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Coupling Reactions of *N*-Propargyl Semi-Salen Compounds Induced by Ruthenium Complex

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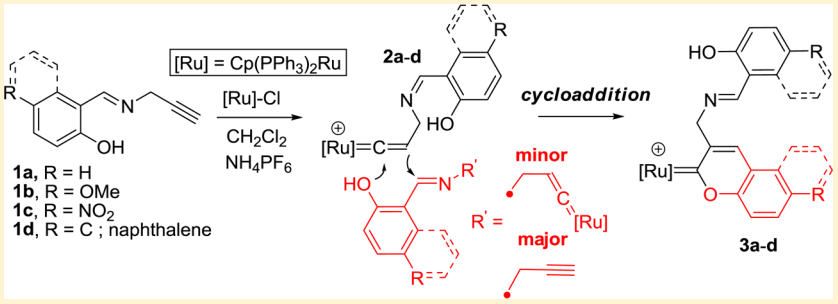
Supporting Information



ABSTRACT: The coupling reaction of *N*-propargyl semi-salen compound **1d** on [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$) generates the carbene complex **3d** containing a substituted 2*H*-chromene unit in 7 d. The precursor vinylidene complex **2d** is isolated from the reaction of the propargyl group of **1d** with [Ru]-Cl in 12 h. Addition of an *o*-cresol moiety to Cα and Cβ of the vinylidene ligand of **2d** takes place in a longer reaction time to yield **3d**. Reactions of [Ru]-Cl with other analogous compounds **1a**, **1b**, and **1c**, in excess, also afford carbene complexes **3a**, **3b**, and **3c**, respectively, in 48 h via a similar coupling process. Their precursor vinylidene complexes **2a**, **2b**, and **2c** are also observed in 12 h. Structures of **2** and **3** are determined on the basis of spectroscopic data. The solid state structure of the dppe analogue **3a′** is further confirmed by X-ray diffraction analysis. The added *o*-cresol part comes from compounds **1**, instead of aldehyde which is confirmed by the cross-coupling reactions of **2** and **1** using mass spectrometry. For comparison, treatment of [Ru]Cl with the amine analogue **13b** retaining the propargyl and phenol moieties yields no coupling product.

INTRODUCTION

During the past decade, chemistry of ruthenium vinylidene complexes has experienced important developments due to their involvement as key intermediates in the stoichiometric reaction as well as catalytic transformation of terminal alkynes.[1] These complexes generally play key roles in many carbon−carbon and carbon−heteroatom coupling processes.[2,3] Reactions of M=C bond of carbene complexes with organic compounds with N=C double bond were found to take place in different ways.[4] Hegedus reported that in the presence of imines, β-lactams formed upon photolysis of $(CO)_5M{=}[C(R)R']$.[5] Imines are normally prepared by a condensation reaction of primary amine with aldehyde and, less commonly, with ketone.[6] Among extensively studied reactions of imine, the aza-Baylis−Hilman reaction[7] and the aza Diels−Alder reaction[8] are well documented. Treatment of imine with mCPBA could further give oxaziridine.[9] Also, various imine compounds are widely used in organic reactions.[10−12] Aromatic Schiff-base, containing an imine functionality and a hydroxyl group, is a ligand commonly used in coordination chemistry.[13] Much less is known on the chemical property of molecules containing both imine and alkynyl groups.

We prepare a series of Schiff base compounds, each tethering a propargyl group on the imine nitrogen atom and explore their reactions with $Cp(PPh_3)_2RuCl$. Unlike a simple nonsubstituted Schiff base, these *N*-propargyl semi-salen compounds display distinctive reactivity. Intermolecular coupling of two molecules via the triple bond and the semi-salen unit on the ruthenium metal center affords the alkoxy carbene complexes with polycyclic structure containing the related skeleton of coumarin with the feature of one Schiff base retained (Scheme 1). Coumarins, a class of fused ring heterocycles, occur widely in nature and show interesting biological activity.[14] In addition to their biosynthesis in plants, coumarins could be prepared by other approaches such as Pechmann condensation.[15,16] Coumarin is also used as gain medium in dye lasers; it is well documented that fluorescence of coumarin-type dyes displays excellent quantum yield.[17] In this paper, we report our investigation on the ruthenium complex-mediated coupling of these *N*-propargyl semi-salen compounds to yield carbene complexes.

RESULTS AND DISCUSSION

***N*-Propargyl Semi-Salen.** The *N*-propargyl semi-salen compound **1a** is prepared from the condensation reaction of 2-hydroxy benzaldehyde and propargyl amine. The ^{1}H NMR

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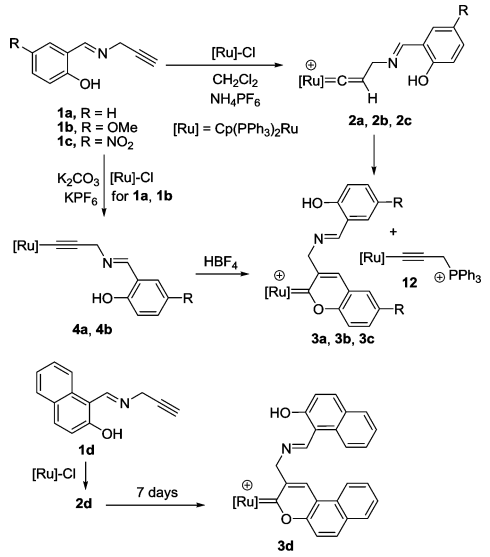
Scheme 1. Reactions of 1a−1d with [Ru]-Cl



signal at δ 8.66 is assigned to the imine N═CH proton of **1a**. Three analogous compounds **1b**, **1c**, and **1d** are prepared similarly, using different aldehydes. As shown in Scheme 1, treatment of [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$) with excess **1a** and NH_4PF_6 in CH_2Cl_2 for 2 d at room temperature affords the carbene complex **3a** in 83% yield. The same reaction in 12 h gives **3a** as the major product and the predecessor vinylidene complex **2a** and the acetylide complex **12** with a phosphonium group as two minor products. Addition of an *o*-cresol moiety to Cα and Cβ of the vinylidene ligand of **2a** yields **3a** containing a substituted 2*H*-chromene unit. Interestingly, the reaction of **1a** in the presence of salicylaldehyde yields **2a** as the major product and a small amount of **3a**, but attempts to purify **2a** by chromatography fail. Spectroscopic data of **2a** are obtained from the crude products. The two singlet ^{31}P NMR signals at δ 42.97 and 49.00 are assigned to **2a** and **3a**, respectively. Treatment of **1b** and **1c** with [Ru]-Cl for 2 days similarly yields complexes **3b** and **3c**, respectively. Addition of salicylaldehyde in the reaction mixture also hinders formation of **3**.

Slightly lower yield of **3c** is possibly attributed to the presence of the electron-withdrawing NO_2 group that may decrease the nucleophilicity of phenol. The electron-donating OMe group in **1b**, on the other hand, enhances the nucleophilic addition of the O atom onto Cα of the vinylidene ligand of **2b**, giving higher yield of **3b**. Moreover, the reaction of **1d** with [Ru]-Cl in 12 h affords only **2d**. Further cycloaddition requires 7 d to afford **3d**, most likely because of the steric effect of the naphthalene moiety. Previously, the reaction of resorcinal with metal alkenylcarbyne complex was reported to yield a cyclic carbene complex.[18]

In the ^1H NMR spectrum of **3b**, two resonances at δ 3.82 and 3.75 clearly reveal the presence of two methoxy-substituted aromatic rings, and the relatively downfield singlet peak at δ 8.83 is assigned to the iminyl N═CH proton. The Cα resonance of the carbene ligand in the ^{13}C NMR spectrum of **3b** appears as a triplet at δ 260.70 with $^2J_{CP}$ = 14.5 Hz. In the mass spectrum, the parent peak at m/z 1014.24 reveals the composition of the ligand on the metal complex which apparently results from dimerization of **1b** on the metal accompanied by loss of the propargyl imine group. Characteristic NMR data of **3a** and **3c** are similar. Separate reactions of [Ru′]-Cl ([Ru′] = Cp(dppe)Ru) with **1a** and **1b** at 45 °C in MeOH result in formation of **3a′** and **3b′**, respectively.

Single crystals of **3a′** are obtained from a bilayer solution of ether/CH_2Cl_2, and the structure is confirmed by an X-ray diffraction analysis. An ORTEP drawing of **3a′** is shown in Figure 1. The bond length of Ru(1)−C(1) (1.986(2)Å) lies in

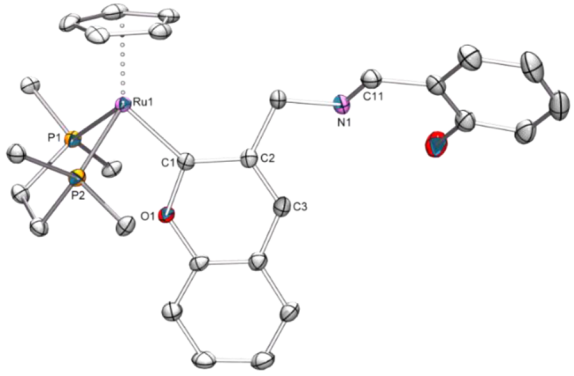


Figure 1. ORTEP drawing of the cationic complex **3a′**. For clarity, hydrogens, PF_6^-, and aryl groups of dppe on Ru except the *ipso* carbons are omitted. Thermal ellipsoid is set at the 50% probability level. Selected distances (Å) and angles (deg): Ru(1)−C(1), 1.986(2); C(1)−C(2), 1.462(3); C(2)−C(3), 1.358(3); O(1)−C(1), 1.374(3); N(1)−C(11), 1.269(3). C(2)−C(1)−Ru(1), 132.01(17).

the range of 1.82−1.99 Å found for many other ruthenium carbene complexes.[19] The bond lengths of the newly formed C(2)−C(3) bond and O(1)−C(1) bond are 1.358(3) Å and 1.374(3) Å, respectively. In addition, the six-membered heterocyclic ring is nearly a plane. The bond length of N(1)−C(11) (1.269(3) Å) reveals the double bond of an imine group.

In order to better understand the formation of **3** from **2**, attempts were thus made to prepare the acetylide complexes **4** from **2**. As expected, the deprotonation at Cβ−H of a vinylidene ligand can be easily achieved with base.[20] When NH_4PF_6 was first used as a salt in the presence of K_2CO_3 in the reaction of **1**, the cationic complex [Ru]-NH_3^+ formed as the major product from free NH_3 released from deprotonation of NH_4^+ cation.[21] Replacement of NH_4PF_6 by KPF_6 in MeOH resulted in formation of [Ru]-H. Probably O-coordination of MeOH to the ruthenium center was followed by a β-hydrogen elimination to give [Ru]-H and formaldehyde.[22] Finally, in the presence of K_2CO_3 and KPF_6 in CH_2Cl_2, syntheses of two stable acetylide complexes **4a** and **4b** were achieved from **1a** and **1b**, respectively, as shown in Scheme 1. Complexes **4a** and **4b** are identified on the basis of spectroscopic data. Aiming at isolation of **2a** and **2b**, protonations of **4a** and **4b**, however, generate the corresponding complexes **3a** and **3b** both in about 30% yield as the final products. It is clear that the vinylidene complex **2** with an imine group is reactive, readily forming the corresponding complex **3** with a substituted 2*H*-chromene unit. We carried out a few experiments in order to find the source of the added *o*-cresol moiety in this cyclization reaction.

Possible Pathways for Formation of 3. Several possible pathways are considered feasible for the formation of **3** from **2**. For example, **3** could be formed by addition of a simple salicylaldehyde molecule to **2**. Presumably hydrolysis of the imine group of **1** could generate the aldehyde. However, as shown in Scheme 2, addition of salicylaldehyde to **2b** resulted in no mixed carbene complex, i.e. no cross addition was

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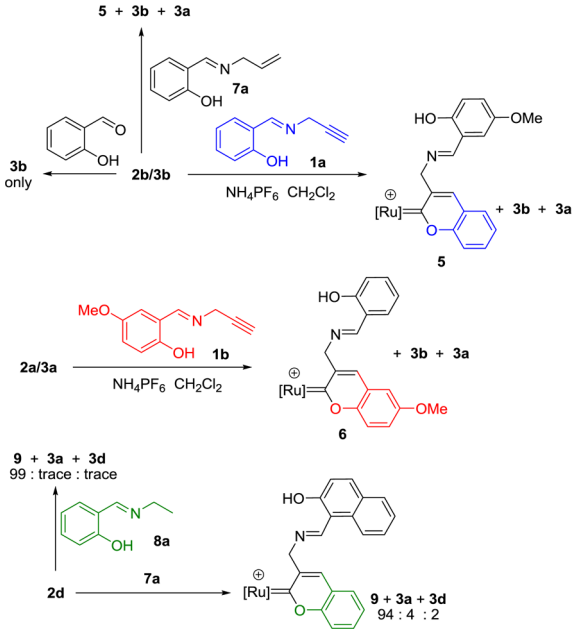
Scheme 2. Formations of the cross addition products

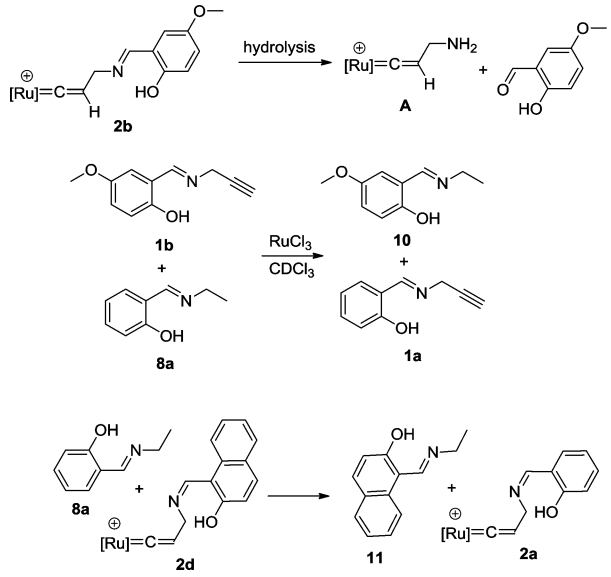


observed. Instead, **3b** was isolated as the only product. Therefore, aldehyde seems to have no effect in the formation of **3**. However, when **1a** was added to the mixture of **2b**/**3b**, the new mixed carbene complex **5**, in addition to **3b**, see Scheme 2, was detected by mass spectra, and **3a** was also observed. Treatment of a mixture of **2a**/**3a** with **1b** also afforded the other mixed carbene complex **6** and **3a**/**3b**. On the basis of these results, it is clear that the imine compound, not aldehyde, plays the vital role for the formation of the coupling products. Two possible imine sources exist in our reaction system i.e. the organic imine compounds **1** and the organometallic vinylidene complexes **2**.

Formation of **3a** in the reaction of **2b**/**3b** with **1a** is reasonably explained by the exchange of the whole vinylidene ligand of **2b** with **1a** generating **2a** then give **3a**. To further explore the reaction, compound **7a**, also a semi-salen but with no propargyl group instead, with an *N*-allylic group, was reacted with **2b**/**3b** to yield two expected products **5** and **3b**, Scheme 2. However, **3a** is also observed in low yield. The ratio of **5**:**3b**:**3a** is approximately 54:42:4. The more stable vinylidene complex **2d** was also reacted separately with **7a** and an ethyl analogue **8a**.[23] In both cases, all three carbene complexes **9**, **3a**, **3d** were detected from mass spectra, with **9** being the major product, see lower part of Scheme 2.

Imine Metathesis. It is interesting that **3a** is also observed in both reactions of **2b** with **7a** and with **8a**. Compounds **7a** and **8a** contain no *N*-propargyl group. Apparently with the whole vinylidene ligand exchange process it would not be possible to generate **2a** in the reaction. However, **3a** is always observed in addition to the anticipated products **5**, **3b**, **9** and **3d**. Formation of **3a** should require **2a**, which could form from exchange of the whole vinylidene ligand of **2b** with **1a**, or alternatively, via hydrolysis of the imine bond of **2b** followed by condensation or a direct imine exchange process. The hydrolysis pathway should require formation of the vinylidene complex **A** with an amine group, see Scheme 3. Our attempts to prepare **A** by directly treating propargyl amine with [Ru]-Cl afford a complicated mixture. Complex **A** is thus believed to be unstable. Therefore, the hydrolysis pathway leading to **2a** is

Scheme 3. Imine metathesis reactions

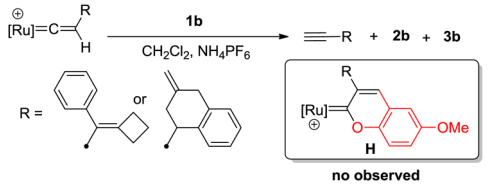


considered not feasible. A direct imine metathesis in the presence of Lewis acid, previously observed by Meyer et al.,[24] is regarded as a reasonable route to give **2a** from the mixture of **2b**/**3b** and **7a** or **8a**. The metathesis process explains the presence of **3a** in the reactions of **2d** or **2b** with **7a** or with **8a**, with no *N*-propargyl group.

Indeed, as shown in Scheme 3, exchange reaction between two Schiff-base-type organic imine compounds **1b** and **8a** in the presence of $RuCl_3$ in $CDCl_3$ gives new imine compounds **10** and **1a** in 32% conversion in 3 days. The direct imine metathesis reaction also occurs for the vinylidene complex **2d** and **8a** giving **11** and **2a**. The quartet and triplet ^1H signals at δ 3.65 and 1.40 with $^3J_{HH}$ = 7.34 Hz are assigned to the ethyl group of **11**. The reaction of **2d** and **7a** forms complex **3a**, albeit in low yield, and **3a** is believed to come from the same imine metathesis reaction. Probably the ruthenium portion plays the role of Lewis acid.

The requirement of the imine moiety in the vinylidene is checked by running the following experiments. Two different vinylidene complexes[25] with no imine group, as shown in Scheme 4, are separately reacted with imine **1b** to yield only **2b**

Scheme 4. Vinylidene Complexes with No Imine Group



and **3b**. If the imine group on the vinylidene ligand is not required, cyclization between the vinylidene ligand and **1b** should give the mixed carbene complex **H**, which is not observed, indicating that the coupling reaction also requires the imine functionality on the vinylidene ligand.

In the reaction of **1a** with [Ru]-Cl, mentioned above, in addition to **2a** and **3a**, the minor side product **12**, see Scheme 1, is detected by NMR and mass spectra in the crude product. In the ^{31}P NMR spectrum of **12**, the triplet and doublet signals at δ 15.79 and 49.73 are assigned to the phosphonium group

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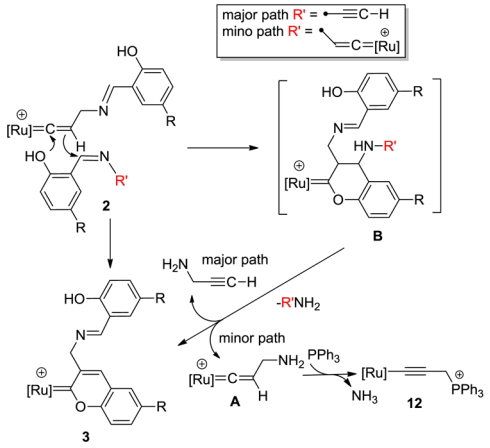
and two phosphine ligands, respectively, showing the pattern of an acetylide product with a cationic phosphonium group. The parent peak in the mass spectrum at m/z 991.23 is consistent with the structure of **12**.

The proposed mechanism for the formation of **3** and **12** is shown in Scheme 5. Complex **3** should be formed mainly from

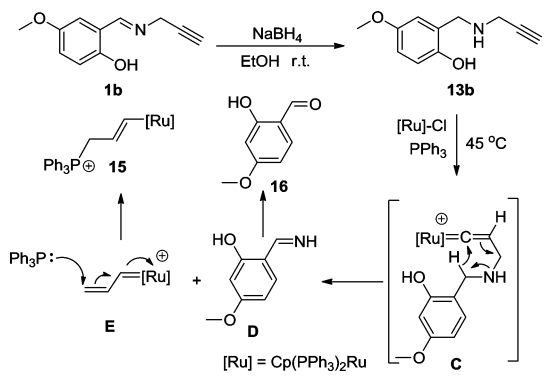
Scheme 5. Formation of 3: Two Possible Pathways



2 and a semi-salen molecule both with imine functionality. The coupling is followed by removal of the nitrogen moiety. Formation of the minor product **12** can be suitably explained by coupling of two vinylidene complexes. Dimerization of **2** involving the vinylidene ligand and the imine/phenol groups gives the dinuclear complex **B**, which undergoes elimination of the metal vinylidene moiety to afford **3** and **A**. Deamination of **A** is accompanied by addition of a phosphine molecule to give **12**. Previously, [2 + 2] cycloaddition between a tungsten vinylidene complex and an imine compound leading to a C–C bond formation has been reported.[26] Nitrogen atom of the imine could serve as a nucleophile. The much lower yield of **12** indicates that this coupling pathway using two organometallic complexes should be a minor route.

Propargyl Amine. As the addition/cyclization reaction of **2** to give **3** requires two imine groups, it is interesting to compare the chemical reactivity of the corresponding propargyl amine. Transformation of the imine group into an amine group was readily achieved by a simple reduction as shown in Scheme 6. Sodium borohydride is used to reduce **1b** to give the corresponding amine **13b**, which was then reacted with [Ru]-Cl in CH_2Cl_2 at 40 °C for 12 h in the presence of NH_4PF_6.

Scheme 6. Reactions of the Amine Analogue



After purification, the desired vinylidene complex with the amine group was not observed; instead, a mixture containing [Ru]-NH_3^+ as the major product was isolated, and the ^{31}P NMR spectrum of the minor product **15** shows a triplet signal at δ 14.92 and a doublet signal at δ 52.64, expected for a cationic complex with a phosphonium group. In the ^1H NMR spectrum of **15**, a multiplet signal at δ 8.22 is assigned to CαH. The mass spectrum displays the parent peak at m/z 993.25 consistent with **15**. Formation of [Ru]-NH_3^+ is probably due to the deprotonation of the ammonium NH_4^+ salt. In addition, as expected, 5-methoxy-2-hydroxy-benzaldehyde was also observed in the ^1H NMR spectrum. In KPF_6, instead of NH_4PF_6, and with excess free phosphine added, the reaction gave **15** and 5-methoxy-2-hydroxybenzaldehyde, **16**, in high yield. As shown in Scheme 6, the vinylidene complex **C** probably forms first, then a 1,5-hydrogen shift takes place to give the imine compound **D** and complex **E**.[27] Free phosphine in solution attacks Cγ of **E** to give **15**, and hydrolysis of **D** gives **16**.

CONCLUSIONS

In summary, reactions of [Ru]-Cl with *N*-propargyl semi-salen compounds first yield vinylidene complexes **2**, followed by an addition reaction, which adds an *o*-cresol moiety across Cα and Cβ of the vinylidene ligand of **2**, to give carbene complexes **3** as the final product. The added cresol portion comes from a molecule with an imine functionality, instead of an aldehyde group. This is confirmed by observation of various cross carbene complexes when **2** is reacted with **1**. The major pathway to yield **3** is the reaction of **2** with excess **1**. The minor route is via a dimerization of two vinylidene complexes **2**, which also yield the acetylide complex **12** with a phosphonium group. In addition, the reaction of [Ru]-Cl with the amine analogue **13b**, which retains the propargyl group and phenol moiety, is also explored. The cationic phosphine addition product **15** is obtained. Cyclization reaction is observed only in the reaction of imine.

EXPERIMENTAL SECTION

General Information. The manipulations were performed under an atmosphere of dry nitrogen using a vacuum-line and standard Schlenk techniques unless mentioned otherwise. 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 at room temperature and are reported in units of δ with residual protons in the solvents as a standard. Electrospray ionization mass spectrometry, elemental analysis and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University. According to the literature methods, [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$)[28] was prepared from $RuCl_3{\cdot}xH_2O$, which was purchased from Steam Chemicals. [Ru′]-Cl ([Ru′] = Cp(dppe)Ru)[29] was prepared from [Ru]-Cl. Preparation of the imine compounds **7a**, **8a** and **11** followed the methods in the literature.[30−32]

Synthesis of 1a. To a Schlenk flask charged with salicylaldehyde (1.98 g, 16 mmol), propargyl amine (1.07 g, 19 mmol) and $MgSO_4$, was added 30 mL of toluene under nitrogen. The resulting solution was stirred at room temperature overnight. The reaction mixture was extracted with ethyl acetate, and the organic phase was washed with aqueous NH_4Cl and dried over $MgSO_4$. Solvent was then removed under reduced pressure to give compound **1a** (2.45 g, 95% yield). Spectroscopic data for **1a**: ^1H NMR (δ, $CDCl_3$): 12.87 (s, 1H, OH); 8.66 (t, $^4J_{HH}$ = 1.79 Hz, 1H, N=CH); 6.86–7.33 (m, 4H, Ph); 4.52 (dd, $^4J_{HH}$ = 1.79 Hz, $^4J_{HH}$ = 2.45 Hz, 2H, CH_2); 2.55 (t, $^4J_{HH}$ = 2.45 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 165.73 (N=C); 160.65 (Ph–

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OH); 132.53, 131.70, 118.75, 116.99 (Ph, =C); 77.47, (C≡); 76.51 (≡CH); 45.38 (CH_2). MS (EI) *m/z*: 159.07

Compound **1b** (1.31 g, 94% yield) was similarly prepared from 5-methoxy salicylaldehyde (1.12 g, 7.4 mmol) and propargyl amine (0.47 g, 8.5 mmol) in toluene. Spectroscopic data for **1b**: ^{1}H NMR (δ, $CDCl_3$): 12.38 (s, 1H, OH); 8.62 (t, $^4J_{HH}$ = 1.81 Hz, 1H, N=CH); 6.82−6.94 (m, 3H, Ph); 4.52 (dd, $^4J_{HH}$ = 1.81 Hz, $^4J_{HH}$ = 2.44 Hz, 2H, CH_2); 3.77 (s, 3H, OCH_3); 2.56 (t, $^4J_{HH}$ = 2.44 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 165.44 (N=C); 154.80, 152.09, 119.64, 118.33, 117.76, 115.16 (Ph, =C); 77.45 (C≡); 76.60 (≡CH); 55.94 (−OCH_3); 45.43 (CH_2). MS (EI) *m/z*: 189.08

Compound **1c** (1.21 g, 95% yield) was prepared from 5-nitro salicylaldehyde (1.04 g, 6.2 mmol) and propargyl amine (0.41 g, 7.4 mmol). Spectroscopic data for **1c**: ^{1}H NMR (δ, $CDCl_3$): 13.98 (s, 1H, OH); 8.78 (t, $^4J_{HH}$ = 1.82 Hz, 1H, N=CH); 8.32 (d, $^4J_{HH}$ = 2.72 Hz, 1H, Ph); 8.22 (dd, $^3J_{HH}$ = 9.16 Hz, $^4J_{HH}$ = 2.72 Hz, 1H, Ph); 7.03 (d, $^3J_{HH}$ = 9.16 Hz, 1H, Ph); 4.60 (dd, $^4J_{HH}$ = 1.82 Hz, $^4J_{HH}$ = 2.45 Hz, 2H, CH_2); 2.65 (t, $^4J_{HH}$ = 2.45 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 170.09 (Ph−OH); 165.90 (N=C); 138.70, 129.95, 129.32, 120.14, 117.97 (Ph, =C); 79.63, (C≡); 78.87 (≡CH); 44.77 (CH_2). MS (EI) *m/z*: 204.05

Compound **1d** (1.17 g, ∼89% yield) was similarly prepared from 2-hydroxy-1-naphthaldehyde (1.08 g, 6.3 mmol) and propargyl amine (0.42 g, 7.6 mmol). After column chromatography, a small amount of starting material, about 8%, remained in the mixture. Spectroscopic data for **1d**: ^{1}H NMR (δ, $CDCl_3$): 14.68 (s, 1H, OH); 9.57 (br, 1H, N=CH); 7.04−9.57 (m, 6H, Ph); 4.65 (dd, $^4J_{HH}$ = 2.44 Hz, $^4J_{HH}$ = 1.44 Hz, 2H, CH_2); 3.11 (t, $^4J_{HH}$ = 2.44 Hz, 1H, ≡CH). ^{13}C NMR (δ, CD_2Cl_3): 166.44 (N=C); 161.59 (Ph−OH); 135.62, 133.62, 129.65, 128.35, 127.94, 123.79, 121.40, 119.62, 108.85 (Ph, =C); 78.27 (C≡); 76.59(≡CH); 44.88 (CH_2). MS (EI) *m/z*: 209.08

Reaction of 1a/Salicylaldehyde with [Ru]-Cl. To a Schlenk flask charged with [Ru]-Cl (0.097 g, 0.13 mmol) and NH_4PF_6 (0.054 g, 0.33 mmol), were added **1a** (0.025 g, 0.16 mmol), salicylaldehyde (0.041 g, 0.33 mmol), and 10 mL of CH_2Cl_2 under nitrogen. The resulting solution was stirred at room temperature overnight. Then the solution was filtered through Celite to remove the insoluble precipitates, and the volatiles of the filtrate were removed under vacuum. The solid residue was extracted with a small volume of CH_2Cl_2 followed by filtration. Addition of 70 mL of diethyl ether and hexane (1:1) to the filtrate gave precipitates which were collected in a glass frit, washed with diethyl ether, and dried under vacuum to give a mixture of **2a** and **3a** in a ratio of ∼3.6:1. (0.104 g). Complex **2a** underwent further reaction to give **3a**. Spectroscopic data for **2a** obtained from the mixture: ^{1}H NMR (δ, $CDCl_3$): 13.22 (s, 1H, OH); 8.14 (s, 1H, N=CH); 6.83−7.75 (m, 34H, Ph); 5.15 (s, 5H, Cp); 5.00 (t, $^3J_{HH}$ = 8.12 Hz, 1H, CβH); 4.40 (d, $^3J_{HH}$ = 8.12 Hz, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.68 (s, PPh_3). MS (ESI^+) *m/z*: 850.20.

Reaction of 1a with [Ru]-Cl. Complex **3a** (0.15 g, 83% yield) was similarly prepared from **1a** (0.067 g, 0.42 mmol), [Ru]-Cl (0.14 g, 0.19 mmol), and NH_4PF_6 (0.083 g, 0.51 mmol) in CH_2Cl_2 but with no salicylaldehyde added. Spectroscopic data of **3a**: ^{1}H NMR (δ, $CDCl_3$): 13.18 (s, 1H, OH); 8.83 (s, 1H, N=CH); 6.92−7.67 (m, 38H, Ph); 5.99 (d, $^3J_{HH}$ = 8.49 Hz, 1H, Ph); 5.18 (s, 2H, CH_2); 4.75 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 264.40 (t, $^2J_{CP}$ = 14.7 Hz, Cα); 169.71 (N=C); 160.91, 160.29 (Ph−OH, Ph−OCα); 147.63 (Ph, =C); 136.27−135.84 (m, PPh_3, P−C); 133.42, 130.20, 128.24 (PPh_3, =C); 114.97−136.41 (Ph, =C); 89.21 (Cp); 62.91 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 48.93 (s, PPh_3). MS (ESI^+) *m/z*: 954.22. Anal. Calcd for $C_{58}H_{48}F_6NO_2P_3Ru$: C, 63.39; H, 4.40; N, 1.27. Found: C, 62.46; H, 4.32; N, 1.21. The minor side product **12** was observed in the crude product without purification. Spectroscopic data for **12**: ^{1}H NMR (δ, $CDCl_3$): 5.91 (d, $^2J_{HP}$ = 9.28 Hz); 4.00 (s, 5H, Cp). ^{31}P NMR (δ, $CDCl_3$): 49.73 (d, J_{PP} = 5.6 Hz, 2P, 2Ru−PPh_3); 15.79 (t, J_{PP} = 5.6 Hz, 1P, PPh_3). MS (ESI^+) *m/z*: 991.23.

A mixture of **2b**/**3b** (1.8:1, total weight 0.18 g) was prepared from **1b** (0.047 g, 0.25 mmol), 5-methoxy-salicylaldehyde (0.079 g, 0.52 mmol), [Ru]-Cl (0.152 g, 0.21 mmol) and NH_4PF_6 (0.091 g, 0.56 mmol) in CH_2Cl_2. Spectroscopic data for **2b** (from the mixture): ^{1}H NMR (δ, $CDCl_3$): 12.70 (s, 1H, OH); 8.17 (s, 1H, N=CH); 6.62−7.84 (m, 36H, Ph); 5.14 (s, 5H, Cp); 5.00 (t, $^3J_{HH}$ = 8.00 Hz, 1H, CβH); 4.38 (d, $^3J_{HH}$ = 8.00 Hz, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.72 (s, PPh_3). MS (ESI^+) *m/z*: 880.20.

Complex **3b** (0.059 g, 85% yield) was prepared from **1b** (0.031 g, 0.164 mmol), [Ru]-Cl (0.048 g, 0.066 mmol) and NH_4PF_6 (0.028 g, 0.17 mmol) in CH_2Cl_2. Spectroscopic data for **3b**: ^{1}H NMR (δ, $CDCl_3$): 12.71 (s, 1H, OH); 8.83 (s, 1H, N=CH); 7.64 (s, 1H, CγH); 6.62−7.67 (m, 48H, Ph); 5.92 (d, $^3J_{HH}$ = 9.26 Hz, 1H, Ph); 5.13 (s, 2H, CH_2); 4.73 (s, 5H, Cp); 3.82, 3.75 (2 s, 6H, 2 OCH_3). ^{13}C NMR (δ, $CDCl_3$): 260.63 (t, $^2J_{CP}$ = 14.7 Hz, Cα); 169.58 (N=C); 156.99, 156.64, 154.98, 152.45 (Ph−OH, Ph−OCα, 2Ph−OMe); 147.57 (Ph, =C); 136.49−135.91 (PPh_3, P−C); 133.31, 130.12, 128.20 (PPh_3, =C); 107.64−136.49 (Ph, =C); 88.72 (Cp); 63.06 (CH_2); 55.99, 55.81 (2 OCH_3). ^{31}P NMR (δ, $CDCl_3$): 48.72 (s, PPh_3). MS (ESI^+) *m/z*: 1014.24. Anal. Calcd for $C_{60}H_{52}F_6NO_4P_3Ru$: C, 62.18; H, 4.52; N, 1.21. Found: C, 61.97; H, 4.24; N, 1.16.

A mixture of **2c**/**3c** (4.1:1, total weight 0.16 g) was prepared from **1c** (0.085 g, 0.42 mmol), 5-nitro-salicylaldehyde (0.14 g, 0.82 mmol) and [Ru]-Cl (0.148 g, 0.20 mmol), NH_4PF_6 (0.088 g, 0.54 mmol) in CH_2Cl_2. Spectroscopic data for **2c** (from the mixture): ^{1}H NMR (δ, $CDCl_3$): 14.00 (s, 1H, OH); 8.78 (s, 1H, N=CH); 6.89−7.40 (m, 33H, Ph); 5.19 (s, 5H, Cp); 5.08 (t, $^3J_{HH}$ = 7.95 Hz, 1H, CβH); 4.45 (d, $^3J_{HH}$ = 7.95 Hz, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.69 (s, PPh_3). MS (ESI^+) *m/z*: 895.18.

Complex **3c** (0.138 g, ∼66% yield) was similarly prepared from **1c** (0.105 g, 0.52 mmol), [Ru]-Cl (0.146 g, 0.20 mmol) and NH_4PF_6 (0.091 g, 0.56 mmol) in CH_2Cl_2. Complex **3c** decomposed in chromatographic column. Pure complex **3c** was not obtained. Spectroscopic data for **3c**: ^{1}H NMR (δ, $(CD_3)_2CO$): 14.38 (s, 1H, OH); 9.08 (s, 1H, N=CH);8.75, 8.55 (2d, $^4J_{HH}$ = 2.77 Hz, 2H, Ph);8.30 (m, 1H, Ph); 8.13 (s, 1H, CγH); 7.05−8.04 (m, 32H, Ph); 6.37 (d, $^3J_{HH}$ = 9.26 Hz, 1H, Ph); 5.63 (s, 2H, CH_2); 5.17 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 268.12 (t, $^2J_{CP}$ = 13.9 Hz, Cα); 169.08 (N=C); 167.53, 161.03 (Ph−OH, Ph−OCα); 148.86, 144.31 (Ph); 135.65−134.93 (PPh_3, P−C); 133.12, 130.54, 128.53 (PPh_3, =C); 115.82−139.53 (Ph, =C); 90.49 (Cp); 61.96 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 48.27 (s, PPh_3). MS (ESI^+) *m/z*: 1044.19.

Synthesis of 2d. To a Schlenk flask charged with [Ru]-Cl (0.097 g, 0.13 mmol) and NH_4PF_6 (0.058 g, 0.36 mmol) were added **1d** (0.070 g, 0.335 mmol) and 10 mL of CH_2Cl_2 under nitrogen. The resulting solution was stirred at room temperature. Similar procedures were used to obtain the final product **2d** (0.104 g, 84% yield) as an orange powder. Spectroscopic data for **2d**: ^{1}H NMR (δ, $CDCl_3$): 14.37 (s, 1H, OH); 8.62 (s, 1H, N=CH); 7.75 (d, $^3J_{HH}$ = 8.25 Hz, 1H, Ph); 7.69 (d, $^3J_{HH}$ = 9.27 Hz, 1H, Ph); 7.58 (d, $^3J_{HH}$ = 8.25 Hz, 1H, Ph); 6.93−7.76 (m, 32H, Ph); 6.95 (d, $^3J_{HH}$ = 9.27 Hz, 1H, Ph); 5.17 (s, 5H, Cp); 5.08 (t, $^3J_{HH}$ = 8.11 Hz, 1H, CβH); 4.42 (d, $^3J_{HH}$ = 8.11 Hz, 2H, CH_2). ^{13}C NMR (δ, $CDCl_3$): 345.72 (t, $^2J_{CP}$ = 15.3 Hz, Cα); 158.53 (N=C); 134.01−133.20 (PPh_3, P−C); 133.00, 130.98, 128.45 (PPh_3, =C); 107.00−133.61 (Ph, =C); 94.85 (Cp); 44.42 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.07 (s, PPh_3). MS (ESI^+) *m/z*: 900.21. Anal. Calcd for $C_{55}H_{46}F_6NOP_3Ru$: C, 63.22; H, 4.44; N, 1.34. Found: C, 63.33; H, 4.21; N, 1.31.

Complex **3d** (0.090 g, ∼43% yield) was prepared from **1d** (0.109 g, 0.52 mmol), [Ru]-Cl (0.145 g, 0.20 mmol) and NH_4PF_6 (0.110 g, 0.67 mmol) in CH_2Cl_2 for 7 days. Complex **3d** decomposed in the chromatographic column. No pure complex **3d** was obtained. Spectroscopic data for **3d**: ^{1}H NMR (δ, $CDCl_3$): 14.94 (s, 1H, OH); 9.58 (s, 1H, N=CH); 8.45 (s, 1H, CγH); 6.78−7.79 (m, 41H, Ph); 6.05 (d, $^3J_{HH}$ = 9.06 Hz, 1H, Ph); 5.32 (s, 2H, CH_2); 4.78 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 258.31 (t, $^2J_{CP}$ = 15.4 Hz, Cα); 171.12 (N=C); 163.16, 162.27 (Ph−OH, Ph−OCα); 147.31 (Ph); 114.66−136.64 (Ph, =C); 88.94 (Cp); 59.35 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 48.69 (s, PPh_3). MS (ESI^+) *m/z*: 1054.25.

Synthesis of 3a′. To a Schlenk flask charged with NH_4PF_6 (0.068 g, 0.417 mmol) and Cp(dppe)RuCl (0.097 g, 0.16 mmol) were added **1a** (0.064 g, 0.402 mmol) and 10 mL of MeOH under nitrogen. The reaction at 45 °C overnight yielded product **3a′** (0.112 g, 84% yield) as a red powder. Single crystals were grown from a CH_2Cl_2/diethyl ether solution. Spectroscopic data of **3a′**: ^{1}H NMR (δ, $CDCl_3$): 13.13 (s,

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1H, OH); 8.72 (s, 1H, N=CH); 6.85−7.49 (m, 26H, Ph); 6.33 (d, $^3J_{HH}$ = 8.53 Hz, 1H, Ph); 4.96 (s, 5H, Cp); 4.89 (d, 2H, CH_2); 3.22, 2.98 (two m, 4H, 2 dppe CH_2). ^{13}C NMR (δ, $CDCl_3$): 264.86 (t, $^2J_{CP}$ = 13.2 Hz, Cα); 169.43 (N=C); 141.21−140.91, 136.44−136.14 (dppe, P−C); 115.21−133.63 (Ph, =C; dppe, =C); 89.35 (Cp); 64.31 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 90.59 (s, dppe). MS (ESI^+) m/z: 828.17. Anal. Calcd for $C_{48}H_{42}F_6NO_2P_3Ru$: C, 59.26; H, 4.35; N, 1.44. Found: C, 59.33; H, 4.33; N, 1.42.

Complex **3b′** (0.179 g, 82% yield) was prepared from **1b** (0.116 g, 0.613 mmol), Cp(dppe)RuCl (0.147 g, 0.245 mmol), and NH_4PF_6 (0.102 g, 0.626 mmol) in MeOH at 45 °C. Spectroscopic data for **3b′**: ^{1}H NMR (δ, $CDCl_3$): 12.72 (s, 1H, OH); 8.70 (s, 1H, N=CH); 6.66−7.72 (m, 27H, Ph); 6.25 (d, $^3J_{HH}$ = 9.14 Hz, 1H, Ph); 5.00 (s, 5H, Cp); 4.85 (s, 2H, CH_2); 3.81, 3.68 (2 s, 2H, 2 OCH_3); 3.16, 2.96 (two m, 4H, 2 dppe CH_2). ^{13}C NMR (δ, $CDCl_3$): 260.13 (t, $^2J_{CP}$ = 13.2 Hz, Cα); 168.87 (N=C); 139.74−139.38, 135.06−134.67 (dppe, P−C); 131.56−128.61 (dppe, =C); 121.54−107.64 (Ph, =C); 107.63−139.74 (Ph, =C); 87.61 (Cp); 63.07 (CH_2); 55.88, 55.64 (2 OCH_3); 28.97 (t, $^2J_{CP}$ = 22.1 Hz, dppe).^{31}P NMR (δ, $CDCl_3$): 90.34 (s, dppe). MS (ESI^+) m/z: 888.20. Anal. Calcd for $C_{50}H_{46}F_6NO_4P_3Ru$: C, 58.14; H, 4.49; N, 2.69. Found: C, 57.97; H, 4.24; N, 2.59.

Synthesis of 4a. To a Schlenk flask charged with [Ru]-Cl (0.147 g, 0.19 mmol), K_2CO_3 (0.052 g, 0.38 mmol), and KPF_6 (0.095 g, 0.52 mmol) were added **1a** (0.048 g, 0.30 mmol) and 15 mL of CH_2Cl_2 under nitrogen. The resulting solution was stirred at room temperature for 3 days, and then CH_2Cl_2 was removed under vacuum. The product was redissolved in CH_2Cl_2, and the mixture was filtered through Celite to remove the insoluble precipitates followed by reprecipitation by addition of 50 mL of MeOH. Precipitates thus formed were collected in a glass frit, washed with MeOH, and dried under vacuum to give the final product **4a** (0.105 g, 61% yield) as light-yellow powder. Spectroscopic data for **4a**: ^{1}H NMR (δ, $CDCl_3$): 14.20 (s, 1H, OH); 8.80 (t, $^4J_{HH}$ = 1.80 Hz, 1H, N=CH); 7.06−7.46 (m, 31H, Ph); 6.90 (d, $^3J_{HH}$ = 8.31 Hz, 1H, Ph); 6.61 (m, 1H, Ph); 6.50 (m, 1H, Ph); 4.74 (d, $^4J_{HH}$ = 1.80 Hz, 2H, CH_2); 4.31 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 164.16 (N=C); 161.73 (Ph−OH); 139.32−138.50 (PPh_3, P−C); 133.79, 130.20, 127.17 (PPh_3, =C); 119.07−116.79 (Ph, =C); 109.39 (t, $^2J_{CP}$ = 24.5 Hz, Cα); 103.66 (Cβ); 84.94 (Cp); 48.80 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 50.63 (s, PPh_3). MS (ESI^+) m/z: 850.19. Anal. Calcd for $C_{51}H_{43}NOP_2Ru$: C, 72.16; H, 5.11; N, 1.65. Found: C, 72.13; H, 5.09; N, 1.63.

Complex **4b** (0.114 g, 62% yield) was similarly prepared from **1b** (0.059 g, 0.31 mmol), [Ru]-Cl (0.152 g, 0.21 mmol), K_2CO_3 (0.050 g, 0.37 mmol), and KPF_6 (0.102 g, 0.55 mmol) in CH_2Cl_2 at room temperature. Spectroscopic data for **4b**: ^{1}H NMR (δ, $CDCl_3$): 13.57 (s, 1H, OH); 8.72 (s, 1H, N=CH); 6.74−7.48 (m, 32H, Ph); 5.86 (d, $^4J_{HH}$ = 2.96 Hz, 1H, Ph); 4.77 (s, 2H, CH_2); 4.30 (s, 5H, Cp); 3.37 (s, 3H, OCH_3). ^{13}C NMR (δ, $CDCl_3$): 163.99 (N=C); 155.43 (Ph−OH); 151.24 (Ph−OMe); 139.39−138.56 (PPh_3, P−C); 133.77, 128.49, 127.18 (PPh_3, =C); 118.87−114.15 (Ph, =C); 109.14 (t, $^2J_{CP}$ = 24.3 Hz, Cα); 103.89 (Cβ); 85.05 (Cp); 55.64 (CH_2); 48.92 (OCH_3). ^{31}P NMR (δ, $CDCl_3$): 50.40 (s, PPh_3). MS (ESI^+) m/z: 880.20. Anal. Calcd for $C_{52}H_{45}NO_2P_2Ru$: C, 71.06; H, 5.16; N, 1.59. Found: C, 71.02; H, 5.13; N, 1.56.

Protonations of **4a** and **4b** by excess HBF_4 for 1 d gave **3a** and **3b** in 31% and 34% yields, respectively, as determined by NMR.

Reaction of 2b with 1a. To a mixture of **2b**/**3b** in a ratio of 2.6:1 (0.155 g) in CH_2Cl_2, prepared as mentioned before, was added **1a** (0.024 g, 0.15 mmol), and the solution was stirred at room temperature overnight. The solution was filtered through Celite to remove the insoluble precipitates followed by precipitation by addition of 60 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 was obtained as a mixture of **3a**, **3b**, and **5** in a ratio of 0.08:0.8:1. Three complexes are not separable by chromatography. Due to extensive overlaps, no attempt was made to obtain complete ^{1}H NMR data of **5** from the mixture. Partial spectroscopic data for **5**: ^{1}H NMR (δ, $CDCl_3$): 8.83 (s, 1H, N=CH); 6.61 (m, 1H, Ph); 5.99 (d, $^3J_{HH}$ = 8.33 Hz, 1H, Ph); 4.76 (s, 5H, Cp). ^{31}P NMR (δ, $CDCl_3$): 49.04 (s, PPh_3). MS (ESI^+) m/z: 984.22.

Reaction of 2a with 1b. A mixture of **2a**/**3a** in a ratio of 3.1:1. (0.113 g) was reacted with **1b** (0.023 g, 0.12 mmol) at room temperature. The final product was similarly obtained as a mixture of **3a**, **3b**, and **6** in a ratio of 0.6:0.4:1. Attempts to obtain the ^{1}H NMR data of **6** failed due to the same reason mentioned above. Partial spectroscopic data for **6**: ^{1}H NMR (δ, $CDCl_3$): 8.82 (s, 1H, N=CH); 6.00 (d, $^3J_{HH}$ = 8.64 Hz, 1H, Ph); 4.75 (s, 5H, Cp); 3.76 (s, 3H, OCH_3). ^{31}P NMR (δ, $CDCl_3$): 48.89 (s, PPh_3). MS (ESI^+) m/z: 984.22.

Synthesis of 9. To a Schlenk flask charged with **2d** (0.062 g, 0.069 mmol) was added **8a** (0.024 g, 0.16 mmol) in 1.5 mL of $CDCl_3$ at room temperature. Similar procedures were used to obtain the final crude products including **9** and trace amount of **3a** and **3d**. Recrystallization from diethyl ether/CH_2Cl_2 gave **9** (0.052 g, 75% yield) as an orange powder. Spectroscopic data for **9**: ^{1}H NMR (δ, $CDCl_3$): 14.77 (s, 1H, OH); 9.40 (s, 1H, N=CH); 8.32 (d, $^3J_{HH}$ = 8.40 Hz, 1H, Ph); 7.77 (d, $^3J_{HH}$ = 9.20 Hz, 1H, Ph); 7.65 (s, 1H, CγH); 6.92−7.63 (m, 37H, Ph); 6.02 (d, $^3J_{HH}$ = 8.40 Hz, 1H, Ph); 5.16 (s, 2H, CH_2); 4.80 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 264.16 (t, $^2J_{CP}$ = 14.5 Hz, Cα); 172.12 (N=C); 163.00, 160.33 (Ph−OH, Ph−OCα); 147.21 (Ph, =C); 136.23−135.80 (PPh_3, P−C); 133.39, 130.23, 128.72 (PPh_3, =C); 136.95−108.28 (Ph, =C); 89.35 (Cp); 58.55 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 48.44 (s, PPh_3). MS (ESI^+) m/z: 1004.25. Anal. Calcd for $C_{62}H_{50}F_6NO_2P_3Ru$: C, 64.81; H, 4.39; N, 1.22. Found: C, 64.97; H, 4.43; N, 1.26.

Metathesis of Imine. To an NMR tube charged with **1b** (0.045 g, 0.24 mmol) and **8a** (0.036 g, 0.24 mmol) were added $RuCl_3$ (12 mg, 0.046 mmol) and 1.5 mL of $CDCl_3$. The resulting solution was kept at room temperature for 3 days. Four compounds **1a**, **1b**, **8a**, and **10** were observed in the final mixture. The **1b**:**10** ratio of 2.1:1 is determined by the ^{1}H NMR spectrum. Spectroscopic data for **10** from the mixture: ^{1}H NMR (δ, $CDCl_3$): 12.87 (br, 1H, OH); 8.29 (br, 1H, N=CH); 6.74−7.33 (m, 4H, Ph); 3.76 (s, 3H, OCH_3); 3.61 (q, $^3J_{HH}$ = 7.30 Hz, 2H, CH_2); 1.30 (t, $^3J_{HH}$ = 7.30 Hz, 3H, CH_3). MS (EI) m/z: 179.12.

Synthesis of 13b. To a Schlenk flask charged with **1b** (0.026 g, 1.38 mmol), were added $NaBH_4$ (0.11g, 2.89 mmol) and 20 mL of EtOH under nitrogen. The resulting solution was stirred at room temperature overnight. The solution was extracted with a mixture of ether/aqueous NH_4Cl solution, and the organic phase was separated and dried over $MgSO_4$. After filtration, solvent was then removed under reduced pressure to give **13b** (0.23 g, 87% yield). Spectroscopic data for **13b**: ^{1}H NMR (δ, $CDCl_3$): 6.52−6.76 (m, 3H, Ph); 5.34 (br, 2H, OH and NH); 4.02 (s, 2H, Ph−CH_2); 3.72 (s, 3H, OCH_3); 3.43 (d, $^4J_{HH}$ = 2.41 Hz, 2H, CH_2); 2.28 (t, $^4J_{HH}$ = 2.41 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 152.51, 151.57 (Ph−OH, Ph−OCH_3); 122.26, 116.69, 114.60, 113.80 (Ph, =C); 80.15 (C≡); 72.71 (≡CH); 55.66 (OCH_3); 50.73 (Ph−CH_2); 36.44 (CH_2). MS (EI) m/z: 191.11

Synthesis of 15. To a Schlenk flask charged with [Ru]-Cl (0.097 g, 0.13 mmol) and KPF_6 (0.068 g, 0.37 mmol) were added **13b** (0.031 g, 0.16 mmol), PPh_3 (0.18 g, 0.69 mmol), and 10 mL of CH_2Cl_2 under nitrogen. After 6 days the resulting solution was filtered through Celite to remove the insoluble precipitates, then the volatiles were removed under vacuum, and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by adding 70 mL of Et_2O. Precipitates thus formed were collected and dried under vacuum to give yellow powder **15** (0.095 g, 72% yield). Spectroscopic data for **15**: ^{1}H NMR (δ, $CDCl_3$): 8.21 (m, 1H, Cα−H); 6.96−7.77 (m, H, Ph); 5.24 (m, 1H, Cβ−H); 4.06 (s, 5H, Cp); 3.83 (dd, $^2J_{HP}$ = 12.59 Hz, $^3J_{HH}$ = 6.35 Hz, 2H, CH_2). ^{13}C NMR (δ, $CDCl_3$): 165.27 (m, Cα); 138.75 (m, Cβ); 139.14−138.34 (PPh_3, P−C); 134.82−118.56 (PPh_3, =C); 85.60 (Cp); 33.25 (d, $^2J_{CP}$ = 42.4 Hz, CH_2). ^{31}P NMR (δ, $CDCl_3$): 52.64 (d, J_{PP} = 4.3 Hz, 2P, 2Ru−PPh3); 14.93 (t, J_{PP} = 4.3 Hz, 1P, PPh3). MS (ESI^+) m/z: 993.25. Anal. Calcd for $C_{62}H_{54}F_6P_4Ru$: C, 65.43; H, 4.78. Found: C, 65.80; H, 4.97.

Single-Crystal X-ray Diffraction Analyses. Single crystals of **3a′** suitable for X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.25 × 0.20 × 0.15 mm^3 was glued to a

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glass fiber and mounted on a CCD diffractometer. The diffraction data were collected using 3-Kw sealed-tube Mo K_α radiation (T = 295 K). Exposure time was 5 s per frame. SADABS[33] (area detector absorption) absorption correction was applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL[34] program. Hydrogen atoms were placed geometrically using riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file giving crystallographic data of compound **3a′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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