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Preparation of Dinuclear Vinylidene Complexes and Their New Deprotonation Reactions

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The dinuclear dicationic vinylidene complex $\{[Ru]{=}C{=}C(Ph)CH_2C(CH_2CN){=}C{=}[Ru]\}^{2+}$ (**7a**, [Ru] = $Cp(PEt_3)_2Ru$) is prepared from the reaction of ICH_2CN with $\{[Ru]{=}C{=}C(Ph)CH_2C{\equiv}C[Ru]\}^{+}$ (**6a**). Deprotonation of **7a** by n-Bu_4NOH is followed by a cyclization process yielding the stable complex **9a**, containing a five-membered carbocyclic ring ligand, which is fully characterized by 2D-NMR analysis and a single-crystal X-ray diffraction analysis. Similarly deprotonation of $\{[Ru]{=}C{=}C(Ph)CH_2C(CH_2COOEt){=}C{=}[Ru]\}^{2+}$ (**8a**) gave the stable product **11a** containing a bridging ligand also with a similar five-membered carbocyclic ring. The cyclization process is affected by an ancillary ligand on the Ru metal center. Thus the analogous dinuclear complex **9b**, with a bistriphenylphosphine ligand on one metal, which is prepared in a similar manner from $\{[Ru]{=}C{=}C(Ph)CH_2C(CH_2CN){=}C{=}[Ru']\}^{2+}$ (**7b**, [Ru′] = $Cp(PPh_3)_2Ru$), is unstable, undergoing isomerization to give the dinuclear complex **10b**, containing a cyclopropenyl ligand.

Introduction

The stabilization of vinylidene[1] upon coordination to a metal center[2] is now a common feature experienced with many transition metals, and chemical properties of metal vinylidene complexes[3] are valuable for novel organic transformations. For example formation of a metal vinylidene intermediate[4] has been used to promote various carbon−carbon bond forming reactions by the addition of a nucleophilic carbon center to the electrophilic vinylidene α-carbon atom. Vinylidene complexes of various metals also function as strategic intermediates[5] for the catalytic conversion of alkynes such as cycloaromatization of conjugated enediynes,[6] the dimerization of terminal alkynes,[7] and the addition of oxygen, nitrogen, and carbon nucleophiles to alkynes.[8] Therefore the synthesis and reactivity of these unsaturated ligands, particularly the ruthenium vinylidene system,[9] are nevertheless under active investigation.[10] While the reactivity of mononuclear vinylidene complexes finds their applications, studies on dinuclear metal complexes with highly unsaturated carbon-rich ligands such as acetylide, vinylidene, and allenylidene have focused more or less on the electron-transfer phenomena mediated by a conjugated bridging ligand.[11] A collection of linkers such as conjugated carboxylates,[12] polyaromatics,[11] polyynes,[13−15] polyenes,[16] or polypyridyl complexes[17] have been used for prospective applications such as molecular wires,[18] dyes,[19] unusual magnetic[20] or nonlinear optical[21] properties, and quantum cell automata.[22] We previously reported the synthesis of a number of mononuclear ruthenium cyclopropenyl complexes[23] by a deprotonation reaction of readily accessible ruthenium vinylidene complexes containing

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a $-CH_2R$ group bound to C_β of the vinylidene ligand. In a slightly different vinylidene system containing a pendant $-CPh_2CH_2CH{=}CH_2$ group bound to C_β of the vinylidene ligand, the ruthenium vinylidene complex displays novel intramolecular metathesis reactivity between the two C=C double bonds.[24] Encouraged by the rich chemistry of ruthenium vinylidene complexes, we set to explore the chemical reactivity of dinuclear bisvinylidene complexes. Since relatively few dinuclear complexes with an odd-numbered carbon bridge have been obtained,[25,26] we therefore started with dinuclear complexes with an unsaturated five-carbon bridge. Herein we report the synthesis of dinuclear vinylidene complexes of ruthenium and osmium and their novel deprotonation reactions.

Results and Discussion

Synthesis of Dinuclear Ruthenium Vinylidene Complexes. The reported preparation of ruthenium acetylide complexes[27] is modified to obtain $[M]-C{\equiv}C-Ph$ (**3a**, $[M] = Cp(PEt_3)_2Ru$; **3c**, $[M] = Cp(PPh_3)_2Os$) in high yield. Treatment of $[M]-Cl$ (**1a**, $[M] = Cp(PEt_3)_2Ru$) with phenylacetylene in the presence of KPF_6 in methanol afforded $\{[M]{=}C{=}C(H)Ph\}PF_6$ (**2a**, $[M] = Cp(PEt_3)_2Ru$), and then deprotonation of **2a** by MeONa yielded complex **3a** as a yellow solid. Complex **3c** was similarly obtained from $Cp(PPh_3)_2OsCl$ (**1c**). Alkylations of acetylide complexes **3a** and **3c** readily gave vinylidene complexes. Thus, the reaction of **3a** with $HC{\equiv}CCH_2Br$ in the presence of KPF_6 yields the air-stable cationic vinylidene complex $\{[Ru]{=}C{=}C(Ph)CH_2C{\equiv}CH\}PF_6$ (**4a**) in high yield. Similarly the osmium complex **4c** was obtained. Spectroscopic data of **4a** including ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra clearly reveal the presence of the vinylidene moiety. For example, in the ^{13}C NMR spectrum of **4a**, the typical downfield resonance of C_α appears as a triplet at δ 345.92 with $^2J_{CP} = 14.7$ Hz. The terminal alkynyl group of **4a** further reacted with $[Ru]-Cl$ to give the bisvinylidene complex **5a**, which upon deprotonation gave the alkynyl vinylidene complex $\{[Ru]{=}C{=}C(Ph)CH_2C{\equiv}C-[Ru]\}PF_6$ (**6a**, $[Ru] = Cp(PEt_3)_2Ru$) in the presence of base. Complex **6a** contains a methylene bridge between the metal vinylidene and the metal acetylide fragments. Similarly complex $\{[Ru]{=}C{=}C(Ph)CH_2C{\equiv}C-[Ru']\}PF_6$ (**6b**, $[Ru'] = Cp(PPh_3)_2Ru$) was isolated from the reaction of **4a** and $Cp(PPh_3)_2RuCl$ (**1b**) in high yield also via **5b**; see Scheme 1.

Spectroscopic data support the description of **5a**, **5b**, **6a**, and **6b**. Interestingly, in the ^{13}C NMR spectrum of **5a**, three typical downfield triplet resonances of C_α are observed at δ 344.76 with $^2J_{CP} = 15.5$ Hz, 344.44 with $^2J_{CP} = 15.1$ Hz, and 343.06 with $^2J_{CP} = 15.1$ Hz, with the former two showing half intensity. The ^{31}P NMR spectrum also displays one singlet signal at δ 37.50 and two singlet resonances with half intensity at 38.89 and 38.87, and the ^1H NMR spectrum shows a broad peak for the vinylidene proton. Low-temperature NMR data indicate that chemical shifts of these resonances are temperature dependent. Below 183 K, the singlet ^{31}P signal at δ 37.50 divides into two broad resonances at δ 37.1 and 40.2, assignable to the triethylphosphine ligands on the phenyl-substituted vinylidene portion (with coalescence temperature at 183 K), while the other two resonances merged into a broad one at δ 39.9, possibly because of lower resolution at low temperature. It is well known that vinylidene complexes of the type $M{=}C{=}CRR'$ exhibit optical isomerism like allenes, however, mostly with a low barrier for the rotation of the M−vinylidene carbon bond. By freezing the rotation, one can observe the optical isomerism.

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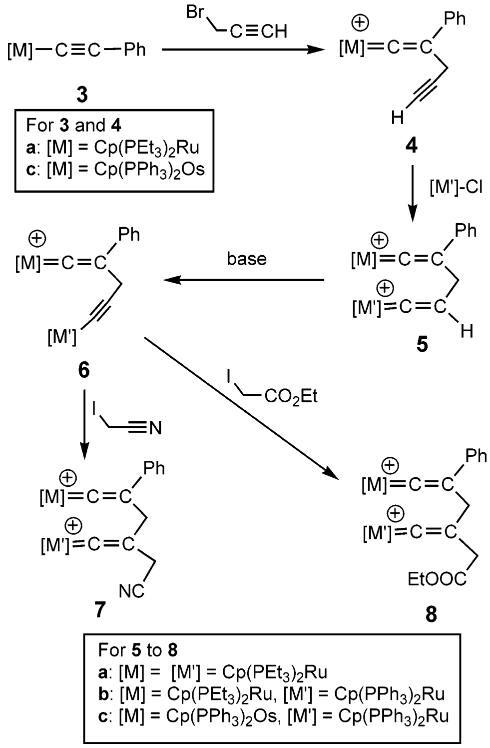
Scheme 1



Particularly for the piano-stool-type cationic ruthenium complex $CpL_2Ru{=}C{=}CRR'^+$ with two identical phosphine ligands, two coupled doublet resonances in the low-temperature ^{31}P NMR spectrum show such an isomerism. The fact that at room temperature the ^{31}P NMR spectrum of **5a** shows all singlet resonances indicates that the rotation of the Ru−vinylidene group remains fast. Temperature-dependent spectra demonstrate that only at low temperature is the fluxional process due to the rotation of the Ru vinylidene group hampered, thus showing diastereomers. Therefore, at room temperature the three C_α resonances as well as three ^{31}P singlet resonances could possibly be due to the existence of two conformational isomers in a 1:1 ratio. No such isomer was observed for **5b**. For dinuclear bisvinylidene complexes with no hydrogen on C_β (complexes **7** and **8** described below), neither do we see the existence of isomers. Thus the existence of isomers seems to require both the presence of triethylphosphine ligands on the nearby metal and the hydrogen atom on C_β of the vinylidene ligand. Since a facile tautomeric interconversion between the vinylidene and the π-bound alkynyl form is expected for the vinylidene ligand with a hydrogen atom, our observation of two species in the NMR spectra could very well be attributed to the presence of conformational isomers via the facile tautomeric interconversion. However, if the P−P couplings between phosphine ligands are negligible, this could be due to the presence of diastereomers. The $^{31}P\{^1H\}$ NMR spectrum of **6a** exhibits two singlet resonances at δ 36.03 and 48.99, with the latter one appearing in the region of the metal acetylide. In the ^{13}C NMR spectrum of **6a** only one downfield triplet resonance at δ 350.44 for C_α of the vinylidene group was observed. These data confirm the existence of both vinylidene and acetylide groups in **6a**.

Addition of base including OH^-, F^-, DBU, and MeLi to **6a** in acetone at room temperature caused no reaction, indicating that the methylene group of complex **6a** would not undergo deprotonation reaction. Complex **6a** is air-stable and decomposes in solution at 70 °C. The solid-state structure of **6b** is determined by an X-ray diffraction analysis. Single crystals of the complex **6b** suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a saturated dichloromethane solution. An ORTEP view of the molecular structure of **6b** is shown in Figure 1, with selected bond distances and angles given in Table 1. X-ray diffraction studies reveal that the dinuclear complex **6b** has vinylidene and acetylide ligands bridged by a methylene group. The Ru(1)−C(1) and C(1)−C(2) bond lengths of 1.834(5) and 1.315(6) Å, respectively, are comparable with the Ru−vinylidene distances found in other ruthenium complexes.[28] The Ru(2)−C(5) and C(4)−C(5) bond lengths are 2.030(5) and 1.201(6) Å, respectively, and are similar to the distances observed in other ruthenium acetylide complexes.[29] The C(3)−C(4)−C(5) bond angle measures 177.2(5)° and confirms the presence of the acetylide ligand on Ru(2). The remaining bond lengths and angles are normal and lie within the expected range.

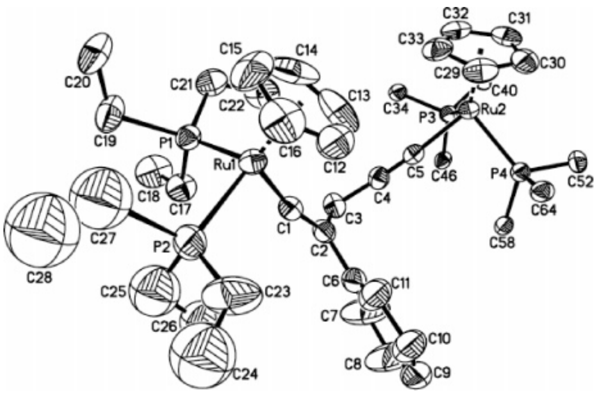


Figure 1. ORTEP plot of complex **6b** drawn at the 30% probability level. Phenyl groups on the phosphine ligands on Ru(2) have been omitted for clarity except the C(ipso) atoms.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complex 6b

Ru(1)−C(1)	1.834(5)	Ru(2)−C(5)	2.030(5)
C(1)−C(2)	1.315(6)	C(2)−C(3)	1.535(7)
C(3)−C(4)	1.463(7)	C(4)−C(5)	1.201(6)
Ru(1)−C(1)−C(2)	166.3(4)	Ru(2)−C(5)−C(4)	174.5(4)
C(1)−C(2)−C(3)	119.1(4)	C(2)−C(3)−C(4)	112.2(4)
C(3)−C(4)−C(5)	177.2(5)		

Alkylations of the two dinuclear complexes **6a** and **6b** each with ICH_2CN in CH_2Cl_2 at room temperature in the presence of KPF_6 afforded bisvinylidene complexes $\{[M]{=}C{=}C(Ph)CH_2{-}C(CH_2CN){=}C{=}[M']\}[PF_6]_2$ (**7a**, [M] = [M′] = $Cp(PEt_3)_2Ru$; **7b**, [M] = $Cp(PEt_3)_2Ru$, [M′] = $Cp(PPh_3)_2Ru$), respectively, both as pink powders. The ^{31}P NMR spectrum of **7a** displays two singlet resonances at δ 36.39 and 35.47. In the ^{13}C NMR spectrum of **7a**, typical downfield triplet resonances of C_α are observed at δ 339.45 and 338.97, both with $^2J_{CP}$ = 14.6 Hz. The corresponding downfield triplet resonances of C_α for **7b** appear at δ 342.91 with $^2J_{CP}$ = 15.2 Hz and at δ 337.96 with $^2J_{CP}$ = 14.3 Hz. Alkylation of complex **6a** with ethyl iodoacetate in CH_2Cl_2 in the presence of KPF_6 gives the bisvinylidene complex $\{[M]{=}C{=}C(Ph)CH_2C(CH_2COOEt){=}C{=}[M]\}[PF_6]_2$ (**8a**, [M] = $Cp(PEt_3)_2Ru$). In the ^1H NMR spectrum of **8a**, two singlet resonances at δ 3.75 and 3.43 and one quartet resonance at δ 4.25 are assigned to protons of three methylene groups. The ^{31}P NMR spectrum of **8a** displays two

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[28] (a) Hill, A. F.; Hulkes, A. G.; White, A. J. P.; Williams, D. J. *Organometallics* **2000**, *19*, 371. (b) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184.

[29] (a) Bruce, M. I.; Ellis, B. G.; Gaudio, M.; Lapinte, C.; Melino, G.; Paul, F.; Skelton, B. W.; Smith, M. E.; Toupet, L.; White, A. H. *Dalton Trans.* **2004**, 1601. (b) Bruce, M. I.; Hall, B. C.; Kelly, B. D.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 3719.

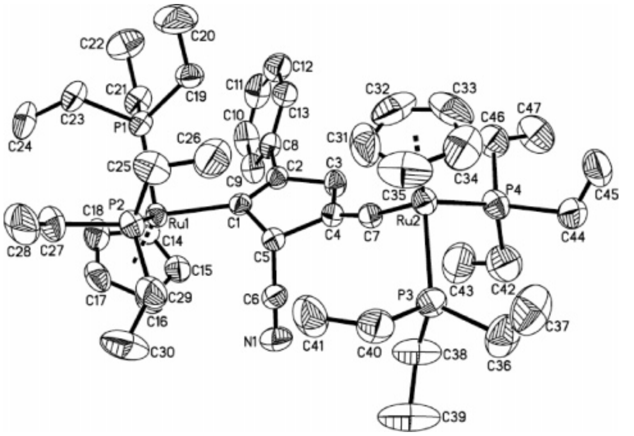
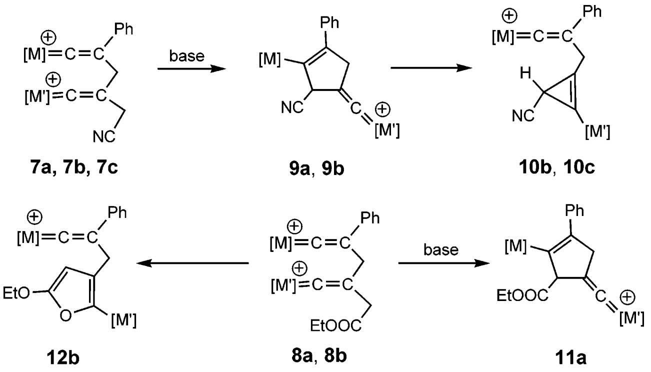


Figure 2. ORTEP plot of complex **9a** drawn at the 30% probability level.

Scheme 2



a: [M] = [M'] = Cp(PEt$_3$)$_2$Ru
b: [M] = Cp(PEt$_3$)$_2$Ru, [M'] = Cp(PPh$_3$)$_2$Ru
c: [M] = Cp(PPh$_3$)$_2$Os, [M'] = Cp(PPh$_3$)$_2$Ru

singlet resonances at δ 36.47 and 35.58. Complex **8b** is also prepared from **6b** and ethyl iodoacetate.

Deprotonation Reactions of Dinuclear Complexes. Treatment of complex **7a** with NaOMe or n-Bu$_4$NOH in acetone at room temperature afforded the air-stable complex **9a** (see Scheme 2) as a deep red powder. Deprotonation of the methylene protons near the CN group followed by a novel cyclization leads to a C−C bond formation at C$_\alpha$ of the remote Ru vinylidene group. Complex **9a**, containing a stereogenic carbon center in the five-membered ring, is characterized by ^{1}H, ^{31}P, ^{13}C, 2D-NMR, and MS spectra. The ^{1}H NMR spectrum of **9a** exhibits a set of two doublet resonances at δ 4.42 and 4.21 with $^2J_{HH}$ = 17.4 Hz corresponding to the *gem*-methylene groups. The proton resonance of the methyne group of the five-membered ring appears as a singlet peak at δ 5.08. The ^{31}P NMR spectrum of **9a**, containing a stereogenic carbon center, displays two sets of two doublet resonances at δ 39.73 and 37.88 ($^2J_{PP}$ = 32.6 Hz) and 29.77 and 29.36 ($^2J_{PP}$ = 45.9 Hz). The ^{13}C NMR spectrum displays one typical downfield triplet resonance at δ 339.81 with $^2J_{CP}$ = 15.0 Hz for C$_\alpha$. Furthermore, 2D NMR data of **9a** reveal the presence of the five-membered carbocyclic ring. In the ^{1}H,^{13}C-HMBC spectrum of **9a**, cross-peaks between the ^{1}H resonance of CH at δ 5.08 and ^{13}C resonances of other four carbocyclic carbon atoms at δ 149.34, 144.31, 121.38, and 46.26 indicated long-range C−H correlation, inferring formation of the five-membered ring. Unequivocal characterization of **9a** was performed by X-ray structure analysis. Figure 2 shows an ORTEP representation of the molecule. Selected bond distances and angles are listed in Table 2. The structure can be described as three-legged piano stool geometry for both Ru centers. The distances Ru(1)−C(1) (2.112(6) Å) and Ru(2)−C(7) (1.854(6) Å) agree with that for a single bond and a double bond, respectively.[28] The angle Ru(2)−C(7)−C(4) of 168.6(6)° involved in the vinylidene group is close to the ideal value. With respect to the cyclic bonds, C(1)−C(2) (1.350(9) Å) is clearly a double bond, while the C(1)−C(5) distance amounts to 1.557(9) Å, in agreement with its single-bond character. The distance C(1)−C(5), next to the Ru(1) moiety, is slightly greater than the other three (C(2)−C(3) 1.523(9) Å, C(3)−C(4) 1.517(9) Å, C(4)−C(5) 1.542(8) Å) and reflects the influence of the metal moiety.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complex 9a

Ru(1)−C(1)	2.112(6)	Ru(2)−C(7)	1.854(6)
C(1)−C(2)	1.350(9)	C(2)−C(3)	1.523(9)
C(3)−C(4)	1.517(9)	C(4)−C(5)	1.542(8)
C(4)−C(7)	1.280(8)	C(1)−C(5)	1.557(9)
Ru(1)−C(1)−C(2)	133.7(5)	Ru(2)−C(7)−C(4)	168.6(6)
C(1)−C(2)−C(3)	115.6(6)	C(2)−C(3)−C(4)	103.3(5)
C(3)−C(4)−C(5)	105.7(5)	C(1)−C(5)−C(4)	106.0(5)
C(2)−C(1)−C(5)	105.7(5)		

We previously reported that the deprotonation reaction of the mononuclear vinylidene complex Cp(PPh$_3$)$_2$Ru=C=C(Ph)CH$_2$CN$^+$ gave a ruthenium complex containing an unsaturated three-membered cyclopropenyl ligand.[23b] Interestingly, in the dinuclear bisvinylidene complex a different cyclization process resulted in formation of a five-membered carbocyclic ring. For comparison, the dinuclear complex **7b**, with one metal containing two triphenylphosphine ligands, was reacted with n-Bu$_4$NOH in acetone. Interestingly the reaction yielded the yellow cyclopropenyl product **10b**; see Scheme 2. The reaction proceeds via formation of a visible red intermediate during the reaction period which could be obtained by replacing the base with NaOMe. By treating the complex **7b** with 5 equiv of NaOMe in acetone for 30 min, a deep red solution showing the presence of a mixture of **9b** and **10b** in a 10:1 ratio was obtained. Complex **10b** is soluble in hexane or ether, but complex **9b** is hexane insoluble and is soluble in CH$_2$Cl$_2$. It is therefore easy to separate **9b** from the mixture. Complex **9b** is air-stable and displays a deep red color in solution but decomposes at about 80 °C. Interestingly, in the absence of base, **9b** in acetone is stable at room temperature, but in the presence of base, formation of complex **10b** is observed. Product **10b** could also be obtained from the deprotonation reaction using NaOMe with longer reaction time, i.e., when the color of the solution turns bright yellow. Extraction with ether gave **10b** in good yield as a yellow powder.

The ^{1}H NMR spectrum of complex **9b** shows two doublet resonances at δ 4.54 and 4.09 with $^2J_{HH}$ = 18.0 Hz for the methylene group. The proton of the methyne group exists as a singlet peak at δ 5.05. The ^{31}P NMR spectrum of **9b** contains four doublet resonances at δ 39.73 and 37.88 ($^2J_{PP}$ = 32.6 Hz) and δ 29.77 and 29.36 ($^2J_{PP}$ = 45.9 Hz). In the ^{13}C NMR spectrum of **9b** the triplet peak at δ 341.46 ($^2J_{CP}$ = 11.8 Hz) is attributed to the typical C$_\alpha$ of the vinylidene ligand. On the basis of these spectroscopic data the structure of **9b** is analogous to **9a**. The spectroscopic data of **10b**, including ^{1}H, ^{31}P, ^{13}C, 2D-NMR, and MS, are consistent with the structure shown in Scheme 2. For example in the ^{1}H NMR spectrum of **10b**, also containing a stereogenic carbon center in the three-memberd ring, two doublet resonances at δ 3.53 and 3.46 with $^2J_{HH}$ = 16.5 Hz are assigned to the methylene group. The stereogenic carbon center is close to the metal center with the bistriphenylphosphine ligands; therefore the ^{31}P NMR spectrum displays a singlet peak at δ 35.78 as well as resonances showing an AB pattern at δ 51.07 and 50.68 with $^2J_{PP}$ = 39.8 Hz assignable to two PEt_3 ligands and two PPh_3 ligands, respectively. It is not possible to convert **9a** to the corresponding cyclopropenyl complex. An electronic effect may play a role in the selectivity of C−C bond formation.

Deprotonation of **8a** was similarly carried out in acetone. From **8a** complex **11a** was observed in 76% NMR yield. Our attempts to isolate **11a** in pure form were unsuccessful. Even though pure complex **11a** was not obtained, NMR characterization indicated that an analogous five-membered carbocyclic ring appears in the bridging ligand. In the 2D HMBC spectrum of **11a**, a long-range C−H correlation was observed between the proton resonance of CH at δ 4.94 and the four cyclic carbon resonances at δ 152.80, 144.33, 123.56, and 47.60, indicating formation of the same five-membered ring as that in **9**. The same long-range coupling pattern was also observed in that of **9a**. Attempts to convert **11a** either to a cyclopropenyl or furyl complex led to decomposition. Interestingly, for **8b**, with two triphenylphosphine ligands, the deprotonation using Bu_4NOH gave complex **12b** in quantitative NMR yield. We could not observe any intermediate during this transformation and, again, failed to isolate complex **12b** in pure form. However, in the ^{31}P NMR spectrum of the reaction mixture, the very clean pattern with two singlet resonances at δ 49.45 and 36.49 clearly reveals formation of the furyl complex in quantitative yield. The ^{31}P resonance at δ 49.45 is in the same region as that of other Ru furyl complexes with a triphenylphosphine ligand.[23b]

On the basis of the reactivity of **7a**, **7b**, **8a**, and **8b** it could be concluded that the phosphine ligand may play a key role in determining the regiochemistry of the cyclization. With a more electron-donating ability, the triethylphosphine ligand could direct the C−C bond formation to take place at C_α of the remote vinylidene ligand. For complex **7b**, with a triphenylphosphine ligand, the less ring-strained energy of the five-membered carbocycle could stabilize the kinetic product **9b**, which eventually transforms to the thermodynamic product **10b**. A series of osmium−ruthenium vinylidene complexes **4c**, **5c**, **6c**, and **7c** all with triphenylphosphine ligands were prepared. The deprotonation of **7c** cleanly and directly gave the cyclopropenyl complex **10c**; see Scheme 2. The reaction did not give the intermediate with the five-membered-ring bridging ligand. In this system the regiochemistry of the cyclization could be readily discriminated by ^{13}C NMR data. Resonances of C_α of the vinylidene ligands for Ru and Os in **7c** appear distinctively at δ 341.51 and 302.24, respectively. The downfield resonance at δ 307.23 for **10c** indicates the presence of an Os vinylidene moiety, revealing the site of cyclization at C_α of the vinylidene ligand on Ru.

In order to check the feasibility for the formation of a cyclopropenyl and furyl complex in mononuclear system containing triethylphosphine ligands, complexes $[Ru]{=}C{=}C(Ph)CH_2R^+$ (**13**, R = CN; **14**, R = CO_2Me; [Ru] = $Cp(PEt_3)_2Ru$) are prepared from the reactions of **3a** with two organic halides, ICH_2CN and $BrCH_2CO_2Me$, respectively, in the presence of KPF_6. Spectroscopic data of **13** and **14** including ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra clearly reveal the presence of the vinylidene moiety. Complexes **13** and **14** undergo deprotonation reaction by Bu_4NOH, yielding the cyclopropenyl complex **15** and the furyl complex **16**, respectively; see Scheme 3. The mononuclear system thus displays normal cyclization. The dinuclear bisvinylidene complex containing bistriethylphosphine ligands therefore exhibits distinctive reactivity from that of the mononuclear system. A multinuclear system could possibly display even more rich chemistry.

Concluding Remark

In summary, dinuclear ruthenium and osmium vinylidene complexes containing bistriethylphosphine or bistriphenylphosphine ligands were synthesized. The deprotonation reaction of the dinuclear bisvinylidene complex **7a** was followed by a novel cyclization reaction with carbon−carbon bond formation between the deprotonated carbon and C_α of the remote vinylidene ligand, giving the dinuclear complex **9a** with a bridging ligand containing a five-membered carbocyclic ring. The deprotonation of **7b** proceeds via a similar pathway, yielding the parallel complex **9b**. However, complex **9b**, with bistriphenylphosphine ligands, is unstable in the presence of base, generating **10b** with a cyclopropenyl ring. Electronic effects of various phosphine ligands can possibly control the regiochemistry of C−C bond formation following deprotonation reactions, leading to various products. Deprotonation of dinuclear complexes with a triphenylphosphine ligand favor formation of a cyclopropenyl product as a thermodynamic product.

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 distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification. Compounds [Ru]Cl (**1a**, [Ru] = $Cp(PEt_3)_2Ru$), [Ru′]Cl (**1b**, [Ru′] = $Cp(PPh_3)_2Ru$), [Os]Cl (**1c**, [Os] = $Cp(PPh_3)_2Os$), and [Os]C≡CPh were prepared by following the methods[30] reported in the literature. Infrared spectra were recorded on a Nicolet-MAGNA-550 spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra (FAB) were recorded using a JEOL SX-102A spectrometer; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker AC-300 instrument (at 300 MHz (^1H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standard) or on a Bruker Avance 500 FT-NMR spectrometer.

Synthesis of {[Ru]=C=C(H)Ph}PF_6 (2a). To a Schlenk flask charged with **1a** (0.42 g, 0.96 mmol) and KPF_6 (0.88 g, 4.80 mmol) was added methanol (20 mL) under nitrogen. The resulting solution was stirred at room temperature, and phenylacetylene (1.05 mL, 9.60 mmol) was added. The clear solution was stirred for 1.5 h, and the color changed from orange to red. After the solvent was removed under vacuum, 30 mL of CH_2Cl_2 was added. The solution was filtered through Celite, and the volume of the solution was reduced to 5 mL under vacuum. Then 60 mL of diethyl ether was added to cause precipitation of a pink powder. After filtration, the precipitate was washed with 10 mL of diethyl ether twice and then dried under vacuum to give **2a** (0.45 g, 72% yield). ^1H NMR ($CDCl_3$): 7.35−6.90 (m, 5H, Ph), 5.54 (s, 5H, Cp), 5.33 (s, 1H, $C_\beta H$), 2.05−1.85 (m, 6H, CH_2), 1.85−1.65 (m, 6H, CH_2), 1.09−1.00 (m, 18H, CH_3). ^{13}C NMR $CDCl_3$: 351.78 (t, $^2J_{CP}$ = 15.3 Hz, C_α), 128.97−125.94 (Ph), 116.84 (C_β), 90.64 (Cp). ^{31}P NMR ($CDCl_3$): 36.92 (s, PEt_3). MS FAB *m/z*: 505.1 ($M^+ - PF_6$), 403.1 ($M^+ - PF_6 - C{=}C(H)Ph$). Anal. Calcd for $C_{25}H_{41}F_6P_3Ru$: C, 46.23; H, 6.36. Found: C, 46.62; H, 6.15.

Synthesis of [Ru]−C≡CPh (3a). To a Schlenk flask charged with **2a** (0.45 g, 0.69 mmol) was added a solution of NaOMe (2.60 g, 4.81 mmol) in methanol (10 mL). The solution was stirred at room temperature for 5 min, and the color changed from pink to yellow. The solvent was removed under vacuum. The desired product was extracted with 4 × 10 mL of diethyl ether and filtered

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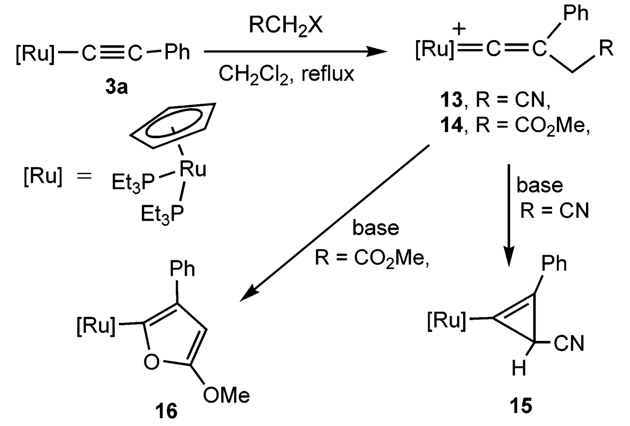
[30] (a) Tadeusz, W.; Maria, B.; Biernat, J. F. *J. Organomet. Chem.* **1981**, *215*, 87. (b) Coto, A.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4392. (c) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471.

Scheme 3



through Celite. The solvent of the filtrate was removed under vacuum to give **3a** (0.34 g, 98% yield). ^{1}H NMR (CDCl$_3$): 7.66−7.03 (m, 5H, Ph), 4.74 (s, 5H, Cp), 1.99−1.90 (m, 6H, CH$_2$), 1.37−1.29 (m, 6H, CH$_2$), 1.07−0.99 (m, 18H, CH$_3$). ^{13}C NMR (CDCl$_3$): 134.68−122.87 (Ph), 118.61 (t, $^2J_{CP}$ = 25.2 Hz, C$_\alpha$), 110.89 (C$_\beta$), 80.78 (Cp). ^{31}P NMR (CDCl$_3$): 40.24 (s, PEt$_3$). MS FAB *m/z*: 504.1(M$^+$), 403.1 (M$^+$ − C=C(H)Ph). Anal. Calcd for $C_{25}H_{40}P_2Ru$: C, 59.62; H, 8.01. Found: C, 59.61; H, 7.92.

Synthesis of {[Ru]=C=C(Ph)CH$_2$C≡CH}[PF$_6$] (4a). To a Schlenk flask charged with **3a** (0.10 g, 0.19 mmol) and KPF$_6$ (0.20 g, 1.08 mmol) in CH$_2$Cl$_2$ (10 mL) was added BrCH$_2$C≡CH (0.2 mL, 2.23 mmol) under nitrogen. The clear solution was stirred for 8 h at room temperature, and the color changed from yellow to red. Then the solution was filtered through Celite, and the volume of the filtrate was reduced to 3 mL under vacuum. Diethyl ether (50 mL) was added to cause precipitation of a pink powder. After filtration, the precipitate was washed with diethyl ether (5 mL) twice and dried under vacuum to give **4a** (0.12 g, 92% yield). ^{1}H NMR (CDCl$_3$): 7.37−7.20 (m, 5H, Ph); 5.56 (s, 5H, Cp); 3.32 (d, $^4J_{HH}$ = 2.6 Hz, 2H, CH$_2$), 2.13 (t, $^4J_{HH}$ = 2.6 Hz, 1H, ≡CH), 1.93−1.58 (m, 12H, CH$_2$), 1.04−0.92 (m, 18H, CH$_3$). ^{13}C NMR (CDCl$_3$): 345.93 (t, $^2J_{CP}$ = 14.7 Hz, C$_\alpha$), 133.49−127.61 (Ph), 123.68 (C$_\beta$), 90.50 (Cp), 82.22 (HC≡*C*), 70.53 (H*C*≡C), 17.10 (CH$_2$). ^{31}P NMR (CDCl$_3$): 36.96 (s, PEt$_3$). MS FAB *m/z*: 543.3 (M$^+$ − PF$_6$), 514.2 (M$^+$ − C$_2$H$_5$). Anal. Calcd for $C_{28}H_{43}F_6P_3Ru$: C, 48.91; H, 6.30. Found: C, 49.05; H, 6.22.

Synthesis of {[Os]=C=C(Ph)CH$_2$C≡CH}[PF$_6$] (4c). To a Schlenk flask charged with [Os]C≡CPh (0.50 g, 0.57 mmol) and KPF$_6$ (0.11 g, 0.6 mmol) were added CH$_2$Cl$_2$ (20 mL) and BrCH$_2$C≡CH (0.4 mL, 4.46 mmol) under nitrogen. The resulting solution was stirred for 8 h at room temperature. Then the solvent was removed in vacuo, and CH$_2$Cl$_2$ (2 × 5 mL) was used to extract the product. After filtration, the volume of the filtrate was reduced to ca. 5 mL. Then the filtrate was added to diethyl ether (60 mL) to yield a pale red precipitate, which was filtered, washed with diethyl ether, and recrystallized from CH$_2$Cl$_2$/hexane to give **4c** (0.60 g, 90%). ^{1}H NMR (CD$_3$COCD$_3$): 7.48−7.06 (m, 35H, Ph), 5.70 (s, 5H, Cp), 3.24 (d, $^4J_{HH}$ = 2.6 Hz, 2H, C*H$_2$*), 2.66 (t, $^4J_{HH}$ = 2.6 Hz, 1H, C*H*). ^{31}P{^{1}H} NMR (δ, d_6-acetone): −5.33 (s, PPh$_3$). MS FAB *m/z*: 1011.2 (M$^+$ − PF$_6$). Anal. Calcd for $C_{52}H_{43}F_6P_3Os$: C, 58.64; H, 4.07. Found: C, 58.72; H, 4.35.

Synthesis of {[Ru]=C=C(Ph)CH$_2$CH=C=[Ru]}[PF$_6$]$_2$ (5a). To a Schlenk flask charged with **4a** (50 mg, 0.073 mmol), KPF$_6$ (0.11 g, 0.60 mmol), and **1a** (32 mg, 0.073 mmol) was added methanol (7 mL) under nitrogen. The solution was stirred at room temperature for 19 h, and the pink precipitate was filtered off and washed with methanol (2 mL) twice and ether (10 mL), then dried under vacuum to give **5a** (72 mg, 80% yield). ^{1}H NMR (CD$_3$COCD$_3$): 7.53−7.37 (m, 5H, Ph), 5.79 (s, 5H, Cp), 5.34, (s, 5H, Cp), 4.46 (t, $^3J_{HH}$ = 8.1 Hz, 1H, =CH), 3.72 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH$_2$), 2.06−1.76 (m, 24H, CH$_2$), 1.10−0.94 (m, 36H, CH$_3$). ^{13}C NMR (CD$_3$COCD$_3$): 344.76 (t, $^2J_{CP}$ = 15.5 Hz, C$_\alpha$), 344.44 (t, $^2J_{CP}$ = 15.1 Hz, C$_\alpha$), 343.06 (t, $^2J_{CP}$ = 15.1 Hz, C$_\alpha$), 131.38−128.04 (Ph), 127.44 (C$_\beta$), 110.48 (C$_\beta$), 90.93 (Cp), 90.83 (Cp), 20.68 (CH$_2$). ^{31}P NMR (CD$_3$COCD$_3$): 38.89, 38.87 (two s, half intensity, PEt$_3$), 37.50 (s, PEt$_3$). MS FAB *m/z*: 1091.2 (M$^+$ + 1 − PF$_6^-$), 945.3 (M$^+$ + 1 − 2PF$_6^-$), 825.2 (M$^+$ + 1 − 2PF$_6^-$ − PEt$_3$), 709.2 (M$^+$ − +1 − 2PF$_6^-$ − 2PEt$_3$), 543.3 (M$^+$ − CpRu(PEt$_3$)$_2$), 441.2 (M$^+$ − CpRu(PEt$_3$)$_2$=C=C(Ph)). Anal. Calcd for $C_{45}H_{78}F_{12}P_6Ru_2$: C, 43.76; H, 6.37. Found: C, 43.80; H, 6.50.

Synthesis of {[Ru]=C=C(Ph)CH$_2$CH=C=[Ru′]}[PF$_6$]$_2$ (5b). To a Schlenk flask charged with **4a** (0.100 g, 0.146 mmol), KPF$_6$ (0.21 g, 1.14 mmol), and **1b** (0.106 g, 0.146 mmol) was added methanol (10 mL) under nitrogen. The solution was stirred at room temperature for 24 h, and the orange-pink precipitate was filtered off and washed with methanol (5 mL) twice, then dried under vacuum to give **5b** (0.182 g, 82% yield). ^{1}H NMR (CDCl$_3$): 7.59−6.86 (m, 35H, Ph); 5.51 (s, 5H, Cp); 4.75 (s, 5H, Cp), 4.54 (t, $^3J_{HH}$ = 8.1 Hz, 1H, =CH), 3.32 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH$_2$), 1.83−1.53 (m, 12H, CH$_2$), 0.96−0.85 (m, 18H, CH$_3$). ^{13}C NMR CDCl$_3$: 350.15 (t, $^2J_{C-P}$ = 13.2 Hz, C$_\alpha$), 342.00 (t, $^2J_{C-P}$ = 13.1 Hz, C$_\alpha$), 141.45−127.56 (Ph, C$_\beta$), 114.15 (C$_\beta$), 94.30 (Cp), 92.11 (Cp), 9.00−7.80 (CH$_2$). ^{31}P NMR (CDCl$_3$): 36.15 (s, PEt$_3$), 42.99 (s, PPh$_3$). MS FAB *m/z*: 1377.0 (M$^+$ + 1 − PF$_6^-$), 1233.1 (M$^+$ + 1 − 2PF$_6^-$), 1114.1 (M$^+$ + 1 − 2PF$_6^-$ − PEt$_3$), 691.1 (M$^+$ − CpRu(PEt$_3$)$_2$=C=C(Ph)CH$_2$C(H)=C), 543.1 (M$^+$ − CpRu(PPh$_3$)$_2$). Anal. Calcd for $C_{69}H_{78}F_{12}P_6Ru_2$: C, 54.40; H, 5.16. Found: C, 54.54; H, 5.48.

Synthesis of {[Os]=C=C(Ph)CH$_2$CH=C=[Ru′]}[PF$_6$]$_2$ (5c). To a Schlenk flask charged with **4c** (0.10 g, 0.09 mmol), KPF$_6$ (0.02 g, 0.10 mmol), and **1b** (0.07 g, 0.10 mmol) was added methanol (15 mL) under nitrogen. The solution was heated to reflux for 4 h. After cooling, the solvent was removed in vacuo, and CH$_2$Cl$_2$ (2 × 5 mL) was used to extract the product. The resulting solution was filtered through Celite, concentrated to ca. 5 mL, and added to diethyl ether (60 mL) to produce a purple precipitate, which was filtered, washed with diethyl ether, and dried under vacuum to give **5c** (0.14 g, 80% yield). ^{1}H NMR (CD$_3$COCD$_3$): 7.79−7.04 (m, 65H, Ph), 5.67 (s, 5H, CpOs), 4.91 (s, 5H, CpRu), 4.70 (t, $^3J_{HH}$ = 5.96 Hz, 1H, C*H*), 3.24 (d, $^3J_{HH}$ = 5.96 Hz, 2H, C*H$_2$*). ^{13}C{^{1}H} NMR CD$_3$COCD$_3$: 345.96 (t, $^2J_{CP}$ = 14.5 Hz, Ru*C*$_\alpha$), 304.62 (t, $^2J_{CP}$ = 9.7 Hz, Os*C*$_\alpha$), 135.22−128.52 (m, Ph and Ru*C*$_\beta$), 114.7 (Os*C*$_\beta$), 94.6 (*Cp*Ru), 92.3 (*Cp*Os), 15.7 (C*H$_2$*). ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$): 42.16 (s, RuPPh$_3$); −4.86 (s, OsPPh$_3$). MS FAB *m/z*: 1756.2 (M$^+$ + 1 − PF$_6^-$), 1611.2 (M$^+$ + 1 − 2PF$_6$), 1347.1 (M$^+$ + 1 − 2PF$_6$ − PPh$_3$), 1085 (M$^+$ + 1 − 2PF$_6$ − 2PPh$_3$). Anal. Calcd for $C_{93}H_{78}F_{12}P_6RuOs$: C, 58.76; H, 4.14. Found: C, 59.02; H, 4.45.

Synthesis of {[Ru]=C=C(Ph)CH$_2$C≡C−[Ru]}PF$_6$ (6a). To a Schlenk flask charged with **5a** (0.10 g, 0.081 mmol) and NaOMe (0.05 g, 0.93 mmol) was added methanol (5 mL). The solution was stirred at room temperature for 30 min, and the color changed from pink to deep yellow. The solvent was removed under vacuum and CH$_2$Cl$_2$ (2 × 5 mL) was used to extract the product. The solution was filtered through a sintered glass with Celite, then the volume of the filtrate was reduced to 3 mL and diethyl ether (50 mL) was added to cause precipitation of an orange powder. After filtration, the precipitate was washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **6a** (82 mg, 93% yield). ^{1}H NMR (CD$_3$COCD$_3$): 7.48−7.18 (m, 5H, Ph), 5.79 (s, 5H, Cp), 4.61 (s, 5H, Cp), 3.63 (s, 2H, CH$_2$), 1.96−1.88 (m, 12H, CH$_2$), 1.50−1.30 (m, 12H, CH$_2$), 1.11−0.95 (m, 36H, CH$_3$). ^{13}C NMR (CD$_3$COCD$_3$): 350.45 (t, $^2J_{CP}$ = 14.8 Hz, C$_\alpha$), 132.57−126.87 (Ph), 119.17 (C$_\beta$), 110.29 (t, $^2J_{CP}$ = 11.8 Hz, C$_\alpha$), 101.30 (C$_\beta$), 87.54 (Cp), 85.85 (Cp), 15.20 (CH$_2$). ^{31}P NMR (CD$_3$COCD$_3$): 38.88 (s, PEt$_3$), 36.03 (s, PEt$_3$). MS FAB *m/z*: 1091.3 (M$^+$ + 1), 945.3 (M$^+$ + 1 − PF$_6$), 826.2 (M$^+$ + 1 − PF$_6$ − PEt$_3$), 709.2 (M$^+$ + 1 − PF$_6$ − 2PEt$_3$),

Table 3. Crystal Data and Structure Refinement Parameters for Complexes 6b and 9a

	6b	9a
empirical formula	$C_{70}H_{79}Cl_2F_6P_5Ru_2$	$C_{47}H_{78}F_6NP_5Ru_2$
fw	1462.22	1128.09
temperature [K]	295(2)	295(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a [Å]	15.3762(2)	9.2924(2)
b [Å]	13.8246(2)	21.0916(4)
c [Å]	32.2115(5)	27.4615(4)
β [deg]	95.0360(4)	90.1850(10)
volume [Å^3], Z	6820.76(17), 4	5382.19(17), 4
ρ_{cacld} [Mg m^{-3}]	1.424	1.392
absorp coeff [mm^{-1}]	0.695	0.762
F(000)	3000	2336
cryst size [mm^3]	0.25 × 0.20 × 0.15	0.15 × 0.15 × 0.10
2θ [deg]	1.27−25.00	2.19−25.00
no. of reflns collected	37 452	29 613
no. of indep reflns	11 803	9259
R(int)	0.0391	0.0549
no. data/restraints/params	11803/0/742	9259/0/544
goodness-of-fit on F^2	1.100	1.089
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0597$, $wR_2 = 0.1679$	$R_1 = 0.0612$, $wR_2 = 0.1544$
R indices (all data)	$R_1 = 0.0734$, $wR_2 = 0.1879$	$R_1 = 0.0980$, $wR_2 = 0.1774$
largest diff peak/hole [e Å^{-3}]	0.998/−0.668	0.674/−0.583

543.3 ($M^+ - CpRu(PEt_3)_2$). Anal. Calcd for $C_{45}H_{77}F_6P_5Ru_2$: C, 49.63; H, 7.13. Found: C, 49.51; H, 7.10.

Synthesis of {[Ru]═C═C(Ph)CH$_2$C≡C−[Ru′]}PF$_6$ (6b). To a Schlenk flask charged with **5b** (0.10 g, 0.066 mmol) and NaOMe (0.05 g, 0.93 mmol) was added methanol (5 mL). The solution was stirred at room temperature under nitrogen for 30 min, yielding a yellow precipitate, which was filtered and washed with diethyl ether and dried under vacuum to give **6b** (0.079 g, 87% yield). Single crystals were grown by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution of **6b**. ^1H NMR (CD_3COCD_3): 7.56−7.09 (m, Ph); 5.75 (s, 5H, Cp); 4.18 (s, 5H, Cp), 3.73 (s, 2H, CH_2), 2.14−1.95 (m, 12H, CH_2), 1.15−1.03 (m, 18H, CH_3). ^{13}C NMR (CD_3COCD_3): 350.23 (t, $^2J_{C-P} = 15.5$ Hz, C_α), 134.61−127.01 (Ph, C_β), 107.05 (C_β), 97.80 (t, $^2J_{C-P} = 24.0$ Hz, C_α), 90.95 (Cp), 85.75 (Cp), 10.08 (CH_2). ^{31}P NMR (CD_3COCD_3): 48.99 (s, PPh_3), 36.15 (s, PEt_3). MS FAB m/z: 1232.1 ($M^+ - PF_6$), 1114.1 ($M^+ - PF_6 - PEt_3$), 970.1 ($M^+ - PF_6 - PPh_3$), 850.9 ($M^+ - PF_6 - PPh_3 - PEt_3$), 729.0 ($M^+ - PF_6 - CpRu(PEt_3)_2{=}C{=}C(Ph)$), 543.1 ($M^+ - CpRu(PPh_3)_2$), 467.0 ($M^+ - CpRu(PPh_3)_2 - Ph$). Anal. Calcd for $C_{69}H_{77}F_6P_5Ru_2$: C, 60.17; H, 5.63. Found: C, 60.05; H, 5.53.

{[Os]═C═C(Ph)CH$_2$C≡C−[Ru′]}[PF$_6$] (6c). To a Schlenk flask charged with **5c** (0.10 g, 0.05 mmol) and NaOMe (0.01 g, 0.20 mmol) was added acetone (10 mL). The resulting solution was stirred at room temperature for 30 min, and the color changed from purple to deep yellow. The solvent was removed in vacuo, and CH_2Cl_2 (2 × 5 mL) was used to extract the product. The resulting solution was filtered through Celite, concentrated to ca. 5 mL, and added to diethyl ether (60 mL) to produce a brown precipitate, which was filtered, washed with diethyl ether, and dried under vacuum to give **6c** (0.08 g, 88% yield). ^1H NMR (CD_3COCD_3): 7.46−7.04 (m, 65H, Ph), 5.62 (s, 5H, CpOs), 4.26 (s, 5H, CpRu), 3.68 (s, 2H, CH_2). ^{13}C NMR (CD_3COCD_3): 301.82 (t, $^2J_{CP} = 10.0$ Hz, OsC_α), 139.14 (t, $^2J_{CP} = 21.2$ Hz, RuC_α), 117.97 (OsC_β), 107.21 (s, RuC_β), 91.59 (*Cp*Ru), 84.74 (*Cp*Os), 17.27(CH_2). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): 48.76 (s, RuPPh_3), −4.05 (s, OsPPh_3). Anal. Calcd for $C_{93}H_{77}F_6P_5RuOs$: C, 63.65; H, 4.42. Found: C, 63.70; H, 4.61.

Synthesis of 7a. To a Schlenk flask charged with **6a** (0.05 g, 0.046 mmol) and KPF_6 (0.11 g, 0.60 mmol) was added CH_2Cl_2 (5 mL) under nitrogen. The resulting solution was stirred at room temperature, and ICH_2CN (0.05 mL, 0.689 mmol) was added. After stirring for 15 min, the color changed from yellow to red. Then the solution was filtered through Celite, and volume of the filtrate was reduced to 3 mL under vacuum. The mixture was slowly added to a solution of diethyl ether (50 mL), giving a pink precipitate. After filtration, the precipitate was washed with diethyl ether and dried under vacuum to give **7a** (0.050 g, 84% yield). ^1H NMR (CD_3COCD_3): 7.59−7.54 (m, 5H, Ph), 5.91 (s, 5H, Cp), 5.39 (s, 5H, Cp), 3.83 (s, 2H, CH_2), 3.03 (s, 2H, CH_2), 2.02−1.91 (m, 24H, CH_2), 1.18−0.97 (m, 36H, CH_3). ^{13}C NMR (CD_3COCD_3): 339.45 (t, $^2J_{CP} = 14.6$ Hz, C_α), 338.97 (t, $^2J_{CP} = 14.6$ Hz, C_α), 131.88−128.21 (Ph), 124.04 (C_β), 119.77 (C_β), 114.20 (C≡N), 25.18 (CH_2-CN), 14.80 (CH_2). ^{31}P NMR (CD_3COCD_3): 36.39 (s, PEt_3), 35.47 (s, PEt_3). MS FAB m/z: 1129.3 ($M^+ - PF_6^-$), 866.2 ($M^+ - PEt_3$), 746.2 ($M^+ - 2PEt_3$), 610.3 ($M^+ - 3PEt_3$), 504.2 ($M^+ - CpRu(PEt_3)_2{=}C{=}C(CH_2CN)CH_2$). Anal. Calcd for $C_{47}H_{79}F_{12}NP_6Ru_2$: C, 44.31; H, 6.25; N, 1.10. Found: C, 44.54; H, 6.48; N, 1.25.

Synthesis of 7b. To a Schlenk flask charged with **6b** (0.05 g, 0.036 mmol), KPF_6 (0.10 g, 0.54 mmol), and CH_2Cl_2 (5 mL) under nitrogen was added ICH_2CN (0.060 mL, 0.827 mmol) at room temperature. The color of the solution changed from yellow to red in 15 min. Then the solution was filtered through Celite, and the volume of the filtrate was reduced to 3 mL under vacuum. The mixture was slowly added to of a solution of diethyl ether (50 mL), giving a precipitate. After filtration, the precipitate was washed with diethyl ether and dried under vacuum to give **7b** (0.046 g, 80% yield). ^1H NMR (CD_3COCD_3): 7.78−7.04 (m, Ph); 5.91 (s, 5H, Cp), 5.09 (s, 5H, Cp), 3.64 (s, 2H, CH_2), 3.47 (s, 2H, CH_2), 2.00−1.91 (m, 12H, CH_2), 1.07−0.95 (m, 18H, CH_3). ^{13}C NMR (CD_3COCD_3): 342.91 (t, $^2J_{CP} = 15.2$ Hz, C_α), 337.96 (t, $^2J_{CP} = 14.3$ Hz, C_α), 135.37−129.08 (Ph), 123.44 (C_β), 119.73 (C_β), 117.42 (C≡N), 95.99 (Cp), 91.93 (Cp), 26.05 (CH_2CN), 13.50 (CH_2). ^{31}P NMR (CD_3COCD_3): 39.46 (s, PPh_3), 35.54 (s, PEt_3). MS FAB m/z: 1272.4 (M^+), 1010.5 ($M^+ - PPh_3$), 892.5 ($M^+ - PPh_3 - PEt_3$), 504.4 ($M^+ - CpRu(PPh_3)_2{=}C{=}C(CH_2CN)CH_2$). Anal. Calcd for $C_{71}H_{79}NF_{12}P_6Ru_2$: C, 54.58; H, 5.10; N, 0.90. Found: C, 54.91; H, 5.04; N, 1.02.

Synthesis of {[Os]═C═C(Ph)CH$_2$C(CH$_2$CN)═C═[Ru′]}[PF$_6$]$_2$ (7c). To a Schlenk flask charged with **6c** (0.090 g, 0.050 mmol), CH_2Cl_2 (10 mL), and KPF_6 (0.010 g, 0.06 mmol) was added ICH_2CN (0.02 mL, 0.276 mmol). The resulting solution was heated to reflux for 8 h. The solvent was removed under vacuum, and CH_2Cl_2 was used to extract the product. Then the solution was filtered through Celite, and the filtrate was concentrated to ca. 5 mL and added to a solution of diethyl ether (60 mL) to produce a purple precipitate. The powder was filtered, washed with diethyl ether, and recrystallized from CH_2Cl_2/hexane to give **7c** (0.080 g, 78% yield). ^1H NMR (CD_3COCD_3): 7.75−6.89 (m, 65H, Ph), 5.86

(s, 5H, CpRu), 4.87 (s, 5H, CpOs), 3.66 (br s, 2H, CH_2), 3.00 (s, 2H, CH_2). ^{13}C NMR (CD_3COCD_3): 341.51 (t, $^2J_{CP}$ = 15.1 Hz, RuC_α), 302.24 (t, $^2J_{CP}$ = 8.7 Hz, OsC_α), 135.43−126.96 (m, Ph), 123.7 (RuC_β), 120.3 (OsC_β), 118.3 (*C*N), 95.9 (*Cp*Ru), 93.5 (*Cp*Os), 22.8 (CH_2CN), 14.1 (CH_2). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): 39.51 (br s, $RuPPh_3$); −6.33 (br s, $OsPPh_3$). Anal. Calcd for $C_{95}H_{79}F_{12}NP_6RuOs$: C, 58.82; H, 4.11; N, 0.72. Found: C, 59.02; H, 4.25; N, 0.81.

Synthesis of {[Ru]═C═C(Ph)CH$_2$C(CH$_2$COOEt)═C═[Ru]}[PF$_6$]$_2$ (8a). To a Schlenk flask charged with **6a** (0.10 g, 0.092 mmol) and KPF_6 (0.10 g, 0.54 mmol) was added CH_2Cl_2 (5 mL). The resulting solution was stirred at room temperature, and ethyl iodoacetate (0.13 mL, 1.09 mmol) was added. After 14 h, the color changed from yellow to red. Then the solution was filtered through Celite, and volume of the filtrate was reduced to 3 mL under vacuum. The mixture was slowly added to a solution of diethyl ether (50 mL). After filtration, the precipitate was washed with diethyl ether and dried under vacuum to give **8a** (0.091 g, 75% yield). ^{1}H NMR (CD_3COCD_3): 7.56−7.37 (m, 5H, Ph), 5.86 (s, 5H, Cp), 5.31 (s, 5H, Cp), 4.25 (q, $^3J_{HH}$ = 6.9 Hz, 2H, OCH_2), 3.75 (s, 2H, CH_2), 3.43 (s, 2H, CH_2), 2.00−1.75 (m, 24H, CH_2), 1.32 (t, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.21−0.85 (m, 36H, CH_3). ^{31}P NMR (CD_3COCD_3): 36.47 (s, PEt_3), 35.58 (s, PEt_3). Anal. Calcd for $C_{49}H_{84}F_{12}O_2P_6Ru_2$: C, 44.55; H, 6.41. Found: C, 44.76; H, 6.58.

Synthesis of {[Ru]═C═C(Ph)CH$_2$C(CH$_2$COOEt)═C═[Ru′]}[PF$_6$]$_2$ (8b). To a Schlenk flask charged with **6b** (0.10 g, 0.073 mmol) and KPF_6 (0.10 g, 0.54 mmol) in CH_2Cl_2 (5 mL) was added ethyl iodoacetate (0.14 mL, 1.18 mmol) at room temperature. After 20 h, the color changed from yellow to red. Then the solution was filtered through Celite, and volume of the filtrate was reduced to 3 mL under vacuum. The mixture was slowly added to a solution of diethyl ether (50 mL), giving a pink precipitate, which, after filtration, was washed with diethyl ether and dried under vacuum to give **8b** (0.102 g, 87% yield). ^{1}H NMR (CD_3COCD_3): 7.70−7.09 (m, 35H, Ph), 5.86 (s, 5H, Cp), 4.99 (s, 5H, Cp), 4.19 (q, $^3J_{HH}$ = 7.2 Hz, 2H, OCH_2), 3.77 (s, 2H, CH_2), 3.37 (s, 2H, CH_2), 1.95−1.87 (m, 12H, CH_2), 1.24 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3), 1.14−0.94 (m, 18H, CH_3). ^{31}P NMR (CD_3COCD_3): 40.40 (s, PPh_3), 35.99 (s, PEt_3). Anal. Calcd for $C_{73}H_{84}F_{12}O_2P_6Ru_2$: C, 54.48; H, 5.26. Found: C, 54.59; H, 5.08.

Synthesis of 9a. A mixture of **7a** (0.050 g, 0.039 mmol) and NaOMe (0.030 g, 0.556 mmol) was dissolved in 10 mL of acetone at room temperature. The solution was stirred under nitrogen for 20 min, and the color changed from pink to deep yellow. After removal of the solvent in vacuo, CH_2Cl_2 was added to the residue, and the extract was filtered with Celite. The volume of the filtrate was reduced to about 3 mL, and hexane (50 mL) was added to cause precipitation of deep brown solid, which was collected by filtration and washed with diethyl ether and hexane, affording **9a** (0.035 g, 80% yield). ^{1}H NMR (CD_3COCD_3): 7.40−7.20 (m 5H, Ph), 5.71 (s, 5H, Cp), 5.08 (s, 1H, CH), 4.82 (s, 5H, Cp), 4.42, 4.21 (two d, $^2J_{HH}$ = 17.4 Hz, 2H, CH_2), 1.97−0.74 (m, 60H, PEt_3). ^{13}C NMR (CD_3COCD_3): 339.81 (t, $^2J_{CP}$ = 15.0 Hz, C_α), 149.34 (t, $^2J_{CP}$ = 14.2 Hz, C_α), 144.31 (C_β), 131.55−126.26 (Ph), 124.82 (CN), 121.38 (*C*Ph), 90.86 (Cp), 79.84 (Cp), 56.04 (CH), 46.26 (CH_2). ^{31}P NMR (CD_3COCD_3): 39.73, 37.88 (two d, $^2J_{PP}$ = 32.6 Hz, PEt_3), 29.77, 29.36 (two d, $^2J_{PP}$ = 45.9 Hz, PEt_3). MS FAB *m/z*: 1129.3 (M^+ + 1), 984.4 (M^+ + 1 − PF_6), 866.3 (M^+ + 1 − PF_6 − PEt_3), 747.2 (M^+ + 1 − PF_6 − $2PEt_3$), 628.1 (M^+ + 1 − PF_6 − $3PEt_3$), 582.3 (M^+ − $3PEt_3$ − $3CH_3$), 403.2 (M^+ − CpRu(PEt_3)$_2$═C═C(CH_2CN)CH_2C(Ph)═C). Anal. Calcd for $C_{47}H_{78}F_6NP_5Ru_2$: C, 50.04; H, 6.97; N, 1.24. Found: C, 50.25; H, 6.78; N, 1.48.

Synthesis of 9b. To a Schlenk flask charged with **7b** (0.050 g, 0.032 mmol) and NaOMe (0.03 g, 0.39 mmol) was added acetone (5 mL). After 30 min, the solvent was removed under vacuum, then CH_2Cl_2 (5 mL) was added and the solution was filtered through Celite. The volume of the filtrate was reduced to 3 mL under vacuum. A solution of diethyl ether (50 mL) was added to cause precipitation of a purple-red powder. After filtration, the precipitate was washed with diethyl ether and dried under vacuum to give **9b**. Single crystals were obtained by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution of **9b**. ^{1}H NMR (CD_3COCD_3): 7.42−7.14 (m, Ph); 5.38 (s, 5H, Cp), 5.05 (s, 1H, CH), 4.82 (s, 5H, Cp), 4.54, 4.09 (two d, $^2J_{HH}$ = 18.1 Hz, 2H, CH_2), 1.75−0.80 (m, 30H, PEt_3). ^{13}C NMR (CD_3COCD_3): 341.46 (t, $^2J_{CP}$ = 11.8 Hz, C_α), 149.07 (t, $^2J_{CP}$ = 11.6 Hz, C_α), 143.22 (C_β), 129.33−127.00 (Ph, C≡N), 125.60 (*C*Ph), 95.09 (Cp), 79.89 (Cp), 54.91 (*C*C≡N), 47.08 (CH_2). ^{31}P NMR (CD_3COCD_3): 39.73, 37.88 (two d, $^2J_{PP}$ = 32.6 Hz, PPh_3), 29.77, 29.36 (two d, $^2J_{PP}$ = 45.9 Hz, PEt_3). MS FAB *m/z*: 1271.2 (M^+ − PF_6), 1154.1 (M^+ − PF_6 − PEt_3), 892.1 (M^+ − PF_6 − PEt_3 − PPh_3), 774.1 (M^+ − PF_6 − $2PEt_3$ − PPh_3), 403.1 (M^+ − CpRu(PPh_3)$_2$═C═C(CHCN)CH_2C(Ph)═C). Anal. Calcd for $C_{71}H_{78}F_6NP_5Ru_2$: C, 60.21; H, 5.55; N, 0.99. Found: C, 60.42; H, 5.12; N, 1.09.

Synthesis of 10b. To a 5 mL acetone solution of **7b** (0.050 g, 0.032 mmol) at room temperature under nitrogen was added n-Bu_4NOH (0.20 mL, 0.20 mmol). After 10 min, the solvent was removed under vacuum and diethyl ether was used to extract the product. Then the solution was filtered through a sintered glass with Celite, and the solvent was removed under vacuum to give **10b**. ^{1}H NMR (CD_3COCD_3): 7.08−6.97 (m, 35H, Ph); 4.76 (s, 5H, Cp), 4.16 (s, 5H, Cp), 3.53, 3.46 (two d, $^2J_{HH}$ = 16.5 Hz, 2H, CH_2). ^{13}C NMR (CD_3COCD_3): 140.37 (t, $^2J_{CP}$ = 5.9 Hz, C_α), 134.93−124.93 (Ph, C_β), 108.53 (C_β), 93.74 (C≡N), 85.68 (Cp), 85.66 (Cp). ^{31}P NMR (CD_3COCD_3): 51.07, 50.68 (two d, $^2J_{PP}$ = 39.8 Hz, PPh_3), 35.78 (s, PEt_3). MS FAB *m/z*: 1271.4 (M^+ − PF_6), 1011.2 (M^+ − PF_6 − PPh_3), 892.2 (M^+ − PF_6 − PEt_3 − PPh_3), 691.2 (M^+ − CpRu(PEt_3)$_2$═C═C(Ph)CH_2C(CHCN)═C), 403.2 (M^+ − CpRu(PPh_3)$_2$═C═C(CHCN)CH_2C(Ph)═C). Anal. Calcd for $C_{71}H_{78}F_6NP_5Ru_2$: C, 60.21; H, 5.55; N, 0.99. Found: C, 60.72; H, 5.65; N, 1.11.

Deprotonation of 7c. To a solution of **7c** (0.10 g, 0.05 mmol) in 15 mL of acetone was added a solution of n-Bu_4NOH (0.2 mL, 1 M in MeOH). The mixture was stirred for 30 min to yield the light yellow microcrystalline powder, which was filtered, washed with 2 × 3 mL of acetone and 2 × 5 mL of diethyl ether, and dried under vacuum to give **10c** (0.075 g, 80% yield). ^{1}H NMR (CD_3COCD_3): 7.42−6.96 (m, 65H, Ph), 5.75 (s, 5H, CpOs), 4.54 (b, 1H, CH), 4.48 (s, 5H, CpRu), 3.02 (br, 1H, CH_2), 3.00 (br, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): 307.23 (t, $^2J_{CP}$ = 9.3 Hz, OsC_α), 139.86 (t, $^2J_{CP}$ = 5.8 Hz, RuC_α), 135.41−126.94 (m, Ph and RuC_β), 124.8 (OsC_β), 95.9 (CN), 93.2 (*Cp*Os), 86.2 (*Cp*Ru), 20.3 (*C*H); 15.5 (CH_2). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): 50.4, 48.4 (two d, J_{pp} = 35.2 Hz, $RuPPh_3$), −3.9, −5.8 (two d, J_{pp}= 19.5 Hz, $OsPPh_3$). Anal. Calcd for $C_{95}H_{78}F_6NP_5RuOs$: C, 63.61; H, 4.38; N, 0.78. Found: C, 63.72; H, 4.71; N, 0.93.

Deprotonation of 8a. A mixture of **8a** (0.050 g, 0.038 mmol) and sodium methoxide (0.02 g, 0.37 mmol) was dissolved in 10 mL of acetone at room temperature. After 70 min, the solvent was removed in vacuo, CH_2Cl_2 was added to the residue, and the extract was filtered through Celite. The volume of the filtrate was reduced to about 3 mL, and 50 mL of hexane was added to cause precipitation of a pink-purple powder. The solid was collected by filtration followed by washing with diethyl ether and hexane. The solid was dried under vacuum to afford the product **11a** and other unidentified side products (0.04 g) in an 8:1 ratio based on NMR data. Attempts to further purify the desired product caused extensive decomposition of **11a**. Spectroscopic data were used to identify **11a**. ^{1}H NMR (CD_3COCD_3): 7.51−7.19 (m, 5H, Ph), 5.57 (s, 5H, Cp), 4.94 (s, 1H, CH), 4.62 (s, 5H, Cp), 4.24 (m, 2H, CH_2), 4.17, 4.05 (m, 2H, OCH_2), 1.30 (m, 3H, CH_3), 2.13−0.70 (m, 60H, PEt_3). ^{13}C NMR (CD_3COCD_3): 339.39 (t, $^2J_{CP}$ = 15.3 Hz, C_α), 175.94 (CO), 152.80 (t, $^2J_{CP}$ = 14.1 Hz, C_α), 144.33 (C_β), 132.03−126.45

(Ph), 123.56 (*C*Ph), 90.04 (Cp), 78.79 (Cp), 69.46 (CH), 60.63 (OCH_2), 47.60 (CH_2), 14.50 (CH_3). ^{31}P NMR (CD_3COCD_3): 39.68, 37.42 (two d, $^2J_{PP}$ = 32.7 Hz, PEt_3), 31.09, 28.92 (two d, $^2J_{PP}$ = 47.9 Hz, PEt_3).

Deprotonation of 8b. Complex **8b** (50 mg, 0.031 mmol) in 0.5 mL of d_6-acetone was treated with n-Bu_4NOH (50 μL, 1 M MeOH solution) at room temperature. The color of the solution turned yellow immediately. The ^{31}P NMR spectrum of the crude product indicated clean formation of the furyl complex **12b**. Attempts to isolate the product resulted in complete decomposition of the desired product. Complex **12b** was characterized only by ^{31}P NMR. Spectroscopic data for **12b**: ^{31}P NMR (CD_3COCD_3): 49.45 (s, PPh_3), 36.49 (s, PEt_3).

Synthesis of {[Ru]═C═C(Ph)CH$_2$CN}[PF$_6$] (13). To a Schlenk flask charged with **3a** (0.100 g, 0.20 mmol) and KPF_6 (0.21 g, 1.08 mmol) in CH_2Cl_2 (10 mL) was added ICH_2CN (0.1 mL, 1.38 mmol). After 30 min at room temperature, the solution was filtered through Celite, and the volume of the filtrate was reduced to 3 mL under vacuum. An aliquot of diethyl ether (50 mL) was added to cause precipitation of a pink powder, which, after filtration, was washed with diethyl ether and dried under vacuum to give **13** (0.126 g, 92% yield). ^{1}H NMR (CD_3COCD_3): 7.45−7.30 (m, 5H, Ph); 5.95 (s, 5H, Cp); 3.87 (s, 2H, CH_2), 2.12−1.94 (m, 12H, CH_2), 1.12−1.01 (m, 18H, CH_3). ^{13}C NMR (CD_3COCD_3): 341.54 (t, $^2J_{CP}$ = 14.6 Hz, C_α), 133.30−128.00 (Ph), 120.05 (C_β), 118.59 (CN), 91.10 (Cp), 16.49 (CH_2). ^{31}P NMR (CD_3COCD_3): 35.51 (s, PEt_3). MS FAB *m*/*z*: 544.2 (M^+), 427.1 ($M^+ - PEt_3$). Anal. Calcd for $C_{27}H_{42}F_6NP_3Ru$: C, 47.09; H, 6.15; N, 2.03. Found: C, 47.24; H, 6.41; N, 2.25.

Deprotonation of 13. To a 5 mL acetone solution of **13** (0.050 g, 0.073 mmol) at room temperature was added n-Bu_4NOH (0.5 mL, 0.42 mmol). After 1 min the solvent was removed under vacuum and diethyl ether (5 mL) was added to extract the product. Then the solution was filtered through a sintered glass with Celite and the solvent was removed under vacuum to give **15** (0.034 g, 87% yield). ^{1}H NMR (C_6D_6): 7.90−7.30 (m, 5H, Ph); 4.94 (s, 5H, Cp); 1.50 (s, 1H, CH), 1.62−0.60 (m, 30H, PEt_3). ^{31}P NMR (C_6D_6): 42.16, 41.67 (dd, $^2J_{PP}$ = 38.0 Hz, PEt_3). MS FAB *m*/*z*: 544.2 ($M^+ + 1$). Anal. Calcd for $C_{41}H_{27}NP_2Ru$: C, 59.76; H, 7.62; N, 2.58. Found: C, 59.90; H, 7.44; N, 2.62.

Synthesis of {[Ru]═C═C(Ph)CH$_2$COOMe}[PF$_6$] (14). To a Schlenk flask charged with **3a** (0.12 g, 0.239 mmol) and KPF_6 (0.20 g, 1.08 mmol) in CH_2Cl_2 (10 mL) was added methylbromoacetate (0.7 mL, 7.37 mmol). After 15 h at room temperature, the solution was filtered through Celite, and the volume of the filtrate was reduced to 3 mL under vacuum. An aliquot of diethyl ether (50 mL) was added to cause precipitation of a pink powder, which, after filtration, was washed with diethyl ether and dried under vacuum to give **14** (0.11 g, 95% yield). ^{1}H NMR (CD_3COCD_3): 7.70−7.15 (m, 5H, Ph); 5.88 (s, 5H, Cp); 3.65 (s, 3H, OCH_3), 3.57 (s, 2H, CH_2), 2.89−2.01 (m, 12H, CH_2), 1.10−0.99 (m, 18H, CH_3). ^{13}C NMR (CD_3COCD_3): 346.87 (t, $^2J_{CP}$ = 14.6 Hz, C_α), 172.83 (CO), 134.55−128.08 (Ph), 123.60 (C_β), 91.75 (Cp), 52.40 (OCH_3), 32.95 (CH_2). ^{31}P NMR (CD_3COCD_3): 35.58 (s, PEt_3). MS FAB *m*/*z*: 577.2 (M^+), 458.1 ($M^+ - PEt_3$), 401.0 ($M^+ - PEt_3 -$ COOMe), 341.0 ($M^+ - 2PEt_3$). Anal. Calcd for $C_{28}H_{45}F_6O_2P_3Ru$: C, 46.60; H, 6.29. Found: C, 46.59; H, 6.24.

Synthesis of Furyl Complex 16. To a 5 mL acetone solution of **14** (0.05 g, 0.08 mmol) at room temperature was added n-Bu_4NOH (0.5 mL, 0.43 mmol). After 5 min the solvent was removed under vacuum and diethyl ether (5 mL) was added to extract the product. The solution was filtered, and the filtrate was dried under vacuum to give **16** (0.04 g, 90% yield). ^{1}H NMR (C_6D_6): 7.78−7.30 (m, 5H, Ph); 5.26 (s, 1H, CH), 4.47 (s, 5H, Cp); 3.52 (s, 3H, OMe), 1.86−0.80 (m, 30H, PEt_3). ^{31}P NMR (C_6D_6): 40.22 (s, PEt_3). MS FAB *m*/*z*: 577.2 ($M^+ + 1$), 459.2 ($M^+ - PEt_3$), 403.2 ($M^+ -$ C═C(Ph)CH_2COOMe). Anal. Calcd for $C_{28}H_{44}O_2P_2Ru$: C, 58.42; H, 7.70. Found: C, 58.30; H, 7.94.

Single-Crystal X-ray Diffraction Analysis of 6b and 9a. Single crystals of **6b** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.25 × 0.20 × 0.15 mm^3 was glued to a glass fiber and mounted on a SMART CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube Mo Kα radiation (T = 295 K). Exposure time was 5 s per frame. SADABS[31] (Siemens area detector absorption) absorption corrections were applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL[32] program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data to give R1 = 0.0597 and wR2 = 0.1679 for 11 803 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. An X-ray diffraction study of **9a** was carried out on a single crystal of dimensions 0.15 × 0.15 × 0.10 mm^3. The structure was similarly solved to give R1 = 0.0612 and wR2 = 0.1554 for 9259 unique observed reflections ($I > 2\sigma(I)$). Appropriate crystal data and structure refinement parameters for complexes **6b** and **9a** are listed in Table 3.

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

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

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