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Article

Carbon−Carbon Bond Formation Involving a Vinylidene Ligand and Ferrocenyl Substituent in Cationic Ruthenium Complexes

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A formal intramolecular olefin metathesis process between the C=C double bond of a vinylidene ligand and a pendant vinyl group in several ruthenium complexes, each with a ferrocenyl group, is followed by an additional intramolecular C−C bond formation between a Cp ligand of the ferrocenyl substituent and the vinylidene ligand. The regioselectivity of the C−C bond formation reaction at either the substituted or the nonsubstituted Cp group of the ferrocenyl group is possibly influenced by a steric effect between the neighboring substituent near the ferrocenyl group and the phosphine ligand on the ruthenium metal center. The structure of one ruthenium complex resulting from such a C−C bond formation has been fully characterized by a single-crystal X-ray diffraction analysis.

Introduction

Metal vinylidene complexes have attracted a great deal of attention, because these compounds offer the possibility for developing new types of organometallic intermediates that could have various interesting and unusual reactivities. Recently, the importance of metal vinylidene intermediates in catalysis,[1] particularly that of ruthenium vinylidene complexes,[2] has been pointed out. The most straightforward route to a metal vinylidene complex arises from the activation of a terminal alkyne.[3,4] The addition reaction at C_β of a σ-alkynyl complex using various electrophilic reagents has also been described as a versatile method to prepare vinylidene derivatives.[5] Vinylidene on a metal is considered as an electron-withdrawing ligand stabilized by electron-rich metal fragments.[6] The reactivity of the metal vinylidene complex is rationalized by taking the electrophilicity of vinylidene C_α, the nucleophilicity of C_β, and the highly unsaturated features of the ligand into consideration. Thus, the formation of metal vinylidene intermediate has been used to promote a new carbon−carbon bond-forming reaction by the addition of carbon nucleophile to the electrophilic vinylidene C_α atom.[7] Ferreocene[8] displayed versatile reactivities of carbon−carbon bond forming reactions and has become very attractive from a commercial point of view.[9] Ferrocenophane ring systems in which the two Cp groups are

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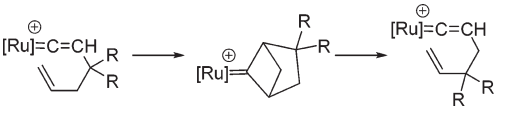
joined by an atomic or a molecular bridge as well as substituted ferrocene have also been developed[10,11] as building blocks for metal-based polymers[12] and also in bioorganometallic chemistry.[13] With both vinylidene and ferrocene groups showing C−C bond forming reactivity, a study has been initiated to explore the intramolecular reactions of a ruthenium vinylidene complex containing a ferrocenyl group. In this study, we use the allenylidene complex[14] with a ferrocenyl group as the starting material for the preparation of the vinylidene complex, since the reactivity of the allenylidene complex is also governed by the electron-deficient character of both C_α and C_γ atoms.[15] Grignard reagent is thus used as a nucleophile to add to C_γ of the allenylidene complex, readily prepared from ferrocenyl-substituted propargylic alcohols, to yield an acetylide complex. This is followed by the electrophilic addition of organic halide to synthesize a variety of specialized vinylidene complexes, each containing a ferrocenyl group and an allylic group at C_γ. Previously, we observed a formal metathesis process, as shown in Scheme 1 for similar vinylidene complexes with an allylic group at C_γ.[16] In this work our study on these ferrocenyl complexes reveals the same reactivity. In addition, a facile C−C bond formation reaction between the vinylidene and the ferrocenyl groups is also observed. This provides a direct approach to ferrocenophane compounds under mild conditions.

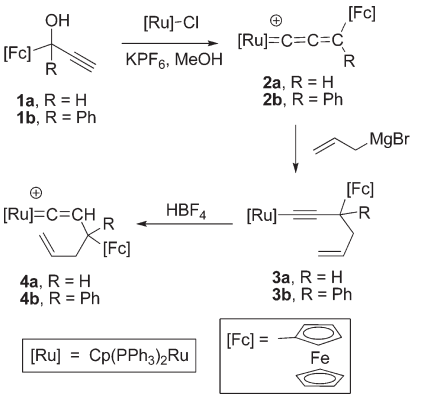
Results and Discussion

Allenylidene, Acetylide, and Vinylidene Complexes. Two ferrocenyl-substituted propargylic alcohols, FcC(OH)-(R^1)C≡CH (**1a**, R^1 = H; **1b**, R^1 = Ph; Fc = CpFe(C_5H_4)), were prepared by following the literature method.[17] The synthesis of allenylidene complexes containing either an [Ru] (=Cp(PPh_3)$_2$Ru) or [Ru′] (=Cp(dppe)Ru) moiety using **1a** or **1b** is straightforward. Namely, the reaction of [Ru]-Cl with **1a** in methanol in the presence of KPF_6 gave the cationic allenylidene complex [Ru]=C=C=CH(Fc)[PF_6] (**2a**) as an intensely deep green solid in good yield (see Scheme 2).

Scheme 1



Scheme 2



The complexes [Ru′]=C=C=CH(Fc)[PF_6] (**2a′**) and [Ru]=C=C=CPh(Fc)[PF_6] (**2b**) were similarly prepared from **1a** and **1b**, respectively. These allenylidene derivatives, each with a ferrocenyl group, are air-stable solids, are readily soluble in most polar solvents such as THF, CH_2Cl_2, chloroform, acetone, and methanol, and have poor solubility in diethyl ether and are insoluble in hexane. The ^{31}P NMR spectrum of **2a** displays a singlet peak at δ 48.15 assigned to PPh_3. Complex **2a′** also shows a singlet resonance at δ 82.9 in the ^{31}P NMR spectrum. These are different from the Tp-substituted congener Tp(PPh_3)$_2$Ru=C=C=CPh(Fc)[SbF_6], where Tp is the tris(pyrazolyl)borate ligand, which exists as two isomers at room temperature.[18] Hartmann et al. proposed that the major isomer of the Tp congener has the less bulky phenyl substituent oriented toward the PPh_3 ligands along the Ru=C=C=C axis. However, for **2a**, the energy barrier for the rotation of the allenylidene moiety is probably not high enough to allow observation of two different rotamers at ambient temperatures. The same phenomenon was also observed in **2a′** and **2b**.

Complex **2a** displays downfield broad ^{1}H resonances at δ 5.21 and 4.90 assigned to the protons of the substituted Cp group of the ferrocenyl moiety bound to C_γ of the allenylidene ligand. The singlet resonance at δ 8.92 assigned to the allenylidene proton is consistent with the structure. The ^{13}C NMR spectrum of **2a** shows a triplet downfield resonance at δ 269.4 with J_{PC} = 19.7 Hz and two singlet resonances at δ 180.4 and 153.8 assigned to C_α, C_β, and C_γ, respectively. The ESI mass spectrum of **2a** displaying a parent ion at m/z 913.1 is consistent with the formula of the proposed allenylidene complex. Recently the chemical reactivity of a metal complex bearing a ferrocenyl group has attracted attention in organometallic chemistry. For example, Dixneuf et al. described the synthesis of heterobimetallic Fe−Ni and Fe−Pd oligomers using diynylferrocene derivatives as precursors.[19] Fischer et al. demonstrated a regioselective insertion of a

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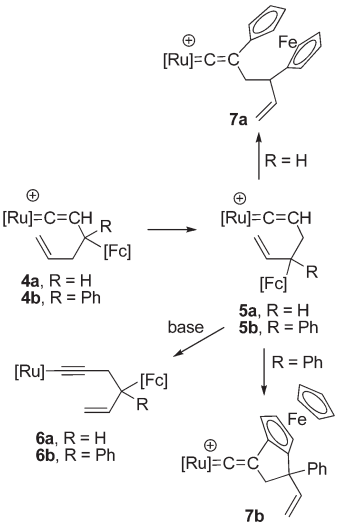
C≡C triple bond into $C_\beta-C_\gamma$ of an allenylidene ligand in a bis(ferrocenyl)-substituted metal complex.[20]

Nucleophilic addition of the Grignard reagent $BrMgCH_2CH{=}CH_2$ to C_γ of the allenylidene ligand of **2a** at −78 °C afforded the neutral acetylide complex [Ru]−C≡CCH(Fc)$CH_2CH{=}CH_2$ (**3a**) as a brown-yellow solid in reasonable yield. Similarly, the complexes [Ru′]−C≡C-CH(Fc)$CH_2CH{=}CH_2$ (**3a′**) and [Ru]−C≡CCPh(Fc)CH_2-$CH{=}CH_2$ (**3b**) were prepared from **2a′** and **2b**, respectively, using the same Grignard reagent. The regiospecific nucleophilic addition takes place exclusively at C_γ of the cumulenic skeleton. This shows that the steric hindrance between the phosphine ligand and the Grignard reagent disfavors addition at C_α. The light yellow acetylide complex is air stable and is soluble in benzene, diethyl ether, acetone, and CH_2Cl_2 but insoluble in methanol. Spectroscopic data of **3a** support the proposed formula. Two doublet resonances at δ 51.3 and 51.1 with $^2J_{P-P}$ = 38.2 Hz in the ^{31}P NMR spectrum of **3a** with a stereogenic carbon center at C_γ appear in the region of a regular ruthenium acetylide complex. In the ^{1}H NMR spectrum of **3a** three multiplet resonances at δ 5.91, 4.89, and 4.79 are assigned to the terminal vinyl group. The multiplet resonances in the region of δ 4.43−4.03 are assigned to the Cp moiety bound to C_γ of the allenylidene ligand. Multiplet resonances at δ 2.42 - 2.30 are assigned to two methylene protons. The ESI mass spectrum of **3a** showing parent ions at m/z 955.2 is consistent with the proposed formula.

Protonation reactions of the acetylide complexes **3a**, **3a′**, and **3b** with HBF_4 in diethyl ether at 0 °C afforded the corresponding cationic vinylidene complexes [M]=C=C-HC(R^1)(Fc)$CH_2CH{=}CH_2[BF_4]$ (**4a**, R^1 = H, [M] = [Ru]; **4a′**, R^1 = H, [M] = [Ru']; **4b**, R^1 = Ph, [M] = [Ru]), which are all red-brown solids. The ^{1}H NMR spectrum of the vinylidene complex **4b** is broad even at low temperature. The formal metathesis reaction described below probably occurred immediately when the vinylidene complex was dissolved in solvent.[16] Fortunately, complex **4a** with no phenyl group at C_γ gives a clear high-resolution ^{1}H NMR spectrum at room temperature if the NMR experiment is quickly conducted in a short period of time for the freshly prepared complex **4a**. The ^{31}P NMR spectrum of **4a** shows two doublet resonances at δ 44.6 and 43.4 with $^2J_{P-P}$ = 26.5 Hz which are in the region of a regular ruthenium vinylidene complex, indicating the presence of the stereogenic center at C_γ. The ^{1}H NMR spectrum of **4a** displays multiplet resonances at δ 6.12, 5.32, and 5.28 assigned to the vinyl group. The resonance of the vinylidene proton appears at δ 4.69. The multiplet resonances in the region of δ 4.24−4.07 are assigned to the Cp moiety of the ferrocenyl group bound at C_γ, and multiplet resonances at δ 2.82−2.35 are assigned to two methylene protons. The ^{1}H NMR spectrum of **4a′** also displays a broad signal possibly due to a fast transformation of **4a′** to **5a′**. Characterization of the vinylidene complex **4a′** relies on the ESI mass and ^{31}P NMR data. The ^{31}P NMR spectrum displays two doublet resonances at δ 78.8 and 78.7 with $^2J_{P-P}$ = 19.5 Hz in the region of a regular ruthenium dppe vinylidene complex. The ESI mass spectrum of **4a′** showing parent ions at m/z 829.1 is consistent with the proposed vinylidene formula. Moreover, deprotonation of **4a′** in methanol by NaOMe immediately formed the acetylide complex **3a′**.

Scheme 3



Intramolecular C−C Bond Formation. Interestingly, complex **4a** displays interesting reactivity owing to the presence of the allylic and the ferrocenyl groups in the vinylidene ligand. As depicted in Scheme 3, a skeletal rearrangement of **4a** is followed by C−C bond formation between C_β of the vinylidene ligand and Cp of the ferrocenyl group, producing the vinylidene complex **7a** in CH_2Cl_2 or MeOH at room temperature (see Scheme 3). When the transformation was monitored by the ^{31}P NMR spectra, a broad resonance at δ 44.20 attributed to the intermediate [Ru]=C=CH-CH_2CH(Fc)CH=CH_2 (**5a**) was observed before two doublet resonances at δ 43.5 and 42.8 with $^2J_{P-P}$ = 27.2 Hz assigned to **7a** appeared. **5a** diminished at the end of the reaction.

The ^{1}H NMR spectrum of **7a** displays multiplet resonances at δ 5.89, 5.02, and 5.06 assigned to the vinyl group, and their coupling patterns reveal that there is no neighboring methylene group. The proton signals of the ferrocenyl group give 6 resonances at δ 4.27, 4.20, 4.17, 4.06, 4.02, and 3.81 with the integral ratio of 1:1:2:2:1:1, and the 10 singlet ^{13}C signals in the region δ 87.62−67.54 are assigned to two Cp rings of the ferrocenyl group. Both indicate that all hydrogen and carbon atoms on the two Cp rings of the ferrocenyl group are in different chemical environments, signifying that both Cp ligands of the ferrocenyl group are substituted. The two ^{13}C resonances at δ 344.6 with $^2J_{P-C}$ = 15.2 Hz and at δ 119.8 assigned to C_α and C_β, respectively, reveal the ruthenium vinylidene character. In the 2D HMBC NMR spectrum of **7a**, both resonances of C_α and C_β are correlated to the ^{1}H resonances at δ 2.54−2.51 assigned to the unique methylene group. The two ^{13}C resonances at δ 87.3 and 78.6 assigned to two tertiary carbons of the ferrocenyl group are both correlated to the methylene protons at C_γ. This implies that the two Cp rings of the ferrocenyl group are separately bonded to C_β and C_δ of the vinylidene ligand. The ESI mass spectrum of **7a** showing the parent peak at m/z 953.17 is also consistent with the proposed vinylidene complex. The HSQC, HMBC, and COSY 2D NMR spectra with the ^{1}H and ^{13}C NMR chemical shifts and coupling patterns clearly reveal the carbon chain of the ligand of **7a**. It is inferred that the transformation of complex **4a** proceeds via the vinylidene intermediate **5a** to yield complex **7a**. However,

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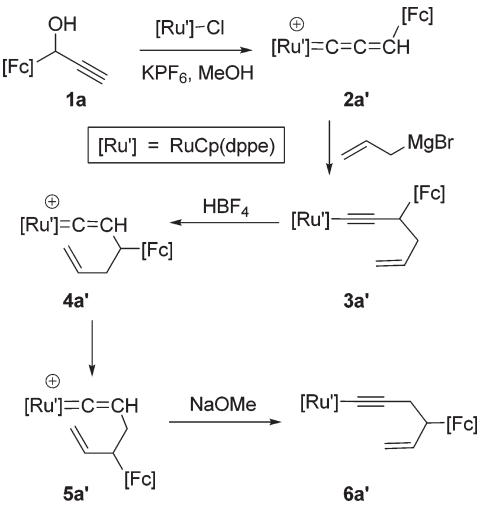
a high-resolution ^{1}H NMR spectrum of **5a** was not obtained, even at low temperature. This is ascribed to the ongoing formal metathesis reaction occurring for **5a** in solution. To indirectly corroborate the structure of the vinylidene intermediate **5a**, subsequent addition of NaOMe to a mixture of **5a** and **7a** afforded the neutral acetylide complex [Ru]−C≡CCH$_2$CH(Fc)CH=CH$_2$ (**6a**) in the reaction mixture. Complex **6a** was separated from the mixture by column chromatography. The ^{31}P NMR spectrum of **6a** displays a broad resonance at δ 51.1 in the region of a regular ruthenium acetylide complex. The broad singlet resonance is ascribed to the relatively long separation between the stereogenic carbon center and the two phosphine ligands. The C−C bond formation in the transformation of **5a** to **7a** provides a direct approach to a ferrocenophane compound under mild conditions. Werner and co-workers reported the reaction of methyl Grignard reagent with a chlororhodium vinylidene complex bearing a ferrocenyl group at C$_\beta$, leading to an interesting C−C coupling reaction mainly due to the steric effect of the ferrocenyl group.[21]

Complexes with dppe Ligand and with Phenyl-Substituted Enyne. The unusual transformation of **4a** to **7a** is interesting; thus, we carried out further studies of the reaction of the dppe analogue **4a′**. Complex **4a′** in solution is gradually converted to the vinylidene complex **5a′** by the same intramolecular formal metathesis reaction of the two C=C double bonds, leading to an equilibrium with a **4a′**:**5a′** ratio of about 1:2 (see Scheme 4).

All resonances of the ^{1}H NMR spectrum of **5a′** are also broad. Addition of NaOMe to the mixture containing **5a′** again afforded the neutral acetylide complex **6a′**. The ^{1}H and ^{31}P NMR spectra of **6a′** indirectly reveal the change of the carbon chain in the transformation of **4a′** to **5a′**. The formal metathesis reaction from **4** to **5** is most probably controlled by a steric effect. The steric hindrance between the dppe and ferrocenyl groups of **4a′** is expected to be less than that of the corresponding groups in **4a**. As a result, the driving force for the formal metathesis process in **4a′** is not as effective. Interestingly, no further C−C bond formation reaction occurred for the dppe vinylidene complex **5a′** in solution, even for a long period of time or at higher temperature. The more electron-donating character of dppe probably makes C$_\beta$ more electron rich, thus disfavoring the nucleophilic addition of the ferrocenyl Cp group to C$_\beta$.

To explore the scope of this novel process, the reaction of the vinylidene complex **4b** containing a slightly different vinylidene fragment with a phenyl group and the same ferrocenyl substituent at C$_\gamma$ was explored. Surprisingly, **4b**, with a phenyl group replacing hydrogen at C$_\gamma$ of **4a**, underwent the same formal metathesis reaction but was followed by a dissimilar C−C bond forming reaction between the ferrocenyl Cp group and C$_\beta$ (see Scheme 3). Complex **4b** in CH$_2$Cl$_2$ or MeOH at room temperature gradually transformed to the metathesis product **5b** and finally converted cleanly to the intramolecular cyclization product **7b** in 7 days. Again, addition of NaOMe to the solution containing **5b** led to the isolation of the neutral acetylide complex [Ru]−C≡CCH$_2$C(Fc)(Ph)CH=CH$_2$ (**6b**). Spectroscopic data of **6b** reveal the expected carbon chain. This sequential formation of complexes **5b** and **7b** from **4b** in solution was observed clearly in the ^{31}P NMR spectra. At the beginning,

Scheme 4



complex **4b** showed two doublet resonances at δ 42.8 and 43.5 with $^2J_{P-P}$ = 26.6 Hz. In 2 days a broad resonance at δ 43.8 assigned to **5b** appeared, and the peaks attributed to **4b** disappeared completely. Finally, the signal of **5b** was converted to two other sets of two doublet resonances at δ 45.8 and 42.9 with $^2J_{P-P}$ = 26.2 Hz and δ 46.1 and 42.6 with $^2J_{P-P}$ = 26.4 Hz in a ratio of 2:1. These are attributed to diastereoisomers of the intramolecular cyclization product **7b**. The ESI mass spectrum of **7b** agrees with the proposed vinylidene cyclization complex with a parent peak at *m*/*z* 1029.20. The ^{1}H NMR spectrum also supports the proposed structure. One isomer shows a doublet of doublets signal at δ 6.27 with $^3J_{H-H}$(trans) = 17.0 Hz and $^3J_{H-H}$(cis) = 10.5 Hz assigned to the internal vinyl proton. From the COSY spectrum, two corresponding doublet signals at δ 5.24 with ^3J = 10.5 Hz and at δ 5.07 with ^3J = 17.0 Hz are assigned to two terminal vinyl protons. The other vinyl signals of the minor isomer appear at δ 5.79 and 4.90 with ^3J = 10.3 Hz and at δ 4.56 with ^3J = 17.1 Hz. These diastereoisomers are due to the presence of a stereogenic center at C$_\gamma$ and the chiral cyclopentadienyl plane in **7b**. On the basis of the structure of **7b** described below, it is reasonable to assume that the major product is the one where the ferrocenyl group and the neighboring phenyl group are in an anti form with less steric hindrance. The minor product should have the ferrocenyl group and the phenyl group in a syn form.

Single crystals of the major isomer of complex **7b** were obtained by vapor diffusion at −5 °C in CH$_2$Cl$_2$/ether. This major isomer of complex **7b** has been further characterized by a single-crystal X-ray crystallographic study. An ORTEP view of **7b** is shown in Figure 1, and selected bond distances and angles are given in Table 1. The molecular structure shows a pseudo-octahedral three-legged piano-stool coordination around the ruthenium atom. The Ru(1)−C(1) distance of 1.852(4) Å is a typical Ru=C double bond, with the Ru(1)−C(1)−C(2) bond angle of 171.2(4)° showing almost linear geometry. In agreement with the sp^2 hybridization at C(2), the bond angle C(1)−C(2)−C(3) is 126.2(4)°. Also, the bond angle C(4)−C(5)−C(6) is 125.6(8)°, indicating the sp^2 hybrid of C(5) and double-bond character of C(5)−C(6).

The transformation from **4a** to **5a** could be interpreted by a formal metathesis process between the terminal vinyl group and the C$_\alpha$=C$_\beta$ bond of the vinylidene ligand of **4a**, as shown in Scheme 5.[15] This mechanism is proposed on the basis

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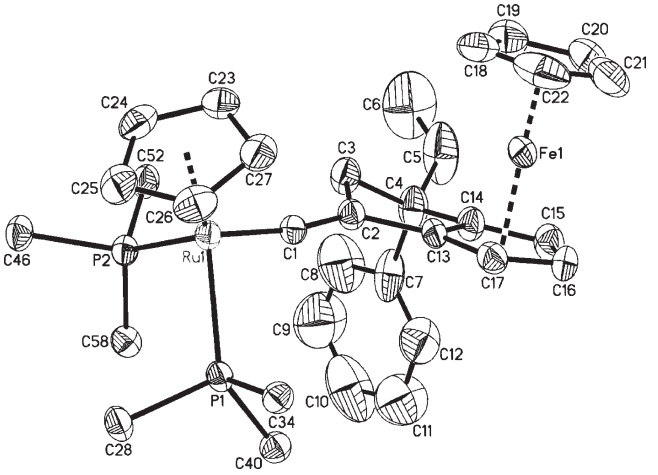


Figure 1. ORTEP drawing of the cationic complex **7b**. For clarity, aryl groups of the triphenylphosphine ligands on Ru except for ipso carbons and PF_6^- are omitted (thermal ellipsoids are set at the 30% probability level).

of many stoichiometric and catalytic reactions of enynes reported in the literature.[16,22] The ruthenium vinylidene complex **4** could first undergo a cyclization to give the carbocationic cyclohexenyl complex **A** or directly proceed via a metal-assisted regiospecific [2 + 2] cycloaddition of two double bonds to yield **C**. The [3.1.0] bicyclic intermediate **B** possibly formed via a 1,2-alkyl shift then serves as a bridge for the transformation between **A** and **C**. Formation of similar bicyclic structures as reaction intermediates has been postulated in many Pt- or Au-catalyzed reactions of enynes.[23] Similarly, a further 1,2-alkyl shift brings about the formation of **D** and **E**. Finally, ring opening of the carbocationic cyclohexenyl complex **E** yields complex **5a**. Alternatively, retrocycloaddition of the four-membered ring of **C** also directly gives **5a**. A complex with a four-membered-ring structure has been reported by Gimeno and co-workers for a ruthenium vinylidene complex containing an allylphosphine ligand which performed a cycloaddition similar to that in **4a**.[22b]

On the basis of the structure of the product **7b**, it is likely that the transformation from **5** to **7** may evolve H_2 gas. An oxidative carbon−carbon bond formation with efficient reductive H_2 evolution has been observed in a photocatalytic system containing colloidal ZnS, water, and organic substrates such as triethylamine, tetrahydrofuran, and methanol.[24] Interestingly, the transformation of **5** to **7** does not require photo energy. The product was obtained from the reaction carried out in a flask covered with aluminum foil. The C−C bond forming reaction may thus be considered as a coupling of two sp^2 carbons induced by the thermal energy. Friedel−Craft alkylation or acylation of the Cp ligand

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7b

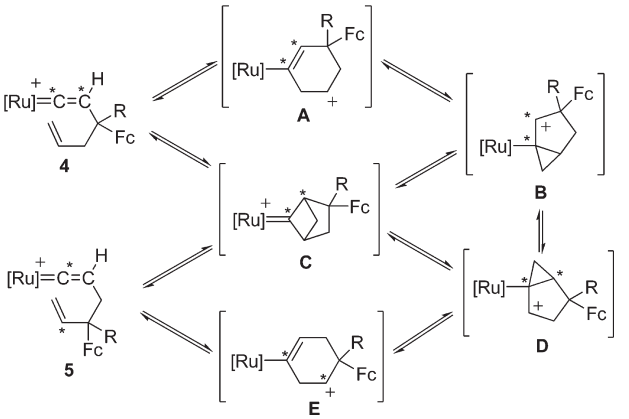
Bond Lengths (Å)

Ru(1)−C(1)	1.852(4)	C(4)−C(5)	1.490(9)
C(1)−C(2)	1.305(6)	C(4)−C(14)	1.513(7)
C(2)−C(3)	1.541(6)	C(5)−C(6)	1.406(12)
C(2)−C(13)	1.470(6)		

Bond Angles (deg)

Ru(1)−C(1)−C(2)	171.2(4)	C(1)−C(2)−C(13)	128.8(4)
C(1)−C(2)−C(3)	126.2(4)	C(13)−C(2)−C(3)	105.0(3)
C(2)−C(3)−C(4)	104.7(4)	C(4)−C(5)−C(6)	125.6(8)

Scheme 5



commonly observed in many ferrocenyl systems may shed light on the transformation of **5** to **7** involving cationic species. A mechanism for the formation of **7b** is proposed as shown in Scheme 6. The vinylidene complex **5b** could undergo a 1,3-hydride shift to give a hydride acetylide intermediate. An alternative access to this intermediate is the formation of a η^2-coordinated alkyne intermediate followed by oxidative addition of the C−H bond to the metal center. Then C−C bond formation between the substituted Cp of the ferrocenyl group and C_β leads to the formation of the cyclic structure, giving the final product **7b**. On the other hand, C−C bond formation could take place at the η^2-coordinated electrophilic alkyne ligand. The transformation from **5a** to **7a** is similar but involves the nonsubstituted Cp. It is clear that the presence of the phenyl group of **5b** alters the reaction path. It could be the steric hindrance between the ferrocenyl group and the phenyl group or an electronic effect that drives the substituted Cp of the ferrocenyl group to move closer to C_β for the C−C bond formation. It is not yet clear how two hydrogen atoms are eliminated.

Since the transformation from **4** to **7** proceeds via the intermediate **5**, with the ferrocenyl group at C_δ, it is interesting to see if other vinylidene complexes bearing a ferrocenyl group at C_δ could undergo the same intramolecular C−C bond formation. Therefore, we prepared **5c** and **5d**, two analogues of **5a**, and the propargyl-substituted vinylidene complex **4e** as shown in Scheme 7 and explored their chemical reactivity. The reaction of [Ru]-Cl and **1c**[17] in the presence of NH_4PF_6 in methanol at room temperature afforded complex **5c**, a vinylidene complex with a ferrocenyl group at C_δ. Another terminal alkyne, **1d**, with a methoxy group and a ferrocenyl group bonded at C_δ, was synthesized by the reaction of **1c** with methanol and HCl. Reaction of [Ru]-Cl with **1d** in the presence of NH_4PF_6 gave the

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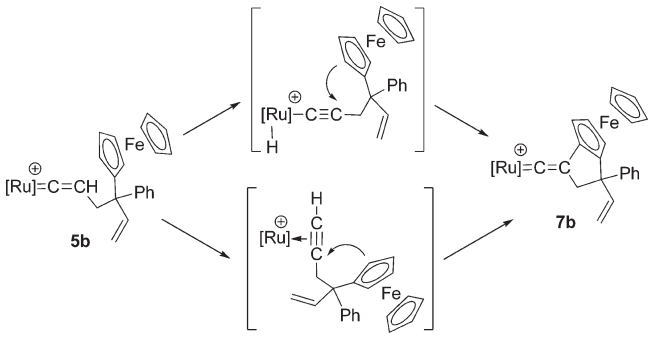
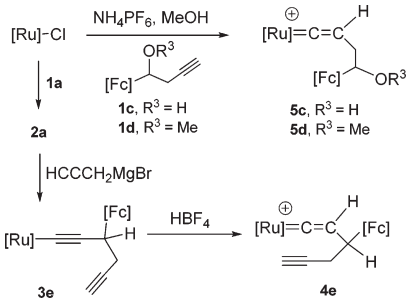
Scheme 6



Scheme 7



vinylidene complex **5d** in reasonable yield. We also synthesized the acetylide complex [Ru]C≡CCH(Fc)CH_2C≡CH (**3e**) using a procedure similar to that for **3a**. Then protonation of **3e** with HBF_4 afforded the corresponding cationic vinylidene complex [Ru]═C═CHCH(Fc)CH_2C≡CH[BF_4] (**4e**).

Unfortunately, all three vinylidene complexes **5c**, **5d**, and **4e** would not undergo transformation to give the desired alkylation product in solution. Complexes **5c**, **5d**, and **4e** are all thermally stable. Attempts to conduct the dehydration of complex **5c** also failed, even at 80 °C. Complex **5d** is also stable in solution at 80 °C. Therefore, it is clear that the terminal vinyl group of **5a** and **5b** plays an important role in the transformation of **5** to **7**.

Concluding Remarks

In several ruthenium vinylidene complexes, each with a substituted ferrocenyl group and an allyl group at C_γ, a formal intramolecular olefin metathesis process between the C═C double bond of the vinylidene ligand and the terminal vinyl group was observed. The extent of such a metathesis process possibly depends on steric effects between the substituted group of the vinylidene ligand and the phosphine on the metal. An additional intramolecular C−C bond formation between the Cp ligand of the ferrocenyl substituent and the vinylidene ligand gave the cyclization product. Steric effects between the neighboring substituent and phosphine ligand on Ru or possibly the electronic effects of the substituent changed the regioselectivity of the C−C bond forming reaction.

Experimental Section

General Procedures. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and were distilled under nitrogen before use. All reagents were obtained from commercial suppliers and were used without further purification. NMR spectra were recorded on a Bruker AC-300, Bruker Avance-400, or a DMX-500 FT-NMR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ at ambient temperature, and chemical shifts are expressed in δ. Proton chemical shifts are referenced to δ 7.26 ($CHCl_3$), and carbon chemical shifts are referenced to δ 77.0 ($CDCl_3$). ^{31}P (121 MHz) NMR spectra were referenced relative to external 85% phosphoric acid. Both $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were proton decoupled. FAB mass spectra were recorded on a JEOL SX-102A spectrometer. According to the literature methods, [Ru]Cl ([Ru] = $Cp(PPh_3)_2Ru$)[25] and [Ru′]Cl ([Ru′] = Cp(dppe)Ru)[26] were prepared from $RuCl_3 \cdot xH_2O$, which was purchased from Steam Chemicals. Compounds **1a**, **1b**, and **1c** were also prepared according to the literature method.[14]

Synthesis of 1-Ferrocenyl-1-methoxy-3-butyne (1d). In a Schlenk flask charged with 1-ferrocenyl-3-propyn-1-ol (0.10 g, 0.39 mmol) and 1 mL of HCl (0.1 M), methanol (30 mL) was added via a syringe. Then the solution was heated to reflux for $^1/_2$ h. The solution turned from yellow to red. Then the solution was dried under vacuum, and the mixture was purified by silica gel chromatography with diethyl ether−hexane (1:5) as eluent to obtain a yellow solution. Removal of the solvent yielded the yellow powder as **1d** (0.05 g, 47%). Spectroscopic data of **1d** are as follows. ^{1}H NMR ($CDCl_3$): δ 4.22 (m, 1H, FcCH), 4.20, 4.19, 4.18, 4.17 (m, 4 × 1H, CH of Cp), 4.14 (s, 5H, Cp), 3.36 (s, 3H, OMe), 2.85−2.69 (m, 2H, CH_2), 2.09 (s, 1H, ≡CH). ^{13}C NMR ($CDCl_3$): δ 87.8 (≡CH), 81.9 (≡C), 77.8 (COMe), 68.8 (5C, Cp), 70.1, 68.3, 67.7, 66.1 (4C, CH of Cp), 56.9 (OMe), 25.6 (CH_2 of allyl). Anal. Calcd for $C_{15}H_{16}FeO$: C, 67.19; H, 6.01. Found: C, 67.32; H, 6.14.

Synthesis of [Ru]═C═C═CH(Fc)[PF_6] (2a). In a Schlenk flask charged with [Ru]Cl (0.25 g, 0.35 mmol), KPF_6 (0.11 g, 0.62 mmol), and **1a** (0.10 g, 0.42 mmol), CH_2Cl_2 (20 mL) was added via a syringe. The mixture was stirred for 30 h at room temperature. The solution turned from red to deep green. The mixture was filtered through Celite. Further purification was performed by three successive precipitations from CH_2Cl_2/hexane. The deep green powder was filtered and washed with ether (5 mL) and hexane (10 mL) and then dried under vacuum to afford **2a** (0.26 g, 83%). Spectroscopic data of **2a** are as follows. ^{1}H NMR ($CDCl_3$): δ 8.92 (s, 1H, ═CH), 7.35−7.13 (m, 30H, Ph), 5.21 (m, 2H, Cp_{Fc}), 4.90 (m, 2H, Cp_{Fc}), 4.86 (s, 5H, Cp_{Fc}), 4.17 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 269.4 (t, $^2J_{P-C}$ = 19.7 Hz, C_α), 180.4 (C_β), 153.8 (C_γ), 135.8−128.2 (Ph), 91.7 (Cp), 72.9, (5C, Cp_{Fc}), 90.7, 79.0, 76.3 (Cp_{Fc}). ^{31}P NMR ($CDCl_3$): δ 48.1 (s, PPh_3), −143.62 (heptet, $^1J_{P-F}$ = 712.7 Hz, PF_6). ESI-MS (m/z): 913.1 (M^+). Anal. Calcd for $C_{54}H_{45}F_6FeP_3Ru$: C, 61.32; H, 4.29. Found: C, 61.16; H, 4.39.

Synthesis of [Ru′]═C═C═CH(Fc)[PF_6] (2a′). Complex **2a′** was similarly prepared from [Ru']Cl (1.01 g, 1.66 mmol), NH_4PF_6 (0.55 g, 3.33 mmol), and **1a** (0.48 g, 1.99 mmol) in methanol (20 mL) for 60 h at room temperature. The deep green powder was dried under vacuum to afford **2a′** (1.06 g, 81%). Spectroscopic data of **2a′** are as follows. ^{1}H NMR ($CDCl_3$): δ 8.07 (s, 1H, ═CH), 7.56−7.11 (m, 30H, Ph), 5.21 (s, 5H, Cp), 4.95 (m, 2H, Cp_{Fc}), 4.43 (m, 2H, Cp_{Fc}), 3.95 (s, 5H, Cp_{Fc}), 2.96−2.92 (m, 4H, dppe). ^{13}C NMR ($CDCl_3$): δ 270.9 (t, $^2J_{P-C}$ = 19.2 Hz, C_α), 180.4 (C_β), 151.0 (C_γ), 138.3−128.3 (Ph), 89.7 (Cp), 72.2 (5C, Cp_{Fc}), 77.9, 68.9, 66.4 (Cp_{Fc}), 29.0 (dppe). ^{31}P NMR ($CDCl_3$): δ 82.9 (s, dppe). ESI-MS (m/z): 787.4 (M^+). Anal. Calcd for $C_{44}H_{39}F_6FeP_3Ru$: C, 56.73; H, 4.22. Found: C, 56.79; H, 4.02.

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Synthesis of [Ru]=C=C=C(Fc)(Ph)[PF$_6$] (2b). Complex **2b** (0.15 g, 65% yield) was similarly prepared from [Ru]Cl (0.25 g, 0.34 mmol), NH_4PF_6 (0.17 g, 1.04 mmol), and **1b** (0.22 g, 0.70 mmol). Spectroscopic data of **2b** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.56−7.05 (m, 35H, Ph), 5.34 (m, 2H, Cp_{Fc}), 5.20 (m, 2H, Cp_{Fc}), 4.92 (s, 5H, Cp), 4.29 (s, 5H, Cp_{Fc}). ^{13}C NMR ($CDCl_3$): δ 263.2 (C_α), 182.3 (C_β), 166.0 (C_γ), 143.2−128.1 (Ph), 91.5, 78.8, 73.6 (Cp_{Fc}), 73.4 (5C, Cp_{Fc}). ^{31}P NMR ($CDCl_3$): δ 47.2 (s, PPh_3), −144.03 (heptet, $^1J_{P-F}$ = 712.7 Hz, PF_6). IR (CH_2Cl_2): ν 1946 cm^{-1} (ν(C=C=C)). Anal. Calcd for $C_{60}H_{49}F_6FeP_3Ru$: C, 63.56; H, 4.36. Found: C, 63.33; H, 4.24.

Synthesis of [Ru]C≡CCH(Fc)CH$_2$CH=CH$_2$ (3a). A 20 mL THF solution of **2a** (0.20 g, 0.22 mmol) was treated with allylmagnesium bromide (0.43 mL, 1 M, 0.43 mmol) at room temperature. The solution turned from deep green to brown immediately, and then 2 mL of water was added to quench the reaction. The resulting solution became brown-green and was dried under vacuum. The solid residue was extracted by diethyl ether, and then the filtered solution was washed with two portions of water. The combined organic extracts were dried over $MgSO_4$ and then filtered. The solid $MgSO_4$ was washed with diethyl ether until the solvent was colorless, and the solvent of the combined extracts was removed by rotary evaporation. Further purification was performed by flash neutral aluminum oxide chromatography (CH_2Cl_2−hexane 2:1) to give **3a** as a yellow powder (0.14 g, 67%). Spectroscopic data of **3a** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.48−7.04 (m, 30H, Ph), 5.91 (m, 1H, =CH), 4.89 (d, $^3J_{H-H}$ (trans) = 17.7 Hz, 1H, =CH$_2$), 4.79 (d, $^3J_{H-H}$ (cis) = 10.2 Hz, 1H, =CH$_2$), 4.43 (m, 1H, CH of Cp_{Fc}), 4.35 (m, 1H, CH of Cp_{Fc}), 4.25 (s, 5H, Cp_{Fc}), 4.19 (s, 5H, Cp), 4.14 (m, 1H, CH of Cp_{Fc}), 4.03 (m, 1H, CH of Cp_{Fc}), 3.69 (m, 1H, C(Fc)(H)), 2.42−2.30 (m, 2H, CH$_2$ of allyl). ^{13}C NMR ($CDCl_3$): δ 139.7−127.0 (Ph), 139.0 (=CH), 114.2 (=C), 112.0 (C_β), 91.8 (t, $^2J_{C-P}$ = 24.8 Hz, C_α), 85.0 (Cp), 68.6 (5C, Cp_{Fc}), 69.4, 68.3, 66.9, 66.7, 66.5 (Fc), 43.3 (C_γ), 35.7 (CH_2). ^{31}P NMR ($CDCl_3$): δ 51.3, 51.1 (two d, $^2J_{P-P}$ = 38.2 Hz). MS (ES): m/z 955.2 (M$^+$). Anal. Calcd for $C_{57}H_{50}FeP_2Ru$: C, 71.77; H, 5.28. Found: C, 71.62; H, 5.49.

Synthesis of [Ru′]C≡CCH(Fc)CH$_2$CH=CH$_2$ (3a′). Complex **3a′** (0.13 g, 62% yield) was similarly prepared from **2a′** (0.20 g, 0.25 mmol) and allylmagnesium bromide (0.40 mL, 1 M, 0.40 mmol). Spectroscopic data of **3a′** are as follows. ^{1}H NMR ($CDCl_3$): δ 8.03−7.27 (m, 30H, Ph), 5.49 (m, 1H, =CH), 4.81 (s, 5H, Cp), 4.70 (m, 1H, =CH$_2$), 4.65 (d, 1H, =CH$_2$), 4.00 (s, 5H, Cp_{Fc}), 3.90, 3.89, 3.78, 3.77 (m, 4 × 1H, CH of Cp_{Fc}), 3.05 (m, 1H, CH(Fc)), 2.78−2.33 (m, 4H, dppe), 1.89−1.68 (m, 2H, CH$_2$ of allyl). ^{13}C NMR ($CDCl_3$): δ 143.3−127.3 (Ph), 138.9 (=CH), 113.6 (=C), 110.0 (C_β), 92.9 (t, $^2J_{C-P}$ = 26.0 Hz, C_α), 82.0 (Cp), 68.5 (5C, Cp_{Fc}), 68.4, 67.7, 66.5, 66.3, 66.1 (Fc), 43.6 (C_γ), 35.1 (CH_2), 27.8 (m, dppe). ^{31}P NMR ($CDCl_3$): δ 87.9, 87.5 (two d, J_{P-P} = 20.8 Hz). Anal. Calcd for $C_{47}H_{44}FeP_2Ru$: C, 68.20; H, 5.36. Found: C, 68.39; H, 5.41.

Synthesis of [Ru]C≡CC(Fc)(Ph)CH$_2$CH=CH$_2$ (3b). Complex **3b** (0.15 g, 72% yield) was similarly prepared from **2b** (0.20 g, 0.20 mmol) and allylmagnesium bromide (0.30 mL, 1 M, 0.30 mmol). Spectroscopic data of **3b** are as follows. ^{1}H NMR (C_6D_6): δ 7.96−6.83 (m, 35H, Ph), 6.08 (m, 1H, =CH), 4.99 (d, J_{H-H} = 17.3 Hz, 1H, =CH$_2$), 4.82 (d, J_{H-H} = 10.4 Hz, 1H, =CH$_2$), 4.43 (s, 5H, Cp), 4.33, 4.21, 4.13 (m, 3 × 1H, CH of Cp_{Fc}), 4.10 (s, 5H, Cp_{Fc}), 3.96 (m, 1H, CH of Cp_{Fc}), 3.18 (m, 2H, CH$_2$ of allyl). ^{13}C NMR (C_6D_6): δ 153.5−124.3 (Ph), 138.8 (=CH), 115.2 (=C), 113.4 (C_β), 93.9 (t, $^2J_{C-P}$ = 23.8 Hz, C_α), 85.6 (Cp), 69.2 (5C, Cp_{Fc}), 68.6, 67.5, 62.2, 66.7, 66.1 (Fc), 50.3 (C_γ), 35.7 (CH_2). ^{31}P NMR (C_6D_6): δ 50.9, 50.3 (two d, J_{P-P} = 37.8 Hz). Anal. Calcd for $C_{63}H_{54}FeP_2Ru$: C, 73.47; H, 5.28. Found: C, 73.62; H, 5.03.

Synthesis of [Ru]C≡CCH(Fc)CH$_2$C≡CH (3e). Complex **3e** (0.14 g, 68% yield) was similarly prepared from **2a** (0.20 g, 0.22 mmol) and propargylmagnesium bromide (0.80 mL, 0.5 M, 0.40 mmol). Spectroscopic data of **3e** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.49−7.06 (m, 30H, Ph), 4.52 (m, 1H, CH of Cp_{Fc}), 4.28 (m, 1H, CH of Cp_{Fc}), 4.27 (s, 5H, Cp), 4.21 (s, 5H, Cp_{Fc}), 4.06, 4.05 (m, 2 × 1H, CH of Cp_{Fc}), 3.88 (m, 1H, CH(Fc)), 2.47−2.39 (m, 2H, CH$_2$), 1.92 (t, $^4J_{H-H}$ = 2.4 Hz, 1H, ≡CH). ^{13}C NMR ($CDCl_3$): δ 134.1−127.1 (Ph), 110.9 (C_β), 94.1 (t, $^2J_{C-P}$ = 24.4 Hz, C_α), 93.2 (≡C), 85.0 (Cp), 84.8 (≡CH), 69.3, 68.9 (5C, Cp_{Fc}), 68.4, 67.5, 67.0, 66.8 (Fc), 35.2 (C_γ), 29.2 (CH_2). ^{31}P NMR ($CDCl_3$): δ 51.3 (s). Anal. Calcd for $C_{57}H_{48}FeP_2Ru$: C, 71.92; H, 5.08. Found: C, 71.77; H, 4.92.

Synthesis of [Ru]=C=CHCH(Fc)CH$_2$CH=CH$_2$[BF$_4$] (4a). A Schlenk flask was charged with **3a** (0.10 g, 0.10 mmol) in diethyl ether (15 mL) under nitrogen. Then HBF_4 (54% in diethyl ether) was added drop by drop at 0 °C to the solution. Immediately, green precipitates formed, and the addition of HBF_4 was continued until no further solid was formed. The precipitates were filtered, washed with diethyl ether (3 × 10 mL), and dried under vacuum to give a brown-yellow powder of **4a** (0.08 g, ca. 77%) with a trace amount of **5a** revealed by NMR. Spectroscopic data of **4a** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.50−6.97 (m, 30H, Ph), 6.12 (m, 1H, =CH), 5.32 (m, 1H, =CH$_2$), 5.28 (m, 1H, =CH$_2$), 5.13 (s, 5H, Cp), 4.69 (m, 1H, =CH), 4.24 (m, 1H, CH of Cp_{Fc}), 4.19 (m, 1H, CH of Cp_{Fc}), 4.14 (m, 1H, CH of Cp_{Fc}), 4.08 (s, 5H, Cp_{Fc}), 3.95 (m, 1H, CH of Cp_{Fc}), 3.42 (m, 1H, C(Fc)(H)), 2.83−2.36 (m, 2H, CH$_2$ of allyl). ^{31}P NMR ($CDCl_3$): δ 45.0, 43.5 (two d, $^2J_{P-P}$ = 26.6 Hz). ESI MS (m/z): 955.19 (M$^+$ − BF_4). Anal. Calcd for $C_{57}H_{51}BF_4FeP_2Ru$: C, 65.72; H, 4.93. No elemental analysis was carried out for **4a**, since the sample is contaminated with a trace amount of **5a**.

Synthesis of [Ru′]=C=CHCH(Fc)CH$_2$CH=CH$_2$[BF$_4$] (4a′). Complex **4a′** (0.17 g, ca. 84% yield) was similarly prepared from **3a′** (0.20 g, 0.24 mmol) and HBF_4 (54% in diethyl ether). Spectroscopic data of **4a′** are as follows. ^{31}P NMR ($CDCl_3$): δ 79.1, 79.0 (two d, $^2J_{P-P}$ = 19.5 Hz). ESI MS (m/z): 829.1 (M$^+$ − BF_4). Anal. Calcd for $C_{47}H_{45}BF_4FeP_2Ru$: C, 61.66; H, 4.95. No elemental analysis was carried out for **4a′**, since the sample is contaminated with **5a′**.

Synthesis of [Ru]=C=CHC(Fc)(Ph)CH$_2$CH=CH$_2$[BF$_4$] (4b). Complex **4b** (0.16 g, 80% yield) was similarly prepared from **3b** (0.20 g, 0.19 mmol) and HBF_4 (54% in diethyl ether). Spectroscopic data of **4b** are as follows. ^{31}P NMR (C_6D_6): δ 43.5, 43.1 (2 d, $^2J_{P-P}$ = 26.8 Hz). ESI MS (m/z): 1031.2 (M$^+$ − BF_4). Anal. Calcd for $C_{63}H_{55}BF_4FeP_2Ru$: C, 67.69; H, 4.96. No elemental analysis was carried out for **4b**, since the sample is contaminated with **5b**.

Synthesis of [Ru]=C=CHCH(Fc)CH$_2$C≡CH[BF$_4$] (4e). Complex **4e** (0.08 g, 84% yield) was similarly prepared from **3e** (0.10 g, 0.11 mmol) and HBF_4 (54% in diethyl ether). Spectroscopic data of **4e** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.39−6.99 (m, 30H, Ph), 5.18 (s, 5H, Cp), 4.74 (d, $^3J_{H-H}$ = 9.5 Hz, 1H, =CH), 4.15, 4.14 (m, 2 × 1H, CH of Cp_{Fc}), 4.06 (s, 5H, Cp_{Fc}), 3.98, 3.91 (m, 2 × 1H, CH of Cp_{Fc}), 3.54 (m, 1H, C(Fc)(H)), 2.89−2.59 (m, 2H, CH$_2$ of allyl), 2.39 (t, $^4J_{H-H}$ = 2.1 Hz, 1H, ≡CH). ^{31}P NMR ($CDCl_3$): δ 44.9, 43.3 (two d, $^2J_{P-P}$ = 26.4 Hz). Anal. Calcd for $C_{57}H_{49}BF_4FeP_2Ru$: C, 65.85; H, 4.75. Found: C, 66.07; H, 5.01.

Synthesis of [Ru]=C=CHCH$_2$CH(Fc)(OH)][PF$_6$] (5c). A Schlenk flask was charged with [Ru]Cl (0.27 g, 0.37 mmol), **1c** (0.10 g, 0.39 mmol), and NH_4PF_6 (0.26 g, 1.59 mmol) under nitrogen. Then 20 mL of methanol was added via a syringe. The solution was stirred for 12 h at room temperature, and the solution turned from orange to yellow. When the reaction ended, a light yellow powder was formed as a precipitate, and the precipitate was filtered, washed with methanol (3 × 10 mL), and dried under vacuum to give a light yellow powder of **5c** (0.25 g, 72%). Spectroscopic data of **5c** are as follows. ^{1}H NMR (CD_2Cl_2): δ 7.47−6.89 (m, 30H, Ph), 4.86 (s, 5H, Cp), 4.44 (m, 1H, =CH), 4.27 (m, 1H, CH of Cp_{Fc}), 4.24 (m, 1H, OH), 4.11 (m, 1H, CH of Cp_{Fc}), 4.11 (s, 5H, Cp_{Fc}), 3.95, 3.52 (m, 2 × 1H, CH of Cp_{Fc}), 3.34 (m, 1H, CH(Fc)), 2.34−1.87 (m, 2H, CH$_2$). ^{13}C NMR (CD_2Cl_2): δ 295.1 (t, $^2J_{P-c}$ = 13.7 Hz, C_α),

136.9−128.5 (Ph), 96.2 (C_β), 91.5 (Cp), 80.2 (COH), 71.0, 70.3, 70.1, 66.6, 62.1 (Fc), 69.4 (5C, Cp_{Fc}), 28.2 (CH_2). ^{31}P NMR (CD_2Cl_2): δ 47.0, 46.7 (two d, $^2J_{P-P}$ = 29.6 Hz). ESI MS (m/z): 945.1 ($M^+ - PF_6$). Anal. Calcd for $C_{55}H_{49}F_6FeOP_3Ru$: C, 60.62; H, 4.53. Found: C, 60.47; H, 4.79.

Synthesis of [Ru]=C=CHCH$_2$CH(Fc)(OMe)[PF$_6$] (5d). A Schlenk flask was charged with [Ru]Cl (0.15 g, 0.20 mmol), **1d** (0.05 g, 0.19 mmol), and NH_4PF_6 (0.15 g, 0.92 mmol) under nitrogen. Then 20 mL of methanol was added via a syringe. The solution was stirred for 12 h at room temperature, and the solution turned from orange to yellow. When the reaction ended, a light yellow powder was formed as a precipitate, which was filtered, washed with methanol (3 × 10 mL), and dried under vacuum to give a light yellow powder of **5d** (0.13 g, 66%). Spectroscopic data of **5d** are as follows. ^1H NMR (CD_3CN): δ 7.46−7.10 (m, 30H, Ph), 5.11 (s, 5H, Cp), 4.89 (m, 1H, =CH), 4.28, 4.23, 4.22, 4.12 (m, 4 × 1H, CH of Cp_{Fc}), 4.03 (s, 5H, Cp_{Fc}), 4.02 (m, 1H, CH(Fc)), 3.38 (s, 3H, OMe), 2.94−2.68 (m, 2H, CH_2). ^{31}P NMR (CD_3CN): δ 44.8, 44.4 (2 d, $^2J_{P-P}$ = 29.6 Hz). ESI MS (m/z): 959.0 ($M^+ - PF_6$). Anal. Calcd for $C_{56}H_{51}F_6FeOP_3Ru$: C, 60.93; H, 4.66. Found: C, 60.79; H, 4.54.

Synthesis of [Ru]C≡CCH$_2$CH(Fc)CH=CH$_2$ (6a). A Schlenk flask was charged with **4a** (0.10 g, 0.10 mmol) in methanol (10 mL). The solution was stirred for 2 days at room temperature. Then NaOMe was added to the solution. A brown precipitate was formed immediately. The mixture was stirred for 30 min. Then the solution was dried under vacuum, and CH_2Cl_2 was added to extract the product. The combined extract solution was filtered through Celite. The filtrate was dried under vacuum. The solid was washed with methanol (3 mL) and dried under vacuum to afford **6a** (0.08 g, 82%). Spectroscopic data of **6a** are as follows. ^1H NMR ($CDCl_3$): δ 7.51−7.06 (m, 30H, Ph), 6.07 (m, 1H, =CH), 4.93 (m, 1H, =CH_2), 4.89 (m, 1H, =CH_2), 4.21 (s, 5H, Cp), 4.19, 4.13 (m, 2 × 1H, CH of Cp_{Fc}), 4.11 (s, 5H, Cp_{Fc}), 4.04, 4.02 (m, 2 × 1H, CH of Cp_{Fc}), 3.05 (m, 1H, CH(Fc)), 2.87−2.67 (m, 2H, CH_2 of allyl). ^{31}P NMR ($CDCl_3$): δ 51.1 (s, PPh_3). Anal. Calcd for $C_{57}H_{50}FeP_2Ru$: C, 71.77; H, 5.28. Found: C, 71.92; H, 5.19.

Synthesis of [Ru′]C≡CCH$_2$CH(Fc)CH=CH$_2$ (6a′). Complex **6a′** (0.16 g, 81%) was similarly prepared from **4a′** (0.20 g, 0.24 mmol). Spectroscopic data of **6a′** are as follows. ^1H NMR (CD_3COCD_3): δ 8.00−7.28 (m, 30H, Ph), 5.53 (m, 1H, =CH), 4.68 (s, 5H, Cp), 4.58 (m, 1H, =CH_2), 4.53 (m, 1H, =CH_2), 3.97 (s, 5H, Cp_{Fc}), 3.91, 3.79, 4.76, 4.74 (m, 4 × 1H, CH of Cp_{Fc}), 2.50−2.32 (m, 4H, dppe), 2.20 (m, 1H, CH(Fc)), 1.76−1.60 (m, 2H, CH_2 of allyl). ^{31}P NMR (CD_3COCD_3): δ 87.1, 86.9 (2 d, J_{P-P} = 22.1 Hz). Anal. Calcd for $C_{47}H_{44}FeP_2Ru$: C, 68.20; H, 5.36. Found: C, 67.97; H, 5.49.

Synthesis of Complex 7a. A Schlenk flask was charged with **4a** (0.10 g, 0.10 mmol) in dried CH_2Cl_2 (10 mL) under nitrogen. The solution was stirred for 1 week at room temperature. The solution changed from brown to red. Then, the solution was concentrated to 2 mL under vacuum, and to the resulting solution was added diethyl ether to give a precipitate, which was filtered. Further purification was performed by flash neutral aluminum oxide chromatography (CH_2Cl_2−acetone 2:1) to give a red-brown powder of **7a** (0.07 g, 70%). Spectroscopic data of **7a** are as follows. ^1H NMR ($CDCl_3$): δ 7.66−6.94 (m, 30H, Ph), 5.89 (m, 1H, =CH), 5.13 (s, 5H, Cp), 5.06 (m, 1H, =CH_2), 5.02 (m, 1H, =CH_2), 4.27, 4.21 (m, 2 × 1H, CH of Cp_{Fc}), 4.17, 4.06 (m, 2 × 2H, CH of Cp_{Fc}), 4.02, 3.81 (m, 2 × 1H, CH of Cp_{Fc}), 2.89 (m, 1H, CH(Fc)), 2.54−2.51 (m, 2H, CH_2 of allyl). ^{13}C NMR ($CDCl_3$): δ 344.6 (t, $^2J_{P-C}$ = 15.2 Hz, C_α), 139.7 (=CH), 134.5−128.2 (Ph), 119.8 (C_β), 115.2 (=CH_2), 94.1 (Cp), 87.3, 78.6, 70.8, 70.7, 70.2, 69.6, 69.5, 69.2, 68.3, 67.5 (Fc), 40.2 (CH(Fc)), 39.5 (CH_2). ^{31}P NMR ($CDCl_3$): δ 43.5, 42.8 (2 d, $^2J_{P-P}$ = 27.2 Hz). ESI MS (m/z): 953.17 ($M^+ - BF_4$). Anal. Calcd for $C_{57}H_{49}BF_4FeP_2Ru$: C, 65.85; H, 4.75. Found: C, 66.15; H, 4.94.

Synthesis of Complex 7b. Complex **4b** (0.10 g, 0.10 mmol) was dissolved in dried CH_2Cl_2 (10 mL) under nitrogen in a Schlenk flask. The solution was stirred at room temperature for 1 week. The solution changed from brown to red. Then, the solution was concentrated to 2 mL under vacuum, and the resulting solution was purified by precipitation from CH_2Cl_2−diethyl ether. Further purification was performed by flash column chromatography using neutral aluminum oxide with CH_2Cl_2−acetone 2:1 as eluent. A red powder identified as **7b** (0.06 g) was obtained in 64% yield. The reaction with no fluorescent light gave no isolable product. For **7b**, two isomers are observed in the ^{31}P NMR spectrum, giving two AB patterns in a 2:1 ratio. For the NMR monitoring reaction carried out in CD_2Cl_2, an intermediate showing a ^{31}P singlet resonance at δ 43.8 attributed to **5b** was observed. Single crystals of the major isomer were obtained by vapor diffusion of ether into a solution of **7b** in CH_2Cl_2 at −5 °C. Attempts to get the pure minor isomer failed. Spectroscopic data of **7b** are as follows. Major isomer: ^1H NMR ($CDCl_3$) δ 7.50−6.68 (m, 35H, Ph), 6.28 (dd, $^3J_{H-H}$(trans) = 17.0 Hz, $^3J_{H-H}$(cis) = 10.5 Hz, 1H, =CH), 5.26 (d, $^3J_{H-H}$(cis) = 10.7 Hz, 1H, =CH_2), 5.09 (br, 6H, =CH_2, Cp), 4.28 (m, 2H, CH of Cp_{Fc}, CH_2), 4.25 (s, 5H, Cp of Fc), 4.16 (d, 1H, $^3J_{H-H}$ = 2.24 Hz, CH of Cp_{Fc}), 3.81 (d, 1H, $^3J_{H-H}$ = 2.29 Hz, CH of Cp_{Fc}), 2.82 (d, 1H, $^2J_{H-H}$ = 13.0 Hz, CH_2); ^{31}P NMR ($CDCl_3$) δ 45.8, 42.9 (two d, $^2J_{P-P}$ = 26.2 Hz). The minor isomer was only observed in NMR: ^1H NMR ($CDCl_3$) δ 7.50−6.68 (m, 35H, Ph), 5.79 (dd, $^3J_{H-H}$(trans) = 16.7 Hz, $^3J_{H-H}$(cis) = 10.0 Hz, 1H, =CH), 5.04 (s, 5H, Cp), 4.88 (d, $^3J_{H-H}$(cis) = 10.8 Hz, 1H, =CH_2), 4.58 (d, $^3J_{H-H}$(trans) = 17.5 Hz, 1H, =CH_2), 4.29−4.01 (m, 4H, CH_2, CH of Cp_{Fc}), 3.91 (s, 5H, Cp), 2.71 (d, 1H, $^2J_{H-H}$ = 13.4 Hz, CH_2); ^{31}P NMR ($CDCl_3$) δ 46.1, 42.6 (two d, $^2J_{P-P}$ = 26.4 Hz). ESI MS (m/z): 1029.20 ($M^+ - BF_4$). Anal. Calcd for the major isomer, $C_{63}H_{53}BF_4FeP_2Ru$: C, 67.82; H, 4.79. Found: C, 67.69; H, 5.01.

Single-Crystal X-ray Diffraction Analysis of 7b. Single crystals of the major isomer of **7b** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.20 × 0.15 × 0.10 mm^3 was glued to a glass fiber and mounted on an SMART CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube Mo Kα radiation (T = 295 K). The exposure time was 5 s per frame. SADABS[27] (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL[28] program. The structure was solved using direct methods and confirmed by Patterson methods refined on intensities of all data to give R1 = 0.0568 and wR2 = 0.1291 for 13 493 unique observed reflections ($I > 2\sigma(I)$). Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times those for the atoms to which the hydrogens are attached and 1.5 times those for the methyl hydrogens.

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Supporting Information Available: A CIF file giving complete crystallographic data for **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

(27) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

(28) *SHELXTL: Structure Analysis Program, version 5.04*; Siemens Industrial Automation Inc., Madison, WI, 1995.