (t, $^3J_{CP}$ = 15.8 Hz, Cα); 149.36-104.18 (Ph and Cβ); 101.40 (CH_2); 94.11 (Cp); 83.11 (CH); 51.21 (OCH_3); 31.77 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 43.28, 42.12 (2d, $^2J_{PP}$ = 26.8 Hz, PPh_3). MS (ESI$^+$) m/z: 893.1887 (M)$^+$. Elemental analysis calcd (%) for $C_{53}H_{45}F_6O_3P_3Ru$: C, 61.33; H, 4.37; found: C, 61.43; H, 4.64.

Synthesis of 3c. The synthesis of **3c** from [Ru]-Cl (0.42 g, 0.58 mmol) and **1c** (0.097 g, 0.60 mmol) for 12 h followed the standard procedure as the synthesis of **3a**. The final product can be obtained as a brown powder identified as **3c** (0.46 g, 78%). Spectroscopic data of **3c**: ^{1}H NMR (δ, $CDCl_3$): 7.38-6.79 (m, 33H, Ph); 5.93 (s, 1H, CH); 5.15 (s, 5H, Cp); 4.47, 3.75 (2d, 2H, $^2J_{HH}$ = 19.0 Hz, CH_2); 3.17 (s, 3H, OCH_3); ^{13}C NMR (δ, $CDCl_3$): 344.04 (t, $^3J_{CP}$ = 15.5 Hz, Cα); 165.14-111.25 (Ph and Cβ); 101.40 (CH_2); 94.36 (Cp); 82.67 (CH); 51.85 (OCH_3); 31.85 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 43.23, 42.27 (2d, $^2J_{PP}$ = 27.1 Hz, PPh_3). MS (ESI$^+$) m/z: 867.1671 (M)$^+$. Elemental analysis calcd (%) for $C_{52}H_{44}F_7OP_3Ru$: C, 61.72; H, 4.38; found: C, 62.01; H, 4.60.

Synthesis of 3f and 8f. A mixture of [Ru]-Cl (0.32 g, 0.44 mmol), **1f** (0.071 g, 0.45 mmol), and KPF_6 (0.083 g, 0.45 mmol), in MeOH (40 mL) was used following the procedure described in the synthesis of **2a** at ambient temperature for 12h. The final product was obtained as a pale pink powder containing a mixture of **3f** and **8f** (total weight 0.35 g) in a ratio of 3:1. Spectroscopic data of **3f**: ^{1}H NMR (δ, $CDCl_3$): 7.50-6.96 (m, 34H, Ph); 5.16 (s, 5H, Cp); 4.18, 3.90 (2s, 2H, CH_2); 3.01 (s, 3H, OCH_3); 1.58 (s, 3H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 348.93 (t, $^3J_{CP}$ = 16.1 Hz, Cα); 142.81-120.33 (Ph and Cβ); 34.36 (Cp); 91.33 (CCH_3); 31.71 (CH_2); 30.77 (CH_3); ^{31}P NMR (δ, $CDCl_3$): 43.05, 41.78 (2d, $^2J_{PP}$ = 27.6 Hz, PPh_3). MS (ESI$^+$) m/z: 863.2157 (M)$^+$. The synthesis of pure **8f** from **1f** is achieved if the reaction was carried out for 1 day at 40 °C. The final product can be obtained as a pale pink powder identified as **8f** (86%).

Synthesis of 2g and 8g. The synthesis of **2g** (0.29 g, 71%) from **1g** (0.083 g, 0.45 mmol) and [Ru]-Cl (0.29 g, 0.40 mmol) followed the standard procedure as the synthesis of **2a** for 8 h. The final product was obtained as a pale yellow powder. Spectroscopic data of **2g**: ^{1}H NMR (δ, $CDCl_3$): 7.42-7.04 (m, 34H, Ph); 5.71 (m, 1H, HC=); 5.17 (s, 5H, Cp); 5.13, 5.04 (2d, 2H, $=CH_2$); 4.11, 3.89 (2d, 2H, CH_2); 2.70, 2.66, 2.58, 2.55 (2dd, 2H, CH_2); 1.86 (s, 1H, OH); ^{13}C NMR (δ, Acetone-d6): 350.60 (t, $^3J_{CP}$ = 15.1 Hz, Cα); 133.82 (=CH), 117.54(=CH_2), 146.11-123.75 (Ph and Cβ); 94.35 (Cp); 86.81 (CCH_2); 48.03 (CH_2); 31.25 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 41.83, 41.41 (2d, $^2J_{PP}$ = 26.8 Hz, PPh_3). MS (ESI$^+$) m/z: 875.2146(M)$^+$. Elemental analysis calcd (%) for $C_{54}H_{47}F_6OP_3Ru$: C, 63.59; H, 4.64; found: C, 63.50; H, 4.38. The reaction of **1g** (0.17 g, 0.92 mmol) with [Ru]-Cl (0.61 g, 0.84 mmol) for one day followed the standard procedure as the synthesis of **3a**. The final product **8g** (0.69 g, 82%) was obtained as a pale green powder. Spectroscopic data of **8g**: ^{1}H NMR (δ, $CDCl_3$): 7.51-6.97 (m, 35H, Ph and HC=); 6.49 (d, 1H, HC=); 5.63 (s, 5H, Cp); 4.94, 4.78 (2d, 2H, $=CH_2$); 3.95 (s, 2H, CH_2); ^{13}C NMR (δ, Acetone-d6): 362.34 (t, $^3J_{CP}$ = 15.4 Hz, Cα); 133.82 (=CH); 127.37 (=CH), 134.9-124.732 (Ph and Cβ); 119.81 (C=CH); 116.81(=CH_2); 94.90 (Cp); 30.27 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 41.45 (s, PPh_3). MS (ESI$^+$) m/z: 857.2040(M)$^+$. Elemental analysis calcd (%) for $C_{54}H_{45}F_6P_3Ru$: C, 64.73; H, 4.53; found: C, 64.51; H, 4.81

Synthesis of 3h and 8h. The synthesis of mixture of **3h** and **8h** from **1h** in MeOH followed the standard procedure as the synthesis of **3a** for 12 h. The final product was obtained as a pale yellow powder identified as a mixture of **3h** and **8h** (5:1) as determined by NMR. Spectroscopic data of **3h**: ^{1}H NMR (δ, $CDCl_3$): 7.69-6.23 (m, 39H, Ph); 5.15 (s, 5H, Cp); 4.16, 4.01 (2d, 2H, $^2J_{HH}$ = 18.3 Hz, CH_2); 3.34, 2.82 (2d, 2H, $^2J_{HH}$ = 13.7 Hz, CH_2); 3.08 (s, 3H, OCH_3); ^{13}C NMR (δ, $CDCl_3$): 347.89 (t, $^3J_{CP}$ = 14.9 Hz, Cα); 142.3-123.770 (Ph and Cβ); 93.82 (Cp); 94.29 ($COCH_3$); 52.04 (OCH_3); 49.27 (CH_2); 31.36 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 43.09, 41.78 (2d, $^2J_{PP}$ = 27.6 Hz, PPh_3). MS (ESI$^+$) m/z: 939.2455(M)$^+$.

Synthesis of 4b. A solution of **3b** (0.050 g, 0.048 mmol) in $CDCl_3$ (3 mL) in a Schlenk tube was warmed under nitrogen to 45°C for 12h. The final product was obtained as red crystal identified as **4b** (0.040g, 81%). Spectroscopic data of **4b**: ^{1}H NMR (δ, CD_2Cl_2): 7.49-6.67 (m, 64H, Ph); 6.24, 6.08 (2s, CH_2); 6.19, 6.06 (2s, CH_2); 5.78 (d, 1H,$^3J_{HH}$ = 9.8 Hz, CH); 5.02 (s, 5H, Cp); 4.93 (s, 5H, Cp); 4.68 (s, 1H, CH); 4.04 (d, 1H, $^2J_{HH}$ = 16.9 Hz, CH); 3.91 (d, 1H, $^3J_{HH}$ = 9.93 Hz, CH); 3.64 (d, 1H,$^3J_{HH}$ = 9.93 Hz, CH); 3.22 (d, 1H, $^2J_{HH}$ =16.9 Hz, CH); 3.00 (s, 3H, OCH_3); ^{13}C NMR (δ, CD_2Cl_2): 340.93 (t, Cα^1 and Cα^2, overlap); 148.48-105.37 (Ph, Cβ^1 and Cβ^2); 102.92 (CH_2); 102.45 (CH_2); 95.11 (Cp^1 and Cp^2, overlap); 81.5179 (CH); 56.64 (OCH_3); 54.56 (CH); 51.18 (CH); 31.30 (CH_2); ^{31}P NMR (δ, CD_2Cl_2): 41.11, 40.08 (2d, $^2J_{PP}$ = 24.3 Hz, PPh_3) 41.54, 39.03 (2d, $^2J_{PP}$ = 25.1 Hz, PPh_3). MS (ESI$^+$) m/z: 876.6722 (M)$^{+2}$.

Synthesis of 5a. A mixture of [Ru]-Cl (0.30 g, 0.41 mmol), **1a** (0.066 g, 0.45 mmol), and KF (0.048 g, 0.83 mmol), in MeOH (40 mL) was stirred at ambient temperature for 2 days. Then the solvent was removed under vacuum and 3 mL of CH_2Cl_2 was used to extract the crude product. The light-yellow solution was filtered through celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under vacuum to give light-yellow complex **5a**. (0.30 g, 87%). Spectroscopic data of **5a**: ^{1}H NMR (δ, CD_2Cl_2): 10.61 (s, 1H, O=CH); 7.88-7.06 (m, 34H, Ph); 4.27 (s, 5H, Cp); 4.21 (s, 2H, CH_2); ^{13}C NMR (δ, CD_2Cl_2): 193.10 (C=O); 145.22-126.62 (Ph); 107.86 (Cβ); 99.3. (t, $^3J_{CP}$ = 24.7 Hz, Cα); 85.40 (Cp); 27.21 (CH_2); ^{31}P NMR (δ, CD_2Cl_2): 50.66 (s, PPh_3). MS (ESI$^+$) m/z: 835.1833 (M+1)$^+$. Elemental analysis calcd (%) for $C_{51}H_{42}OP_2Ru$: C, 74.36; H, 5.08; found: C, 74.43; H, 5.24.

Synthesis of 6d. The synthesis of **6d** from **1d** (0.066 g, 0.41 mmol) and [Ru]-Cl (0.28 g 0.38 mmol) followed the standard procedure as the synthesis of **2a** for 16 h. The final product can be obtained as a pale pink powder identified as **6d** (0.28 g, 73%). Spectroscopic data of **6d**: ^{1}H NMR (δ, $CDCl_3$): 7.72-6.82 (m, '34H, Ph); 5.28 (s, 5H, Cp); 5.23 (s, CH); 4.93, 4.60 (2d, 2H, $^1J_{HH}$ = 11.7 Hz, CH_2); 3.65 (s, 1H, OH); ^{13}C NMR (δ, $CDCl_3$): 338.1 (t, $^3J_{CP}$ = 15.0 Hz, Cα); 153.77(O-Ph); 134.59-116.79 (Ph and Cβ); 94.39 (Cp); 61.27 (CH_2); 57.85 (CH); ^{31}P NMR (δ, $CDCl_3$): 42.48, 40.73 (2d, $^2J_{PP}$ = 25.6 Hz, PPh_3). MS (ESI$^+$) m/z: 851.1776 (M)$^+$. Elemental analysis calcd (%) for $C_{51}H_{43}F_6O_2P_3Ru$: C, 61.51; H, 4.35; found: C, 61.55; H, 4.31.

Synthesis of 6e. The synthesis of **6e** from **1e** (0.074g, 0.42 mmol) and [Ru]-Cl (0.29 g 0.40 mmol) followed the standard procedure as the synthesis of **2a** for 16h. The final product was obtained as a pale pink powder identified as **6e** (0.26 g, 64%) by NMR. Spectroscopic data of **6e**: ^{1}H NMR (δ, $CDCl_3$): 7.09-6.88 (m, 34H, Ph); 5.49 (s, 1H, CH); 5.26 (s, 5H, Cp); 4.06, 3.06 (2d, 2H , $^1J_{HH}$ = 12.6 Hz , CH_2); 3.77 (s, 1H, OH); ^{13}C NMR (δ, $CDCl_3$): 340.16 (t, $^3J_{CP}$ = 15.9 Hz, Cα); 136.17-120.01 (Ph and Cβ); 94.72 (Cp); 63.29 (CH); 19.2 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 42.61, 41.80 (2d, $^2J_{PP}$ = 26.6 Hz, PPh_3). MS (ESI$^+$) m/z: 867.1548 (M)$^+$. Elemental analysis calcd (%) for $C_{51}H_{43}F_6OP_3RuS$: C, 60.53; H, 4.28; found: C, 60.51; H, 4.31

Synthesis of 6d and 7d. A mixture of [Ru]-Cl (0.32 g, 0.44 mmol), **1d** (0.064 g, 0.40 mmol), and KPF_6 (0.085 g, 0.46 mmol), in MeOH (40 mL) was used following the procedure described in the synthesis of **2a** at ambient temperature for 16h. The final product was obtained as a pale pink powder containing a mixture of **6d** and **7d** (total weight 0.30 g, ca. 75%) in a ratio of 6:1. Spectroscopic data of **7d**: ^{1}H NMR (δ, $CDCl_3$): 7.44-6.85 (m, 34H, Ph); 5.10 (s, 5H, Cp); 4.94 (s, 1H, CH); 4.82, 4.67 (2d, 2H , $^1J_{HH}$ = 11.15 Hz , CH_2); 3.58 (s, 3H, CH_3); ^{31}P NMR (δ, $CDCl_3$): 42.55, 41.31 (2d, $^2J_{PP}$ = 25.5 Hz, PPh_3). MS (ESI$^+$) m/z: 865.1933 (M)$^+$

Synthesis of 6e and 7e. A mixture of [Ru]-Cl (0.30 g, 0.41 mmol), **1e** (0.077 g, 0.44 mmol), and KPF_6 (0.085 g, 0.46 mmol), in MeOH (30 mL) was used following the procedure described in the synthesis of **2a** at ambient temperature for 12h. The final product was obtained as a pale pink powder containing a mixture of **6e** and **7e** (total weight 0.27 g, ca. 70%) in a ratio of 6:1. Spectroscopic data of **7e**: ^{1}H NMR (δ, $CDCl_3$): 7.35-6.91 (m, 34H, Ph); 5.30 (s, 5H, Cp); 4.94 (s, 1H, CH);; 4.06, 3.20 (2d, 2H , $^1J_{HH}$ = 9.92 Hz , CH_2) ; 3.56 (s, 3H, CH_3); ^{31}P NMR (δ, $CDCl_3$): 42.94, 41.07 (2d, $^2J_{PP}$ = 26.3 Hz, PPh_3). MS (ESI$^+$) m/z: 881.1705 (M)$^+$

Synthesis of fluorene 9g. The synthesis of **8g** and fluorene **9g** from **1g** (0.081 g, 0.44 mmol) and [Ru]-Cl (0.31 g 0.43 mmol) followed the standard procedure as the synthesis of **2a** for 3 days but in MeOH at 50 °C. The green precipitates thus formed was filtered and washed with diethyl ether and dried under vacuum to give green powder identified as **8g**. The filtrate was evaporated to dryness under vacuum and the crude product purified by column chromatography (SiO_2, EA/hexane, 1:10) to afford organic product fluorene **9g** (0.019 g, 27%). Spectroscopic data of **9g**: ^{1}H NMR (δ, $CDCl_3$): 7.83-7.31 (m, 8H, Ph); 3.92 (s, 2H, CH_2); ^{13}C NMR (δ, $CDCl_3$): 143.2-119.8 (Ph); 36.9 (CH_2). MS (ESI$^+$) m/z: 167.0622(M+1)$^+$

Synthesis of 8h. The synthesis of **8h** (0.38 g, 82%) from **1h** (0.122 g, 0.50 mmol) and [Ru]-Cl (0.32 g 0.44 mmol) in CH_2Cl_2 followed the standard procedure as the synthesis of **3a** for one day. The final product was obtained as a green powder identified as **8h**. Spectroscopic data of **8h** (major): ^{1}H NMR (δ, $CDCl_3$): 7.39-6.76 (m, 40H, Ph and CH=); 5.33 (s, 5H, Cp); 3.90 (s, 2H, CH_2); ^{13}C NMR (δ, $CDCl_3$): 361.27 (t, $^3J_{CP}$ = 15.9 Hz, Cα); 142.36-120.01 (Ph, HC=C and Cβ); 94.37 (Cp); 30.31 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 41.27 (s, PPh_3). MS (ESI$^+$) m/z: 907.2197(M)$^+$. Elemental analysis calcd (%) for $C_{58}H_{47}F_6P_3Ru$: C, 66.22; H, 4.50; found: C, 66.06; H, 4.48.

Synthesis of Complex 10k. The synthesis of **10k** (0.38 g, 86%) from **1k** (0.082 g, 0.48 mmol) and [Ru]-Cl (0.32 g 0.44 mmol) followed the standard procedure as the synthesis of **1a** and **2a** but in MeOH for 12 h. The final product can be obtained as a pink powder identified as **10k**. Spectroscopic data of **10k**: ^{1}H NMR (δ, $CDCl_3$): 7.97- 6.51 (m, 34H, Ph); 5.00 (s, 5H, Cp); 3.75, 3.67 (2d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2); 3.10 (m, 1H, CH); 2.74 (m, 2H, CH_2); 1.35 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3); ^{13}C NMR (δ, $CDCl_3$): 349.8 (t, $^3J_{CP}$ = 15.1 Hz, Cα); 202.0 (C=O); 141.4-123.8 (Ph and Cβ); 94.2 (Cp); 49.4 (CH_2); 27.8 (CH); 26.6 (CH_2); 22.4 (CH_3); ^{31}P

NMR (δ, $CDCl_3$): 43.32, 41.55 (2d, $^2J_{PP}$ = 26.0 Hz, PPh_3). MS (ESI^+) m/z: 861.1942$(M)^+$.

Synthesis of 10l. The synthesis of **10l** (0.25 g, 81%) from **1l** (0.061 g, 0.33 mmol) and [Ru]-Cl (0.22 g 0.30 mmol) followed the standard procedure as the synthesis of **3a** for 12h. The final product was obtained as a pink powder identified as **10l** (0.31 g, 85%). Spectroscopic data of **10l**: ^{1}H NMR (δ, $CDCl_3$): 7.97- 6.51 (m, 34H, Ph); 5.00 (s, 5H, Cp); 3.75, 3.67 (2d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2); 3.10 (m, 1H, CH); 2.74 (m, 2H, CH_2); 1.35 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3); ^{13}C NMR (δ, $CDCl_3$): 349.77 (t, $^3J_{CP}$ = 15.1 Hz, Cα); 202.01 (C=O); 141.44-123.77 (Ph and Cβ); 94.17 (Cp); 49.36 (CH_2); 27.83 (CH); 26.63 (CH_2); 22.41 (CH_3); ^{31}P NMR (δ, $CDCl_3$): 43.32, 41.55 (2d, $^2J_{PP}$ = 26.0 Hz, PPh_3). MS (ESI^+) m/z: 875.2146$(M)^+$. Elemental analysis calcd (%) for $C_{54}H_{47}F_6OP_3Ru$: C, 63.59; H, 4.64; found: C, 63.53; H, 4.55.

Synthesis of 10m. The synthesis of **10m** (0.32 g, 88%) from **1m** (0.075 g, 0.41 mmol) and [Ru]-Cl (0.26 g 0.36 mmol) followed the standard procedure as the synthesis of **3a** for 12 h. The final product can be obtained as a pink powder identified as **10m**. Spectroscopic data of **10m**: ^{1}H NMR (δ, $CDCl_3$): 7.89-6.76 (m, 34H, Ph); 5.02 (s, 5H, Cp); 3.81, 3.73 (2d, 2H, $^2J_{HH}$ = 16.7 Hz, CH_2); 3.19, 2.19 (m, 2H, CH_2); 3.13 (m, 1H, CH); 1.14 (d, 3H, $^3J_{HH}$ = 6.1 Hz, CH_3); ^{13}C NMR (δ, $CDCl_3$): 349.32 (t, $^3J_{CP}$ = 15.4 Hz, Cα); 204.90 (C=O); 142.00-124.13 (Ph and Cβ); 93.99 (Cp); 43.91 (CH); 29.66 (CH_2); 28.70 (CH_2); 15.28 (CH_3); ^{31}P NMR (δ, $CDCl_3$): 43.61, 41.96 (2d, $^2J_{PP}$ = 26.6 Hz, PPh_3). MS (ESI^+) m/z: 875.2151$(M)^+$. Elemental analysis calcd (%) for $C_{54}H_{47}F_6OP_3Ru$: C, 63.59; H, 4.64; found: C, 63.76; H, 4.84.

Synthesis of 11n. The synthesis of **11n** (0.21 g, 81%) from **1n** (0.065g, 0.33 mmol) and [Ru]-Cl (0.18 g 0.25 mmol) followed the standard procedure as the synthesis of **3a** for 16 h. The final product can be obtained as a pink powder identified as **11n**. Spectroscopic data of **11n**: ^{1}H NMR (δ, $CDCl_3$): 8.39-6.97 (m, 34H, Ph); 5.65 (s, 1H, HC=); 5.26 (s, 5H, Cp); 3.72 (s, 2H, CH_2); 3.02 (s, 3H, OCH_3); 1.22 (s, 6H, $(CH_3)_2C$); ^{13}C NMR (δ, $CDCl_3$): 361.03 (t, $^3J_{CP}$ = 15.7 Hz, Cα); 137.05 (C=); 129.77 (HC=); 142.65-127.31 (Ph and Cβ); 94.39 (Cp); 75.66 ($C(CH_3)_2$); 50.33 (OCH_3); 30.05 (CH_2); 27.55 (CH_3); ^{31}P NMR (δ, $CDCl_3$): 41.29 (s, PPh_3). MS (ESI^+) m/z: 903.2458$(M)^+$. Elemental analysis calcd (%) for $C_{56}H_{51}F_6OP_3Ru$: C, 64.18; H, 4.91; found: C, 63.98; H, 4.79.

Synthesis of 11n'. The synthesis of **11n'** from **1n** (0.077g, 0.39 mmol) and [Ru]-Cl (0.26 g 0.36 mmol) followed the standard procedure as the synthesis of **3a** in ethanol for one day. The final product was obtained as a pink powder identified as **11n'** (0.28 g, 68%). Spectroscopic data of **11n'**: ^{1}H NMR (δ, $CDCl_3$): 8.47-6.97 (m, 34H, Ph); 5.70 (s, 1H, HC=); 5.27 (s, 5H, Cp); 3.72 (s, 2H, CH_2); 3.23 (q, 2H, $^3J_{HH}$ = 7.0 Hz, OCH_2); 1.24 (s, 6H, $(CH_3)_2C$); 1.00 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3); ^{13}C NMR (δ, $CDCl_3$): 361.17 (t, $^3J_{CP}$ = 15.5 Hz, Cα); 136.91 (C=); 130.84 (HC=); 142.40-124.12 (Ph and Cβ); 94.18 (Cp); 74.90 ($C(CH_3)_2$); 57.87 (OCH_2); 29.83 (CH_2); 27.82 (CH_3); 15.77 (CH_3);^{31}P NMR (δ, $CDCl_3$): 41.34 (s, PPh_3). MS (ESI^+) m/z: 917.2615$(M)^+$. Elemental analysis calcd (%) for $C_{57}H_{53}F_6OP_3Ru$: C, 64.46; H, 5.03; found: C, 64.67; H, 4.89.

Synthesis of 12o, 12o', 12p and 12p'. The synthesis of complex **12o** (0.21 g, 68%) from **1o** (63 mg, 0.34 mmol) and [Ru]-Cl (0.22 g, 0.30 mmol) followed the standard procedure as the synthesis of **3a** in methanol for one day. Spectroscopic data of **12o**: ^{1}H NMR (δ, $CDCl_3$): 8.27-6.57 (m, 34H, Ph); 4.66 (s, 5H, Cp); 4.40 (s, 2H, OCH_2); 3.21 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2); 2.58 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2); ^{13}C NMR (δ, $CDCl_3$): 339.56 (t, $^3J_{CP}$ = 14.2 Hz, Cα); 201.31 (C=O); 157.93-119.29 (Ph and Cβ); 94.75 (Cp); 70.61 (OCH_2); 41.74 (CH_2); 22.40 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 41.07 (s, PPh_3). MS (ESI^+) m/z: 877.1922$(M)^+$. Elemental analysis calcd (%) for $C_{53}H_{45}F_6O_2P_3Ru$: C, 62.29; H, 4.44; found: C, 62.37; H, 4.39. The synthesis of complex **12o'** (0.35 g, 59 %) from **1o'** (0.15g, 0.63 mmol) and [Ru]-Cl (0.40 g, 0.55 mmol) followed the standard procedure as the synthesis of **5a** in methanol for one day. Spectroscopic data of **12o'**: ^{1}H NMR (δ, $CDCl_3$): 8.84-6.87 (m, 38H, Ph); 4.61 (s, 5H, Cp); 4.54 (s, 2H, OCH_2); 3.21 (t, 2H, $^3J_{HH}$ = 6.8 Hz, CH_2); 2.64 (t, 2H, $^3J_{HH}$ = 6.8 Hz, CH_2); ^{13}C NMR (δ, $CDCl_3$): 341.40 (t, $^3J_{CP}$ = 14.4 Hz, Cα); 204.74 (C=O); 156.98-120.15 (Ph and Cβ); 94.61 (Cp); 70.30 (OCH_2); 44.00 (CH_2); 22.51 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 41.26 (s, PPh_3). MS (ESI^+) m/z: 927.2094$(M)^+$. Elemental analysis calcd (%) for $C_{53}H_{45}F_6O_2P_3Ru$: C, 63.87; H, 4.42; found: C, 63.57; H, 4.39. Synthesis of complex **12p** (0.16 g, 59%) in methanol from **1p** (61 mg, 0.30 mmol) and [Ru]-Cl (0.19 g, 0.26 mmol) followed the standard procedure as the synthesis of **5a** for one day. Spectroscopic data of **12p**: ^{1}H NMR (δ, $CDCl_3$): 8.49-6.86 (m, 34H, Ph); 4.74 (s, 5H, Cp); 3.73 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2); 3.32 (s, 2H, SCH_2); 2.56 (t, 2H, $^3J_{HH}$ = 6.9 Hz , CH_2); ^{13}C NMR (δ, $CDCl_3$): 343.36 (t, $^3J_{CP}$ = 12.0 Hz, Cα); 203.05 (C=O); 142.93-119.29 (Ph and Cβ); 94.67 (Cp); 40.29 (CH_2); 30.94 (SCH_2); 22.65 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 40.79 (s, PPh_3). MS (ESI^+) m/z: 893.1730$(M)^+$ Elemental analysis calcd (%) for $C_{53}H_{45}F_6OP_3RuS$: C, 61.33; H, 4.37; found: C, 62.37; H, 4.39. The synthesis of complex **12p'** (0.23 g, 64%) from **1p'** (0.11g, 0.51 mmol) and [Ru]-Cl (0.25 g, 0.30 mmol) followed the standard procedure as the synthesis of **5a** in methanol for one day. Spectroscopic data of **12o**: ^{1}H NMR (δ, $CDCl_3$): 8.45-6.71 (m, 34H, Ph); 5.04 (m, 1H, CH); 4.69 (s, 5H, Cp); 3.21 (m, 2H, OCH_2); 2.31 (m, 2H, CH_2); 1.15 (d, 3H, $^3J_{HH}$ = 5.0 Hz, CH_2); ^{13}C NMR (δ, $CDCl_3$): 343.71 (t, $^3J_{CP}$ = 11.9 Hz, Cα); 206.02 (C=O); 142.50-120.83 (Ph and Cβ); 94.67 (Cp); 42.46 (SCH_2); 31.22 (CH_2); 30.71 (CH_2); 16.58 (CH_3); ^{31}P NMR (δ, $CDCl_3$): 40.85 (dd, PPh_3). MS (ESI^+) m/z: 907.1866$(M)^+$. Elemental analysis calcd (%) for $C_{54}H_{47}F_6OP_3RuS$: C, 61.65; H, 4.50; found: C, 61.47; H, 4.45.

Synthesis of isochromene 14h. A mixture of [Ru]-Cl (0.20 g, 0.28 mmol), **1h** (0.33 g, 1.40 mmol) and $CDCl_3$ (3 mL) in a tube was heated at 50 °C for 6 h under nitrogen. Then $CDCl_3$ was removed *in vacuo* and CH_2Cl_2 (1 mL) was used to extract the product. Then diethyl ether (10 mL) was added to the extract. The pale-orange precipitates thus formed were filtered and washed with diethyl ether and dried under vacuum to give [Ru]-Cl. The filtrate was evaporated to dryness under vacuum and the crude product purified by column chromatography (SiO_2, EA/hexane, 1:10) to afford compound **14h** (0.24 g, 73%) as yellow oil. Spectroscopic data of **14h**: ^{1}H NMR (δ, $CDCl_3$): 7.72-6.93 (m, 9H, Ph); 6.12 (=CH); 5.67 (=CH); 2.12 (s, 3H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 151.9 (=C); 149.3 (=C); 136.0-122.5 (Ph); 101.2 (=CH); 100.8 (=CH); 19.3 (CH_3). MS (ESI^+) m/z: calcd: 234.1045 $(M)^+$; expt: 235.1123$(M+1)^+$.

Synthesis of isochromene 13q. The synthesis of complex 13q (0.21 g, 75%) from **1q** (0.063 g, 0.34 mmol) and [Ru]-Cl (0.20 g, 0.28 mmol) followed the standard procedure as the synthesis of **2a** in methanol for one day. Spectroscopic data of 12o: ^{1}H NMR (δ, $CDCl_3$): 10.02 (s, 1H, CHO); 7.71-6.71 (m, 34H, Ph); 5.25 (s, 5H, Cp); 4.72, 4.41 (2d, 2H, OCH_2) 4.23 (d, 1H, CH); 3.54, 2.78 (2d, 2H, CH_2); ^{13}C NMR (δ, $CDCl_3$): 340.47 (t, $^3J_{CP}$ = 14.7 Hz, Cα); 201.64 (C=O); 154.18-116.95 (Ph and Cβ); 94.92 (Cp); 57.94 (OCH2); 51.22 (CH2); 27.88 (CH); ^{31}P NMR (δ, $CDCl_3$): 43.38, 40.18 (2d, $^2J_{PP}$ = 25.7 Hz, PPh_3). MS (ESI^+) m/z: 877.1935 $(M)^+$. Elemental analysis calcd (%) for $C_{53}H_{45}F_6O_2P_3Ru$: C, 62.29; H, 4.44; found: C, 62.32; H, 4.35.

Synthesis of 15j. The synthesis of **15j** (0.08 g, 74%) from **1j** (0.1 g, 0.45 mmol) and [Ru]-Cl (0.016 g, 0.022 mmol) followed the standard procedure as the synthesis of **14h** in $CDCl_3$ for 10h. Spectroscopic data of **15j**: ^{1}H NMR (δ, $CDCl_3$): 7.78-7.25 (m, 9H, Ph); 3.95 (s, 2H, CH_2); 2.16 (s, 3H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 205.46 (O=C); 198.20 (O=C); 137.88-126.34 (Ph); 48.11 (CH_2); 29.84 (CH_3). MS (ESI^+) m/z: calcd: 238.0994 $(M)^+$; expt: 239.1003$(M+1)^+$.

Single-crystal X-ray diffraction analyses: Single crystals of complexes **4a** and **10l** suitable for X-ray diffraction study were grown as mentioned above. Single crystals were glued to a glass fiber and mounted on a SMART CCD diffractometer. The diffraction data were collected by using a 3-kW sealed-tube Mo K_α radiation (T = 295 K). Exposure time was 5 s per frame (Siemens area detector absorption). SADABS[37] absorption correction was applied, and decay was negligible. Data were processed and the structure was solved and refined by the SHELXTL[38] program. Hydrogen atoms were placed geometrically by using a riding model with thermal parameters set to 1.2 times that for the atoms to which they are attached and 1.5 times for the methyl hydrogen atoms.

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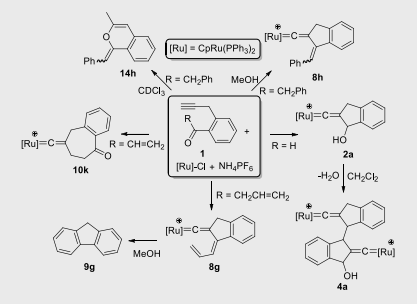
A number of Ru vinylidene complexes were obtained by metal mediated cyclization of aryl propynes with *ortho*-substituted aldehyde or ketone groups. With either terminal or internal α,β-unsaturated olefinic groups on the carbonyl group, the C-C bond formation occurs on the olefinic group. An unusual intermolecular dehydrative coupling was observed for the aryl propyne with simple *ortho*-substituted aldehyde group.



Author(s), Pi-Yeh Chia,[a] Cheng-Chen Kuo,[a] Shou-Ling Huang,[a] Yi-Hong Liu,[a] Ling-Kang Liu,[a] and Ying-Chih Lin,[a]*

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