Reactions of Ruthenium Acetylide and Vinylidene Complexes Containing a 2-Pyridyl Group

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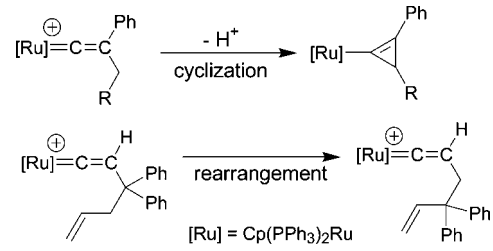
Two ruthenium acetylide complexes [Ru]C≡C(C_5H_3RN) (**1a**, R = H; **1b**, R = Me; [Ru] = Cp(PPh_3)$_2$Ru) containing 2-pyridyl groups are prepared and their chemical reactivities are explored. Protonation of the ruthenium acetylide complex **1a** with HBF_4 takes place at both the nitrogen atom and Cβ, giving the dicationic pyridiniumvinylidene complex {[Ru]=C=C(H)(C_5H_4NH)}(BF_4)$_2$ (**3a**). Addition of BF_3 to **1a** yields the Lewis acid/base adduct [Ru]C≡C($C_5H_4N\rightarrow BF_3$) (**4a**). In the presence of moisture both complexes **3a** and **4a** in solution transform into the cationic heterocyclic carbene complex {[Ru]=C(O)CH_2-($C_5H_4N\rightarrow BF_2$)}BF_4 (**6a**), for which the structure is confirmed by X-ray structure determination. The formation of **6a** involves the intermediate {[Ru]=C=C(H)($C_5H_4N\rightarrow BF_2OH$)}$BF_4$ (**5a**), characterized by spectroscopic methods. DFT calculations show that the Gibbs free energy change of the exothermic transformation of **5a** to **6a** is −20.59 kcal/mol. N-Alkylation reactions of **1b** with two alkyl bromides $BrCH_2R'$ (R′ = CH=$CHCO_2$Me and CO_2Me) yield two pyridiniumacetylide complexes {[Ru]C≡C($C_5H_3MeNCH_2R'$)}Br (**7b**, R′ = CH=$CHCO_2$Me; **7c**, R′ = CO_2Me, respectively). Complex **7c**, characterized by X-ray structure determination, undergoes further protonation to give the pyridiniumvinylidene complex {[Ru]=C=C(H)($C_5H_4NCH_2R'$)$^{2+}$ (**8c**). Interestingly, the acetylide complex **7b** undergoes a C−C coupling reaction of the acetylic Cβ with the C=C double bond to give the vinylidene complex **9b**, characterized also by X-ray structure determination.

Introduction

During the past decade, chemistry of transition metal complexes containing vinylidene ligands has attracted a great deal of attention because of their occurrence as key intermediates in many stoichiometric and catalytic transformations of organic molecules.[1] Since the method for the preparation of cationic bisubstituted vinylidene complexes via electrophilic attack of metal acetylides was established, the diversity and applications of these metal vinylidene complexes have further expanded. Previously we have shown that ruthenium vinylidene complexes [Ru]=C=C(Ph)CH_2R^+ ([Ru] = Cp(PPh_3)$_2$Ru) bearing an electron-withdrawing group R attached at Cγ undergo intramolecular cyclization under mild basic conditions.[2] On the basis of this approach, various mono- and multinuclear neutral metal cyclopropenyl or furyl complexes have been prepared. Recently, serendipitous results showed that the ruthenium vinylidene complex with a pendant terminal vinyl group exhibits excellent metathesis reactivity of C=C double bonds so that skeletal rearrangement and cyclization are observed.[3]



Rich chemistry has been demonstrated for molecules containing various pyridyl moieties. For example, *ortho*-substituted pyridyl groups usually act as building blocks in templating metal centers by means of coordination, which leads to supramolecules.[4] Very recently the metal-mediated C−H activation was reported to cause formation of pyridine/quinolidene *ortho*-carbene complexes.[5] *ortho*-Substitution of an ethynyl group on pyridine has been under investigation in the development of nonlinear optics.[6] The coordination ability of the N atom of platinum acetylide complexes with 2-pyridyl functional groups has also been investigated.[4d,e] We therefore set a goal to study

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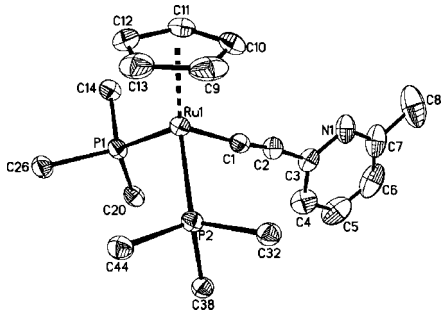


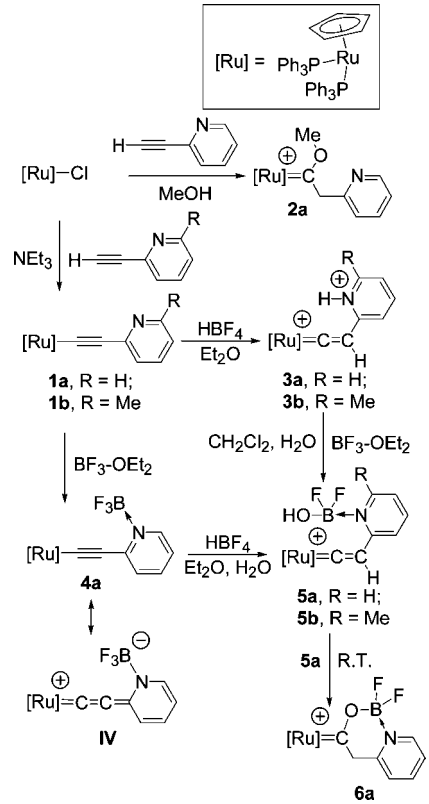
Figure 1. ORTEP drawing (30% thermal ellipsoid) of **1b** with phenyl groups on phosphine ligands (except *ipso* carbon) and hydrogen atoms eliminated for clarity. Selected bond distances (Å) and bond angles (deg): Ru1−C1, 2.007(3); C1−C2, 1.216(4); C2−C3, 1.422(4); Ru1−C1−C2, 174.7(2); C1−C2−C3, 172.5(3).

the chemistry of ruthenium acetylide and vinylidene complexes containing *ortho*-pyridyl groups. Herein we report the synthesis and reactivities of these acetylide and vinylidene complexes toward protic acids, Lewis acids, and electrophilic alkyl groups.

Results and Discussion

Preparation and Reactions of Ruthenium Pyridylacetylides. A convenient method was utilized to prepare a ruthenium pyridylacetylide complex from ruthenium chloride. Thus the reaction of [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$) with 2-ethynylpyridine in a mixed solvent ($CHCl_3$/MeOH/NEt_3) at room temperature exclusively gave the pyridylacetylide complex **1a** as a yellow powder in good yield. Complex **1a** shows a ^{31}P resonance at δ 51.0 and Cα resonance at δ 124.30 with J_{CP} = 25.8 Hz in the ^{31}P and ^{13}C NMR spectra, respectively. These are comparable with those of analogous phenylacetylide derivatives.[7a,b] The mass spectrum of **1a** shows parent peaks at m/z = 794.0 for $M^+ + 1$. Similarly the reaction of [Ru]-Cl with 6-methyl-2-ethynylpyridine yielded complex **1b**, which has been characterized by single-crystal X-ray diffraction analysis. The molecular structure of complex **1b** with selected bond lengths and bond angles is shown in Figure 1. The coordination sphere surrounding the ruthenium center of **1b** adopts a three-legged piano-stool structure with a typical acetylide skeleton. The methyl and N atom in the pyridyl group face the same direction as the bonding of Ru toward the Cp ring centroid. The Ru−C(1) distance of 2.007(3) Å is a typical Ru−C single bond and is comparable to the corresponding one in [Ru]C≡CPh (**I**, 2.017(5) Å)[7a] and [Ru]C≡C(C_6H_4-*p*-NO_2) (**II**, 1.994(5) Å).[7b] The C(1)−C(2) distance of 1.216(4) Å, which is a C≡C triple bond, is also comparable to that in **I** (1.214(7) Å) and the nickel analogue Cp(PPh_3)NiC≡C(C_5H_3N-*p*-NO_2) (**III**, 1.215(7) Å),[7b] but is slightly longer than that in **II** (1.202(8) Å).

Scheme 1



On the other hand, when the reaction was carried out in a mixed solvent of CH_2Cl_2/MeOH at room temperature, the 2-picolylmethoxycarbene complex **2a** was obtained (Scheme 1). This result is different from that in the ruthenium 4-pyridylacetylide complex reported by Lin et al.[8a] The cationic complex **2a** exhibits spectroscopic features different from those of **1a**. The ^{13}C NMR spectrum shows a characteristic carbenoic triplet resonance of Cα at δ 306.0 with J_{CP} = 12.8 Hz. The ^{31}P NMR spectrum of **2a** shows a singlet at δ 46.6. Furthermore the ^{31}P NMR results indicate that during the reaction a singlet resonance at δ 42.0 appeared and diminished as **2a** gradually formed. This intermediate is proposed to be the pyridylvinylidene complex $\{[Ru]{=}C{=}C(H)(C_5H_4N)\}^+$. Because of its instability in the presence of alcohol and in the absence of NEt_3, the intermediate complex will spontaneously undergo nucleophilic addition to yield the cationic methoxycarbene complex. The electron-withdrawing *ortho*-pyridine substituent seems to play a role in this reaction. Similar reactions involving various vinylidenes of the type $Cp(PR_3)_2Ru{=}C{=}CRH$ can lead to alkoxycarbene in the presence of alcohol, albeit at elevated temperature.[9] This phenomenon prompted us to study the reactivities of the pyridine moiety implanted in the ruthenium acetylide backbone. The reactions of complex **1** toward protic acids, Lewis acids, and a

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few alkyl halides are thus investigated. Their further transformations into vinylidene and heterocyclic carbene complexes are also studied.

Although many reports deal with the coordination ability of the N atom of the transition metal 2-pyridylacetylides,[4d,e] their interaction with protic acids and Lewis acids have not been thoroughly described. Furnished with acetylide and pyridyl groups both complexes **1a** and **1b** are expected to undergo electrophilic addition. Treatment of complex **1a** with excess HBF_4 in diethyl ether produces the bright orange pyridiniumvinylidene complex $\{[Ru]{=}C{=}C(H)(C_5H_4NH)\}(BF_4)_2$ (**3a**) in high yield (Scheme 1). The ^{31}P NMR spectrum of **3a** shows a singlet resonance at δ 37.3. The ^1H NMR spectrum shows the characteristic broad proton resonance of N*H* at δ 12.7 and the relatively downfield singlet resonance of the vinylidene proton at Cβ at δ 5.90. This reveals that both the pyridyl group and Cβ are protonated; thus the basicity of the pyridine moiety is not diminished in forming a complex of this system.[8] Addition of D_2O causes the exchange of the pyridinium and vinylidene protons of **3a** as shown in the ^1H NMR spectrum. Surprisingly, this two-proton adduct is sufficiently acidic and can even protonate D_2O to effectively restore **1a** if excess D_2O was added (observed in nearly 100% NMR yield). In a similar vein, protonation of complex **1b** also gives the dicationic complex $\{[Ru]{=}C{=}C(H)(C_5H_3MeNH)\}(BF_4)_2$ (**3b**).

On the other hand, a Lewis acid/base interaction was observed only at the pyridyl group, and the BF_3 adduct of the pyridiniumacetylide complex $[Ru]C{\equiv}C(C_5H_4N{\rightarrow}BF_3)$ (**4a**) was obtained when complex **1a** was treated with excess $BF_3{-}OEt_2$ (Scheme 1). Binding of the BF_3 group is indicated by the singlet resonance at δ −152.2 in the ^{19}F NMR spectrum, which is similar to that of the structurally similar BF_4^- group at δ −152.0. The ^{31}P NMR spectrum of **4a** shows a singlet resonance at δ 50.9, which is comparable to that of BF_3-free **1a** at δ 51.0. The ^{13}C NMR triplet resonance of Cα at δ 173.98 with J_{CP} = 23.0 Hz is closer to the carbene region (generally at ca. δ 200) than that of complex **1a** (δ 124.30 with J_{CP} = 25.8 Hz), which is attributed to the partial contribution of the allenylidene structure (**IV**) in the ground-state geometry of complex **4a** (Scheme 1).[8c]

Complex **4a** is air and moisture sensitive and in chloroform can be cleanly transformed to **5a** in the presence of moisture. In addition, treatment of **3a** or **1a** with an excess amount of $BF_3{-}OEt_2$ in the presence of moisture also affords complex **5a** (Scheme 1). The reaction of complex **4a** with HBF_4 in the presence of H_2O at room temperature also gives **5a** as a brown solid in good yield. Complex **5a** is believed to be the cationic pyridiniumvinylidene complex $\{[Ru]{=}C{=}C(H)(C_5H_4N{\rightarrow}BF_2OH)\}BF_4$ with a BF_2OH group on the pyridine N atom. The ^1H NMR spectrum of **5a** shows a singlet resonance at δ 5.90 and a broad peak at δ 12.33 assigned to the vinylidene β-proton and the OH group, respectively. The vinylidene backbone of **5a** is reflected by the ^{13}C NMR resonances of α- and β-carbons at δ 344.56 and 112.46, respectively. A 2D NMR $^{13}C{-}^1H$ HSQC experiment also confirms the vinylidene group by displaying a cross-peak between δ_H of 5.90 and δ_C of 112.46.

Interestingly, in $CDCl_3$ solution, complex **5a** further transforms into the new complex **6a** in 4 days at room temperature in ca. 60% yield (Scheme 1). The cationic complex **6a** contains a heterocyclic carbene ligand with a boron atom in the ring.[10] The carbenoic triplet resonance of **6a** at δ_C 292.65 with J_{CP} = 12.7 Hz shifts slightly upfield than the corresponding Cα resonance of the methoxy derivative **2a** at δ 306.0. The IR spectrum of **6a** reveals an absorption band at ν = 1350.5 cm^{-1}, indicating the presence of a C−O single bond skeleton.[10g] Complex **6a** has been characterized by X-ray structural determination. Figure 2 displays an ORTEP drawing and selected bond lengths and angles of **6a**. The Ru−C(1) bond distance of 1.944(3) Å is a typical Ru=C carbenoic double bond but is slightly longer than that of the methoxy derivative $\{[Ru]{=}C(OMe)Me\}^+$ (**V**, 1.931(9) Å),[10e] whereas the C(1)−O(1) bond length of 1.308(4) Å is shorter than that in complex **V** (1.321(9) Å). The partial delocalization of the cationic charge around Ru−C(1)−O(1) bonds can be rationalized by the much upfield-shifted Cα resonance of **6a** in the ^{13}C spectrum. The O(1)−B(1) bond distance of 1.484(5) Å is slightly shorter than those in iron complexes[10d] and in rhodium complexes.[10a] For comparison, in a trinuclear Ru cluster the bond distances between B−O, O−C, and average C−Ru[10b] are 1.508(5), 1.262(4), and 2.004 Å, respectively.

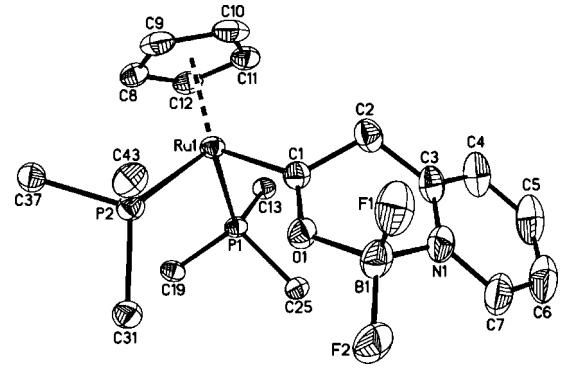

Figure 2. ORTEP drawing (30% thermal ellipsoid) of **6a** with phenyl groups on the phosphine ligands (except the *ipso* carbon) and hydrogen atoms eliminated for clarity. Selected bond distances (Å) and bond angles (deg): Ru1−C1, 1.944(3); C1−C2, 1.520(4); C2−C3, 1.484(5); C1−O1, 1.308(4); O1−B1, 1.484(5); B1−F1, 1.369; B1−F2, 1.352; Ru1−C1−C2, 123.4(2); C1−C2−C3, 113.7(3); Ru1−C1−O1, 124.7(2); C2−C1−O1, 111.8(3); C1−O1−B1, 125.4(3); O1−B1−N1, 105.9(3); F1−B1−F2, 112.8(3).

In addition to complex **4a**, the pyridiniumvinylidene complex **3a** with two BF_4^- counteranions in solution also yielded **6a** in the presence of moisture. Upon NMR monitoring of a sealed tube containing a $CDCl_3$ solution of **3a** under nitrogen, complex **6a**, [Ru]-CO^+, and triphenylphosphine oxide were observed in a 2:1:1 ratio based on ^{31}P NMR integration after 5 days at room temperature. The ^{31}P NMR resonances of [Ru]-CO^+ and $O{=}PPh_3$ appear at δ 42.5 and 30.0, respectively.[11] The ^1H and ^{13}C signals of the Cp group at δ 5.00 and 91.4, respectively, confirm the formation of [Ru]-CO^+. Perhaps trace moisture in the solution caused decomposition of the BF_4^- anion of complex **3a** to form BF_3,[12] which then reacted with **3a** to result in the formation of **5a** and finally **6a**. The methyl derivative **1b** sequentially gave complexes **3b** and **5b**. However, complex **5b**

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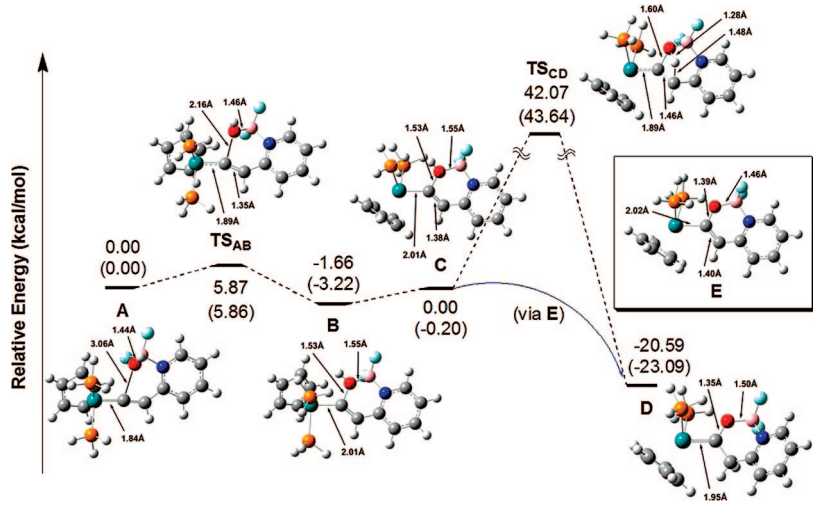

Figure 3. Optimized geometries and relative Gibbs free energies (kcal/mol) for the conversion of $\{Cp(PH_3)_2Ru{=}C{=}C(H)(C_5H_4N{\rightarrow}BF_2OH)\}^+$ (**A**) to heterocyclic carbene $\{Cp(PH_3)_2Ru{=}CCH_2(C_5H_4N{\rightarrow}BF_2O)\}^+$ (**D**). Values in parentheses are relative electronic energies.

is relatively more stable toward cyclization in solution. Attempts to promote cyclization of **5b** led to decomposition.

Given that the aforementioned transformations require the existence of moisture (either from the air or the solvent), a deuterium labeling experiment was carried out. To the complex **4a** was added an equivalent amount of HBF_4 in the presence of excess D_2O. The ^{31}P NMR spectrum of the product shows the resonance at δ 46.9 of **6a**, while the disappearance of the methylene resonance at δ 5.15 in the ^1H NMR spectrum reveals the doubly deuterated complex (**6a-*d*$_2$**). As described below, because the protonation of a pyridiniumacetylide complex to give a pyridiniumvinylidene complex is easily achieved, we believe that the protonation of **4a** here involves the formation of the pyridiniumvinylidene intermediate. Interestingly, no alkoxycarbene product from the addition at Cα was observed during the reaction. This probably indicates that the pyridyl-BF_3 group is more reactive than the vinylidene group so that the substitution of F by OH proceeds faster than the nucleophilic attack at Cα. When the 2-pyridyl group is bound to a less electron-deficient BH_3 group, no substitution was observed. Namely, by treating the pyridylacetylide complex **1a** with excess BH_3-THF we prepared the pyridylacetylide complex $[Ru]C{\equiv}C(C_5H_4N{\rightarrow}BH_3)$ (**4c**), which is sufficiently stable at ambient temperature even in solution for at least 1 week.[13]

The mechanism for the formation of **6a** is thus suggested as followed. Treatment of **4a** with HBF_4 immediately affords the vinylidene intermediate $\{[Ru]{=}C{=}C(H)(C_5H_4N{\rightarrow}BF_3)\}^+$ (**VI**). Substituting one fluoride of the pyridinium-BF_3 group by a hydroxyl group subsequently gives the OH-substituted pyridylvinylidene **5a** with the formation of a B−OH bond.[14] Then two possible pathways were considered, namely, intramolecular nucleophilic addition of the OH group onto the vinylidene Cα and 1,3-proton shift and direct nucleophilic addition of the O−H group onto the vinylidene C$\alpha{=}$Cβ bond, affording the final product **6a**.[15]

According to this mechanism, it can be visualized that complex **6** can be prepared directly via a one-pot procedure from [Ru]-Cl. Actually, in chloroform solution, 10 molar equiv of $BF_3{-}OEt_2$ and 2-ethynylpyridine were first mixed for 10 min followed by the addition of [Ru]-Cl. The resulting solution was stirred for 3 days at room temperature. Workup of the solution afforded complex **6a** in high yield. However, without an excess amount of BF_3, only [Ru]-Cl was obtained. Excess BF_3 probably induces dissociation of the chloride ligand and initiates the reaction. The reaction of [Ru]-Cl with 2-ethynylpyridine in the presence of CH_3I leads to [Ru]-I only.

Theoretical Calculations. DFT calculations at the B3LYP/LanL2DZ[16] level by Gaussian 03 were performed to study the reaction of **5** to **6** in an effort to distinguish two pathways for the addition of OH to the C=C bond.[17] The phenyl groups of the PPh_3 were replaced by hydrogen in our study. Figure 3 displays the optimized geometries and corresponding Gibbs free energy changes of the conversion of **A** to **D**, modeling the transformation of complex **5** to **6**. The Ru−C bond of 1.95 Å, C−O bond of 1.35 Å, and O−B bond of 1.50 Å of the optimized structure reasonably match the experimental result obtained from

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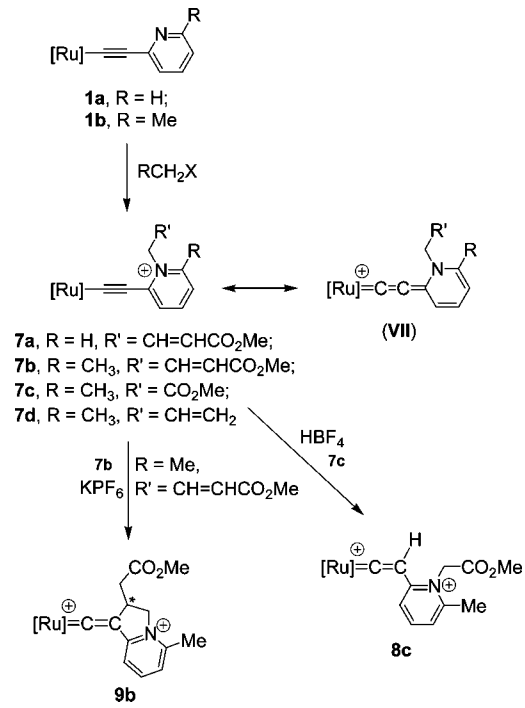
the crystal structure of complex **6a** (1.944(3), 1.308(4), and 1.484(5) Å, respectively). In addition, the Ru−C−O bond angle of 121.4° and C−O−B bond angle of 124.6° also resemble those of **6a** (123.4(2)° and 125.4(3)°, respectively). NBO analysis[18] of **D**, the modeling complex of **6a**, reveals that the Ru−C and C−O bond orders are 1.46 and 1.95, respectively, indicating partial delocalization of π-electrons and positive charge at the carbene moiety. For compound **A**, the modeling complex of **5a**, the LUMO and LUMO+1 orbitals are largely localized at Cα, showing that an electrophilic attack might take place there (see Figure S1 in the Supporting Information). Consequently, the approach of the hydroxyl group of BF_2OH to Cα in **A** caused the formation of the intermediate **B**, which is lower in Gibbs free energy than **A** by −1.66 kcal/mol. **B** is formally an intramolecular cyclization product of **A**, where the oxygen atom is bound to boron, Cα, and a proton. The transition state ($\mathbf{TS_{AB}}$) is 5.87 kcal/mol higher in free energy than **A**. Following the reaction coordinate, the conversion of **B** to **D** first requires the rotation of the Ru−C bond to become the rotamer **C**, which is higher in free energy than **B** by 1.66 kcal/mol. This can be rationalized by the metal−carbon π-bonding resulted from different preferred orbital overlap of metal d_π-orbital with the carbene and vinylidene p-orbital.[19] The conversion of **C** to **D** is exothermic by −20.59 kcal/mol. However, this conversion via the transition state $\mathbf{TS_{CD}}$ has an activation free energy of 42.07 kcal/mol. Since experimentally we have observed that complex **5** spontaneously undergoes isomerization to give **6** at room temperature in solution, the pathway **C** → $\mathbf{TS_{CD}}$ → **D** is thus unfavorable. That is, the direct O−H addition is less likely. Alternatively, another pathway via a stepwise deprotonation−protonation process through the intermediate **E** is suggested. Although we cannot accurately calculate the relative energy of **E** in this system, this **C** → **E** → **D** pathway is much preferred due to the fact that the spontaneous transformation of **5** to **6** often occurs in acidic conditions, i.e., in the presence of an excess amount of HBF_4 during the synthesis of **6**. The overall conversion of **A** to **D** is exothermic by a free energy of −20.59 kcal/mol, which reasonably matches our experimental observation.

Alkylation Reactions. Reactions of **1** with various alkyl halides are also studied. At room temperature, treatment of **1a** with 4-bromomethylcrotonate produces the air-stable golden-yellow product **7a** in high yield. The alkylation takes place at the nitrogen atom. Similarly, facile N-alkylation is observed in the case of **1b**. Treatment of **1b** with functionalized alkyl halides also generates **7b**, **7c**, and **7d** in high yield (Scheme 2). Complexes **7a**−**7d** were characterized by ^1H, ^{31}P, and ^{13}C NMR and mass spectra. 2D NMR HMBC and HSQC techniques were also applied to confirm the connectivity between the pyridiyl and the alkylated group. For example, the ^{13}C NMR spectrum of **7c** shows a triplet resonance assigned to the Ru−Cα carbon at δ 181.8 with J_{CP} = 22.3 Hz. The ^1H NMR spectrum of **7c** displays a singlet downfield shift resonance of the methylene protons of the ester group at δ 5.96. Of the most important is the $^1H-^{13}C$ HMBC spectrum, which shows long-range couplings between the methylene protons at δ 5.96 of the ester group to both Cβ at δ 114.9 and one of the pyridyl carbons at δ 153.7, but no cross-peak is observed with the Cα resonance at δ 181.8. This demonstrates that the methylene protons of the ester group are not in the vicinity of Cα.

Scheme 2



The molecular structure of complex **7c** established by single-crystal X-ray diffraction analysis is shown in Figure 4 with selected bond lengths and bond angles. Bonding of the pyridinium N−C bond faces the direction parallel to that of the Ru center to the Cp centroid. The Ru−C(1) single bond distance (1.977(4) Å) is slightly shorter than that in complex **1b** (2.007(3) Å), whereas the C(1)−C(2) triple bond distance (1.219(5) Å) is slightly longer than that in **1b** (1.216(4) Å) but is shorter that in the chromium allenylidene complex.[8c] The Ru−C1−C2 bond angle is approximately the same as that in **1b** (174.4(7)°). This fact might indicate partial contribution of the allenylidene resonance structure **VII** shown in Scheme 2 in the solid state. The ^{13}C resonance of Cα of **7d** at δ 181.8 compared to that of **1b** at δ 117.6 provides further support.

The fact that complexes **1a** and **1b** underwent addition exclusively at the N atom rather than at Cβ might stem from the intrinsic reactivity of the pyridyl group. A similar event was observed in the alkylation reaction of tungsten and chromium pyridylacetylide and indolylacetylide complexes to give alle-

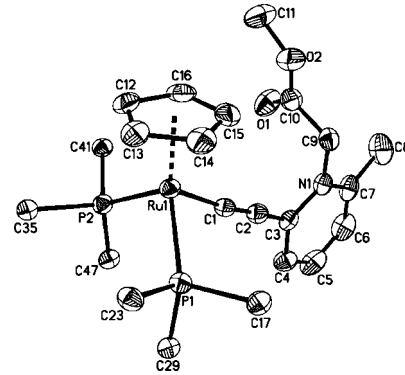


Figure 4. ORTEP drawing (30% thermal ellipsoid) of **7c** with phenyl groups on the phosphine ligands (except the *ipso* carbon), hydrogen atoms and the anion eliminated for clarity. Selected bond distances (Å) and bond angles (deg): Ru1−C1 1.977(4), C1−C2 1.219(5), C2−C3 1.400(5), N1−C9 1.458(5), Ru1−C1−C2 174.7(2), C1−C2−C3 174.1(3).

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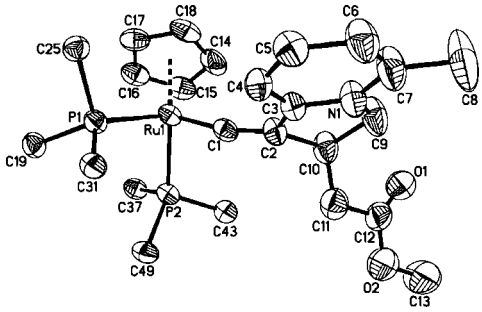

Figure 5. ORTEP drawing (30% thermal ellipsoid) of **9b** with phenyl groups of PPh_3 ligands (except *ipso* carbon atoms), hydrogen atoms and the anion are eliminated for clarity. Selected bond distances (Å) and bond angles (deg): Ru1−C1, 1.820(6); C1−C2, 1.330(9); C2−C3, 1.447(9); C3−N1, 1.333(8); N1−C9, 1.473(9); Ru1−P1, 2.3715(16); Ru1−P2, 2.3560(16); Ru1−C1−C2, 166.0(5); C1−C2−C3, 126.3(6); C3−C2−C10, 108.3(5); P1−Ru1−P2, 99.93(5); C1−Ru1−P1, 97.94(17); C1−Ru1−P2, 94.01(19).

nylidene complexes.[8c] Also in ruthenium 4-pyridylacetylide complexes, the dangling pyridine was protonated, methylated, or ligated to tungsten carbonyl fragments to give various pyridiniumacetylide complexes.[8a] Interestingly, when the alkylation reaction of **1b** was carried out in methanol at 60 °C, no reaction was observed. On the other hand, protonation took place when strong acid-like HBF_4 was used. Treatment of **7a**, **7b**, **7c**, and **7d** with excess HBF_4 in CH_2Cl_2 at 0 °C produced various dicationic pyridiniumvinylidene complexes **8**. However, among these spectroscopically observed pyridiniumvinylidene complexes only complex **8c**, with the CH_2CO_2Me group, was isolated. The ^{31}P resonance of phosphorus ligands and ^1H resonance of the Cp group of complex **8c** resemble that of complex **3**. Other protonated products could not be isolated, since the β-hydrogen of the product is relatively acidic, and these revert rapidly to pyridiniumacetylides in the presence of a weak base such as trace amounts of water in the solvent.[20]

Surprisingly, addition of KPF_6 to an acidic solution of **7b** at room temperature resulted in the formation of the brown dicationic ruthenium vinylidene complex **9b** (Scheme 2). A cyclization by the formation of a C−C bond takes place between Cβ of the vinylidene ligand and one of the olefinic carbons, leading to a heterocyclic fused-ring ligand. The ^{31}P NMR spectrum of **9b** displays a set of doublets of doublets at δ 41.3 and 39.6 with $J_{PP} = 24.6$ Hz due to the presence of a stereogenic center. The ^1H NMR spectrum shows this methine resonance at δ 4.72, while the ^{13}C NMR spectrum displays a resonance of this carbon at δ 32.62. The two methylene groups both split into multiplets in the ^1H NMR spectrum (δ 2.14 and 2.42 for NCH_2; δ 2.38 and 2.42 for the other CH_2) because of the adjacent stereogenic center. Finally, the characteristic α-carbon resonance at δ_C of 343.42 and the downfield-shifted Cp resonance at δ_H of 5.77 and δ_C of 97.55 indicate the presence of a vinylidene structure. 2D NMR COSY, HSQC, and HMBC techniques are also applied in the structure determination of **9b**. The HSQC spectrum clearly displays C−H cross-peaks of the two methylene groups, and cross-peaks in the HMBC between the methine and two methylene groups clearly indicate their connectivity. The structure of **9b** is confirmed by X-ray diffraction analysis. Figure 5 shows an ORTEP drawing and selected bond lengths and angles of **9b**. The Ru(1)−C(1) bond length of 1.820(6) Å and the C(1)−C(2) bond length of 1.330(9) Å reveal a typical vinylidene skeleton. The Ru(1)−C(1)−C(2) bond angle of 166.0(5)° is bent from linear arrangement, which is possibly due to the steric effect between the CO_2Me group and two PPh_3 ligands.[2h] Attempts to promote a similar coupling reaction for complex **7d** failed to yield the desired product, indicating the requirement of the activating ester group in this C−C bond forming reaction.

On the basis of the aforementioned protonation reactions of pyridylacetylides **1** and pyridiniumacetylides **7**, it is reasonable to assume that formation of **9b** from **7b** proceeds via an addition of the activated olefin to Cβ, leading to C−C bond formation generating the Ru=C=C vinylidene moiety. Addition of a proton possibly from acid or moisture at the other olefinic carbon atom then gave the final product. This C−C coupling reaction occurs between the internal carbon of the allylic moiety and the acetylide Cβ without cleavage of the C−N bond. Reactions involving coupling of the allylic terminal carbon with transition metal acetylide complexes have been reported in the literature.[21] Preparations of transition metal vinylidene complexes with monosubstituted Cβ are well known in the literature. Yet preparation of vinylidenes with quarternary Cβ directly via highly substituted alkyl halides[5a,b] were only scarcely demonstrated.[22] The established alkylating protocol for metal acetylides provided by Bruce[11,23] in reactions with alkyl halides is limited to primary ones. To our knowledge, these highly branched ruthenium pyridiniumvinylidenes are unprecedented. Our observation in the formation of **9b** unequivocally serves as an alternative approach to prepare Cβ,Cβ-disubstituted vinylidenes with a stereogenic center simultaneously generated at Cγ.

Conclusion

Protonation of the two ruthenium pyridylacetylide complexes **1a** and **1b** gave pyridiniumvinylidene complexes **3a** and **3b**, respectively. Additions of BF_3 to **1a** take place at the N atom of the pyridyl group, yielding **4a**. This reaction is rationalized by the Lewis acid/base interaction. Subsequent protonation of **4a** in the presence of moisture caused substitution of one F in the BF_3 bonded to the 2-pyridyl group of **4a** by an OH group, giving the vinylidene complex **5a**. This is followed by a spontaneous cyclization reaction, resulting in the formation of the cationic carbene complex **6a**. This spontaneous transformation of **5a** to **6a** is further confirmed by DFT calculations using model complexes. Analogous vinylidene complex **5b** could be obtained from **1b**. However, the cyclization process is not observed in the case of complex **5b**. Alkylation of **1a** and **1b** also took place preferentially at the N atom of the pyridyl group, yielding the pyridiniumacetylide complexes **7**, which could be protonated to give pyridiniumvinylidene complexes **8** detected

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spectroscopically. For the pyridiniumacetylide complex **7d**, containing an unsaturated functional group $CH_2CH{=}CHCO_2Me$ on the pyridinium moiety, the C−C coupling of the acetylide Cβ with the C=C double bond yielded **9b**.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, glovebox, and standard Schlenk techniques unless mentioned otherwise. Hexanes and CH_2Cl_2 were distilled from CaH_2, diethyl ether and THF from sodium benzophenone ketyl, and methanol from Mg/I_2. All other solvents were of reagent grade and were used as received. NMR spectra were recorded on Bruker Avance-400 and DMX-500 FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvents as a standard ($CDCl_3$, δ 7.24; d_6-acetone, δ 2.04). FAB mass spectra were recorded using a JEOL SX-102A spectrometer using 3-nitrobenzyl alcohol (NBA) as the matrix. Infrared spectra were recorded on a Nicolet-MAGNA-550 spectrometer. X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at the National Taiwan University. All reagents were obtained from commercial suppliers. $RuCl_3 \cdot xH_2O$ was purchased from Strem Chemicals. $Cp(PPh_3)_2RuCl$[24] was prepared following the method reported in the literature.

Synthesis of [Ru]C≡C(C_5H_3RN) (R = H, 1a; R = CH_3, 1b). In a Schlenk flask containing a mixed solvent of $CHCl_3$/MeOH/NEt_3 (15:15:1 mL) were added at ambient temperature [Ru]Cl (1.03 g, 1.42 mmol) and 2-ethynyl-6-methylpyridine (406 mg, 3.1 mmol), and the resulting solution was stirred for 18 h. After that the volatiles were removed to obtain an oily product, which was redissolved in 10 mL of CH_2Cl_2 followed by filtration via a small pack of Celite into 60 mL of methanol. The precipitate thus formed was collected by filtration and dried under vacuum to afford **1b** as a yellow powder (824 mg, 72.0% yield). The rest of the methanol solution was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2/cold pentane to bring about more desired product **1b** as a brown microcrystal, 34.09 mg (yield ca. 18.3%). Anal. (%) Calcd for $C_{49}H_{41}NP_2Ru$: C, 72.94; H, 5.12; N, 1.74. Found: C, 72.78; H, 5.10; N, 1.82. FAB mass (*m*/*z*): 807.3 (M^+), 546.1 ($M^+ - PPh_3$), 468.1, 429.1 ($[Cp(PPh_3)Ru]^+$). IR (KBr, cm^{-1}): ν 2064.6 (C≡C). ^{1}H NMR ($CDCl_3$): δ 7.46−7.04 (Ph and Py), 6.70 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Py), 6.43 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Py), 4.35 (s, 5H, Cp), 2.50 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 132.86, 131.98, 131.22, 128.98 (Py), 138.66−127.35 (Ph), 123.38 (Py), 117.57 (RuC*C*), 115.38 (t, $^2J_{CP}$ = 5.2 Hz, Ru*C*), 86.02 (Cp), 23.39 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 51.2 (s).

Complex **1a** was prepared in 73% yield from 2-ethynylpyridine following the same procedure as that of **1b**. Spectroscopic data for **1a**: Anal. (%) Calcd for $C_{48}H_{39}NP_2Ru$: C, 72.71; H, 4.96; N, 1.77. Found: C, 71.88; H, 4.91; N, 1.63. ESI mass (*m*/*z*): 794.0 (M^+ + 1). ^{1}H NMR ($CDCl_3$): δ 8.39 (d, $^3J_{HH}$ = 7.6 Hz, Py), 7.30 (t, $^3J_{HH}$ = 7.6 Hz, Py), 7.43−7.05 (Ph), 6.83 (t, $^3J_{HH}$ = 7.6 Hz, Py), 6.64 (d, $^3J_{HH}$ = 7.6 Hz, Py), 4.36 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 149.03, 147.81 (Py), 139.11−127.01 (Ph), 125.51 (Py), 124.30 (t, $^2J_{CP}$ = 25.8 Hz, Ru*C*), 117.73 (Py), 116.52 (RuC*C*), 85.65 (Cp). ^{31}P NMR ($CDCl_3$): δ 51.0.

Synthesis of {[Ru]=C(OMe)CH_2(C_5H_4N)}PF_6 (2a). To a Schlenk flask charged with [Ru]Cl (254.2 mg, 0.35 mmol) and $NaPF_6$ (56.0 mg, 0.47 mmol) were added 2-ethynylpyridine (0.5 mL, 0.5 mmol) and 35 mL of mixed solvent (CH_2Cl_2/methanol, 3:4, v/v) under nitrogen. The resulting solution was stirred at room temperature for 13 h. After that, volatiles were removed and the solid residue was extracted with 5 mL of CH_2Cl_2 followed by reprecipitation with 60 mL of diethyl ether. The precipitate thus formed was collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as a brown powder and was identified as complex **2a** (255.7 mg, 75% yield). Anal. (%) Calcd for $C_{49}H_{44}F_6NOP_3Ru$: C, 60.62; H, 4.57; N, 1.44. Found: C, 60.71; H, 4.71; N, 1.32. FAB mass (*m*/*z*): 826.3 (M^+), 719.2, 564.1 ($M^+ - PPh_3$), 429.1 ($[Cp(PPh_3)Ru]^+$). IR (KBr, cm^{-1}): ν 1588.9 (Ru=C), 1263.7 (br, C−O). ^{1}H NMR ($CDCl_3$): δ 8.26 (d, $^3J_{HH}$ = 6.8 Hz,1H, Py), 7,90 (t, $^3J_{HH}$ = 6.8 Hz, 1H, Py), 7.65 (t, $^3J_{HH}$ = 6.8 Hz, 1H, Py), 7.96−6.38 (Ph and Py), 4.99 (s, 2H, C*H*$_2$), 4.78 (s, 5H, Cp), 3.38 (s, 3H, OC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 306.0 (t, $^2J_{CP}$ = 12.8 Hz, Ru*C*), 154.77, 148.91, 137.82 (Py) 136.16−127.62 (Ph), 124.49, 122.30 (Py), 91.84 (s, Cp), 64.05 (s, *C*H$_2$), 62.23 (s, OCH$_3$). ^{31}P NMR ($CDCl_3$): δ 46.6.

Protonation of 1a and 1b. Complex **1a** (182.2 mg, 0.23 mmol) was dissolved in 80 mL of diethyl ether. The resulting solution was cooled to 0 °C followed by addition of HBF_4 (54 wt % in diethyl ether, 0.5 mL) via a syringe, and the solution was allowed to warm to room temperature and stirred for 1 day. After that, the precipitate was collected by a glass frit, washed with diethyl ether, and dried under vacuum to afford **3a** as an orange powder (211.7 mg, 95% yield). Anal. (%) Calcd for $C_{48}H_{41}B_2F_8NP_2Ru$: C, 59.53; H, 4.27; N, 1.45. Found: C, 59.83; H, 4.10; N, 1.52. ^{1}H NMR ($CDCl_3$): δ 12.7 (br, 1H, N*H*), 8.29 (1H, Py), 8.14 (1H, Py), 7.93 (1H, Py), 7.59−6.89 (Ph), 5.90 (s, 1H, =C=C*H*), 5.51 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 346.41 (t, $^2J_{CP}$ = 14.6 Hz, Ru*C*), 145.96, 139.47 (Py), 133.22−128.00 (Ph), 125.86, 122.35 (Py), 112.40 (RuC*C*), 96.58 (Cp). ^{31}P NMR ($CDCl_3$): δ 37.3 (s).

Complex **3b** was similarly obtained from **1b** in 91% yield. Spectroscopic data for**3b**: Anal. (%) Calcd for $C_{49}H_{43}B_2F_8NP_2Ru$: C 59.90, H 4.41, N 1.43. Found: C, 59.78; H, 4.50; N, 1.52. ^{1}H NMR ($CDCl_3$): δ 12.28 (br, 1H, N*H*), 8.13 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Py), 7.59 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Py), 7.60−7.03 (Ph and Py), 6.10 (s, 1H, RuCC*H*), 5.50 (s, 5H, Cp), 2.65 (s, 3H, CH_3). ^{31}P NMR ($CDCl_3$): δ 37.8 (s).

Synthesis of [Ru]C≡C(C_5H_4N→BY_3) (Y = F, 4a; Y = H, 4c). At room temperature complex **1a** (90.3 mg, 0.11 mmol) was weighted into a Schlenk flask under nitrogen. Diethyl ether (80 mL) was added into the flask via a cannula followed by addition of BF_3-OEt_2 (ca. 48%, 0.02 mL) under nitrogen. The resulting orange cloudy solution was then stirred for 8 h. After that, the mixture was filtered through a glass frit under nitrogen, and the solid was washed with diethyl ether and dried under vacuum to afford **4a** as a golden powder (85.9 mg, 88% yield). Anal. (%) Calcd for $C_{48}H_{39}BF_3NP_2Ru$: C, 66.99; H, 4.57; N, 1.63. Found: C, 66.79; H, 4.60; N, 1.52. ^{1}H NMR ($CDCl_3$): δ 8.29 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Py), 7.68 (t, $^3J_{HH}$ = 8.3 Hz, 1H, Py), 7.11−7.39 (Ph), 7.04 (t, $^3J_{HH}$ = 8.3 Hz, 1H, Py), 6.70 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Py), 4.54 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 173.98 (t, $^2J_{CP}$ = 23.0 Hz, Ru*C*), 142.53, 139.58, 136.41 (Py), 137.78−127.45 (Ph), 117.15 (Py), 113.08 (RuC*C*), 87.44 (Cp). ^{31}P NMR ($CDCl_3$): δ 50.9. ^{19}F NMR ($CDCl_3$): δ −152.2.

Complex **4c** was similarly synthesized from **1a** and BH_3-THF in 61% yield. Spectroscopic data for **4c**: Anal. (%) Calcd for $C_{48}H_{42}BNP_2Ru$: C, 71.47; H, 5.25; N, 1.74. Found: C, 71.68; H, 5.10; N, 1.62. ^{1}H NMR ($CDCl_3$): δ 8.51 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Py), 7.07−7.44 (Ph and Py), 6.82 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Py), 4.51 (s, 5H, Cp), 2.5−3.5 (br, 3H, B*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 153.47 (t, $^2J_{CP}$ = 23.5 Hz, Ru*C*), 147.37, 143.20, 136.55, 128.23 (Py), 138.71−127.39 (Ph), 117.03 (Py), 115.39 (RuC*C*), 86.58 (Cp). ^{31}P NMR ($CDCl_3$): δ 51.5.

Synthesis of {[Ru]=C=C(H)(C_5H_3RN→BF_2OH)}BF_4 (5a, R = H; 5b; R = Me). To a Schlenk flask containing a CH_2Cl_2 solution (25 mL) of complex **1a** (139.8 mg, 0.18 mmol) was added BF_3-OEt_2 (1.25 mL) at room temperature, and the resulting solution was stirred for 12 h, while the color of the solution turned from yellow to orange-red. Then volatiles of the solution were removed

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Table 1. Crystal Data and Refinement Parameters for Complexes 1b, 6a, 7c, and 9b

	1b	6a	7c	9b
formula	$C_{49}H_{41}NP_2Ru$	$C_{52}H_{51}B_2F_6NO_2P_2Ru$	$C_{53}H_{50}BrCl_2NO_3P_2Ru$	$C_{58}H_{57}F_{12}NO_3P_4Ru$
mass (amu)	806.84	1020.57	1062.76	1269.00
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.83500(10)	10.34010(10)	11.4830(3)	12.0479(2)
b (Å)	18.3860(2)	18.5289(2)	11.9140(3)	15.3359(2)
c (Å)	24.0340(2)	25.4882(2)	20.4030(4)	16.6007(3)
α (deg)	90	90	95.1040(10)	72.3710(10)
β (deg)	94.5170(1)	92.3180(10)	103.5170(10)	81.1360(10)
γ (deg)	90	90	112.4140(10)	86.1200(10)
V (Å^3); Z	3891.96(7); 4	4879.31(8); 4	2459.21(10); 2	2887.56(8); 2
θ range (deg)	1.40 to 27.49	1.60 to 27.49	1.05 to 27.47	1.71 to 27.46
no. of data	27 035	33 479	15 898	23 576
no. of indep data	8922	11 035	10 814	13 211
R1 for $I > 2\sigma(I)$	0.0387	0.0513	0.0512	0.0877
wR2, all data	0.1140	0.1560	0.1575	0.2862
goodness-of-fit on F^2	1.124	1.090	1.094	1.110

under vacuum, and 60 mL of diethyl ether was added into the flask. The resulting mixtures were stirred vigorously under nitrogen for 1.5 h. Precipitates thus formed were collected by a glass frit, washed with diethyl ether, and dried in vacuo to give complex **5a** as a pale orange powder (120.9 mg, 72%). Anal. (%) Calcd for $C_{48}H_{41}B_2F_6NOP_2Ru$: C, 60.91; H, 4.37; N, 1.48. Found: C, 60.74; H, 4.10; N, 1.48. ^{1}H NMR ($CDCl_3$): δ 12.33 (br, 1H, O*H*), 8.14 (t, $^3J_{HH}$ = 7.2 Hz, Py), 7.71 (d, $^3J_{HH}$ = 7.2 Hz, Py), 7.43−6.95 (Ph and Py), 5.90 (s, 1H, =C=C*H*), 5.49 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 344.56 (t, $^2J_{CP}$ = 15.7 Hz, Ru*C*), 146.02, 145.94, 139.46 (Py), 133.48−126.50 (Ph), 125.93, 122.42 (Py), 112.46 (RuC*C*), 96.62 (Cp). ^{31}P NMR ($CDCl_3$): δ 37.6 (s). ^{19}F NMR ($CDCl_3$): δ −149.6 (br, BF_2), −150.7 (BF_4).

Complex **5b** was prepared using the same procedure as that of **5a** in 79% yield. Spectroscopic data for **5b**: ^{1}H NMR ($CDCl_3$): δ 12.14 (br, 1H, OH), 7.99−7.67 (m, Py), 7.54−6.99 (Ph and Py), 6.09 (s, 1H, =CH), 5.46 (s, 5H, Cp), 2.58 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 345.82 (t, $^2J_{CP}$ = 16.2 Hz, Ru*C*), 151.96, 145.77, 145.46 (Py), 134.58−128.55 (Ph), 123.05, 122.59 (Py), 112.48 (RuC*C*), 96.44 (Cp), 19.47 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 37.7 (s). ^{19}F NMR ($CDCl_3$): δ −150.4 (BF_4).

Synthesis of {[Ru]=C(O)CH$_2$(C$_5$H$_4$NBF$_2$)}BF$_4$ (6a). To a 10 mL chloroform solution of 2-ethynylpyridine (0.4 mL, 3.96 mmol) at room temperature was added an aliquot of BF_3−OEt_2 (ca. 48% in ether, 2 mL, 7.57 mmol). The solution was stirred for 10 min under nitrogen. Subsequently the solution was transferred to a 25 mL chloroform solution containing [Ru]Cl (514.3 mg, 0.71 mmol) under nitrogen. After stirring for 2 days the solvent of the resulting solution was removed and the crude product was extracted with CH_2Cl_2. The solution was concentrated and added into diethyl ether, and the precipitate thus formed was collected by a glass frit, washed with diethyl ether and hexane, and dried under vacuum to afford the yellow product **6a** (485.2 mg; 85% yield). Anal. (%) Calcd for $C_{49}H_{43}B_2F_6NOP_2Ru$: C, 61.27; H, 4.51; N, 1.46. Found: C, 61.51; H, 4.60; N, 1.42. FAB mass (*m*/*z*): 860.4 (M$^+$). IR (KBr, cm^{-1}): ν 1350.5 (νCO), 1081.9 (m, BF), 1030.2 (m, BF). ^{1}H NMR ($CDCl_3$): δ 8.46 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Py), 8.30 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Py), 8.03 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Py), 7.51 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Py), 7.31−6.95 (Ph), 5.15 (s, 2H, C*H*$_2$), 4.94 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 292.65 (t, $^2J_{CP}$ = 12.7 Hz, Ru*C*), 148.54, 145.31, 140.21 (Py), 135.96−128.04 (Ph), 126.60, 124.16 (Py), 92.18 (Cp), 63.11 (*C*H$_2$). ^{31}P NMR ($CDCl_3$): δ 46.9 (s). ^{19}F NMR ($CDCl_3$): δ −155.8 (br, 2F, B*F*$_2$), −152.4 (4F, B*F*$_4$).

Synthesis of Complexes {[Ru]C≡C(C$_5$H$_3$RNCH$_2$R′)}X (R = H, R′ = CH=CHCO$_2$CH$_3$, 7a; R = Me, R′ = CH=CHCO$_2$CH$_3$, 7b; R = Me, R′ = CO$_2$CH$_3$, 7c; R = Me, R′ = CH=CH$_2$, 7d). Two synthetic methods are used. Method A for **7d**: an aliquot of allyl iodide (1 mL) was added into a 20 mL of CH_2Cl_2 solution of **1b** (507 mg, 0.63 mmol) under nitrogen, and the solution was stirred at 0 °C overnight. The volume of the resulting solution was reduced to 5 mL and was added into 50 mL of diethyl ether. A bright yellow precipitate thus formed was filtered through a glass frit, washed three times with diethyl ether and hexane, and dried under vacuum to obtain complex **7d** (432 mg, 81% yield). Method B: to a Schlenk flask containing 50 mL of a diethyl ether solution of **1b** (47.5 mg, 0.06 mmol) was added 0.1 mL of allyl iodide and the resulting solution stirred overnight. The golden precipitate thus formed was collected, washed, and dried under vacuum to afford **7d**. The yield is comparable. Anal. (%) Calcd for $C_{52}H_{46}INP_2Ru$: C, 64.07; H, 4.76; N, 1.44. Found: C, 64.18; H, 4.60; N, 1.52. FAB mass (*m*/*z*): 848 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 7.68 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Py), 7.41−7.05 (Ph and Py), 6.57 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Py), 5.89 (s, 2H, C*H*$_2$), 5.03 (s, 1H, =C*H*), 4.45 (s, 5H, Cp), 3.71 (s, 2H, =C*H*$_2$), 2.82 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 181.33 (t, $^2J_{CP}$ = 22.5 Hz, Ru*C*), 166.86 (=CH$_2$), 152.97, 141.26, 139.26 (Py), 137.40−127.75 (Ph), 127.38, 120.53 (Py), 114.32 (RuC*C*), 90.82 (=CH), 87.05 (Cp), 55.01 (*C*H$_2$), 53.18 (*CH*$_2$), 22.46 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 49.8.

Complexes **7a**, **7b**, and **7c** were prepared following the same procedure as that in **7d**. Spectroscopic data for **7a** (method B, in 85% yield): Anal. (%) Calcd for $C_{53}H_{46}BrNO_2P_2Ru$: C, 65.50; H, 4.77; N, 1.44. Found: C, 65.74; H, 4.81; N, 1.32. ^{1}H NMR ($CDCl_3$): δ 9.30 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Py), 7.72 (t, $^3J_{HH}$ = 8.1 Hz, 1H, Py), 7.40−6.89 (Ph and Py), 6.75 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Py), 6.17 (d, $^3J_{HH}$ = 15.6 Hz, 1H, =C*H*), 5.89 (s, 2H, NC*H*$_2$), 4.45 (s, 5H, Cp), 3.67 (s, 3H, OC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 181.15 (t, $^2J_{CP}$ = 22.6 Hz, Ru*C*), 165.56, 141.39, 140.05 (Py), 137.41−127.23 (Ph), 124.56, 118.82 (Py), 113.39 (RuC*C*), 86.85 (Cp), 57.01 (N*C*H$_2$), 51.60 (O*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 49.5.

Spectroscopic data for **7b** (method B, in 98% yield): Anal. (%) Calcd for $C_{54}H_{48}BrNO_2P_2Ru$: C 65.79, H 4.91, N 1.42. Found: C, 65.78; H, 5.04; N, 1.41. FAB mass (*m*/*z*): 906.3 (M$^+$), 719.3, 645.3, 429.0. ^{1}H NMR ($CDCl_3$): δ 7.62−6.98 (Ph, =CH and Py), 6.66 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Py), 6.03 (d, $^3J_{HH}$ = 2.7 Hz, 2H, CH_2), 5.77 (m, 1H, =C*H*CO$_2$Me), 4.47 (s, 5H, Cp), 3.67 (s, 3H, OC*H*$_3$), 2.91 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 180.27 (t, $^2J_{CP}$ = 22.5 Hz, Ru*C*), 165.35 (C=O), 152.48, 140.86, 140.15 (Py), 137.40−127.24 (Ph), 122.81, 120.69 (Py), 114.18 (RuC*C*), 97.50 (=*C*H), 90.78 (=*C*H), 86.93 (Cp), 54.62 (*C*H$_2$), 51.69 (O*C*H$_3$), 22.08 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 49.6.

Spectroscopic data for **7c** (method A, in 86% yield): Anal. (%) calcd for $C_{52}H_{46}BrNO_2P_2Ru$: C, 65.07; H, 4.83; N, 1.46. Found: C, 65.17; H, 4.91; N, 1.48. FAB mass (*m*/*z*): 880.1 (M$^+$ + 1). ^{1}H NMR ($CDCl_3$): δ 7.70 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Py), 7.26−7.12 (Ph and Py), 6.56 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Py), 5.96 (s, 2H, C*H*$_2$), 4.46 (s, 5H, Cp), 3.72 (s, 3H, OC*H*$_3$), 2.87 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 181.76 (t, $^2J_{CP}$ = 22.3 Hz, Ru*C*), 167.54 (C=O), 153.74, 141.90, 139.95 (Py), 138.06−128.37 (Ph), 128.00, 121.18 (Py), 114.95 (RuC*C*), 87.68 (Cp), 55.76 (*C*H$_2$), 53.78 (O*C*H$_3$), 23.15 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 49.8.

Synthesis of {[Ru]=C=C(H)($C_5H_3MeNCH_2CO_2CH_3$)}(BF_4)$_2$ (8c). To a Schlenk flask containing a solution of **7c** (45.5 mg, 0.05 mmol) in 20 mL of CH_2Cl_2 at 0 °C was added HBF_4 (54 wt % diethyl ether solution, 0.1 mL) via a syringe. The resulting solution was allowed to warm to room temperature in 10 min, and the color of the solution turned from yellow to brown. Volatiles were removed under vacuum, and the residue was washed with diethyl ether. A brown solid thus formed was collected and dried in vacuo to afford **8c** (38.3 mg, 77% yield). ^{1}H NMR ($CDCl_3$): δ 8.20 (t, $^3J_{HH}$ = 8.2 Hz, Py), 7.72−6.98 (Ph, Py), 5.85 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Py), 5.58 (s, 5H, Cp), 5.01 (s, 2H, NC*H*$_2$), 4.27 (m, 1H, =C=C*H*), 3.77 (s, 3H, OC*H*$_3$), 2.65 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 341.77 (t, $^3J_{CP}$ = 14.6 Hz, Ru*C*), 189.28 (C=O), 153.58−129.03 (Ph, Py), 101.38 (RuC*C*), 97.82 (Cp), 54.03 (O*C*H$_3$),19.85 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 38.9.

Transformation of Complex 7b to 9b. A $CHCl_3$ solution (4 mL) containing complex **7b** (80.4 mg, 0.08 mmol) and KPF_6 (33.9 mg, 0.18 mmol) was stirred at ambient atmosphere for 3 days. Volatiles were removed and the residue was extracted with CH_2Cl_2 (10 mL), which was added into diethyl ether to form a precipitate, which was collected, washed with diethyl ether and cold THF, and dried under vacuum to afford **9b** as a brown powder (48.4 mg, 50% yield). Anal. (%) Calcd for $C_{54}H_{49}F_{12}NO_2P_4Ru$: C, 54.19; H, 4.13; N, 1.17. Found: C, 54.07; H, 4.10; N, 1.12. FAB mass (*m*/*z*): 906.4 ($M^+ + 1$), 726.1, 644.2 ($M^{2+} - PPh_3$), 429 ([Cp(PPh_3)Ru]$^+$). ^{1}H NMR ($CDCl_3$): δ 7.40−6.90 (Ph and Py), 5.77 (s, 5H, Cp), 5.59 (m, 1H, NC*H*), 4.72 (br, 1H, C*H*), 4.42 (d, $^3J_{HH}$ = 11.3 Hz, 1H, NC*H*), 3.53 (s, 3H, OC*H*$_3$), 2.74 (s, 3H, C*H*$_3$), 2.42 (m, 2H) and 2.38 (dd, J_{HH} = 7.0 Hz, 1H, C*H*), 2.14 (d, $^3J_{HH}$ = 16.1 Hz, 1H, C*H*). ^{13}C NMR ($CDCl_3$): δ 343.42 (t, $^3J_{CP}$ = 13.4 Hz, Ru*C*), 171.38 (*C*O), 152.21, 149.21, 143.44 (Py), 133.87−128.43 (Ph), 124.75, 120.70 (Py), 97.55 (Cp), 61.03 (N*C*H$_2$), 52.01 (O*C*H$_3$), 39.59 (*C*H$_2$), 32.62 (*C*H), 20.79 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 41.3, 39.6 (2 d, $^2J_{PP}$ = 24.6 Hz).

X-ray Structure Determinations. Details of the structure analyses carried out on complexes **1b**, **6a**, **7c**, and **9b** are given in Table 1. A single crystal of **1b** suitable for an X-ray diffraction study was glued to a glass fiber and mounted on a Nonius Kappa CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube molybdenum Kα radiation (T = 295 K). Exposure time was 5 s per frame. Multiscan absorption correction was applied, and decay was negligible. Data were processed, and the structures were solved and refined by the SHELXTL program.[25] The structure was solved using direct methods and confirmed by Patterson methods, and refining on intensities of all data gave R1 and wR2 for unique observed reflections ($I > 2\sigma(I)$). Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. Structures of complexes **6a**, **7c**, and **9b** were similarly determined. Table 1 lists the crystal data and refinement parameters for complexes **1b**, **6a**, **7c**, and **9b**.

Computational Methods. Theoretical calculations have been carried out using the Gaussian 03 program[17] at the DFT level by means of the Becke 3 and Lee−Yang−Parr (B3LYP) composite exchange−correlation functional.[16] The LanL2DZ basis sets was used throughout the calculation, where for the Ru atom the innermost electrons are replaced by a relativistic ECP and the 18 valence electrons are explicitly treated by a double-ξ basis set. Full geometry optimization without symmetry restrictions was performed for all structure. Before performing optimization of ground-state geometries at the B3LYP/LanL2DZ level of theory, the molecular structures were initially optimized at the semiempirical PM3[26] level of calculation. Harmonic frequencies were calculated at the optimization level using the same basis sets, and the nature of the stationary points was determined in each case according to the right number of negative eigenvalues of the Hessian matrix. For each of the stationary points, the presence of one imaginary frequency indicates a transition state, while no imaginary frequency indicates a local minimum. The intrinsic reaction coordinate (IRC) pathways[27] from the transition structures have been followed using a second-order integration method[28] to verify the expected connections of the first-order saddle points with the correct local minima found on the potential energy surface.

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Supporting Information Available: Complete crystallographic data for **1b**, **6a**, **7c**, and **9b** (CIF) and detailed computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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