Addition of Acetylenes to Olefins. Oxidative Coupling versus [2+2] Cycloaddition to a Vinylidene Intermediate

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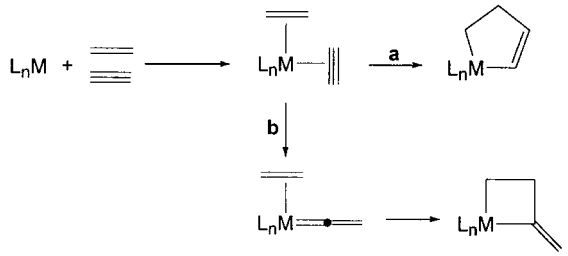
The reaction of [RuCp(κ^1(P),η^2-$PPh_2CH_2CH_2CH{=}CH_2$)(CH_3CN)]PF_6 (**1**) with HC≡CPh in the absence of base results in the formation of the η^4-butadiene complexes [RuCp(κ^1(P),η^4-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH{=}CH{-}CH{=}CHPh$)]$PF_6$ (**2a**) and [RuCp(κ^1(P),η^4-(3*Z*)-$PPh_2CH_2CH_2CH{=}CH{-}CPh{=}CH_2$)]$PF_6$ (**2b**). When the reaction is carried out in the presence of base (NaOEt), in addition to **2a** and **2b**, the η^3-butadienyl complex RuCp(κ^1(P),(3,4,5-η)-$PPh_2CH_2CH_2CHCHCCHPh$) (**2c**) is obtained. The C−C coupling reactions take place also with internal alkynes $R^1C{\equiv}CR^2$ ($R^1 = R^2$ = Ph, Et; R^1 = Ph, R^2 = Et) to give the η^4-butadiene complexes [RuCp(κ^1(P),η^4-(3Z,5Z)-$PPh_2CH_2CH_2CH{=}CH{-}CR^1{=}CHR^2$)]$PF_6$ (**3**−**5**). In the case of terminal acetylenes two distinct reaction modes are observed proceeding via either metallacyclopentene complexes or the successive intermediacy of vinylidene and metallacyclobutane complexes. With internal alkynes, the metallacyclopentene route is followed. X-ray structures of representative complexes are reported.

Introduction

The coupling of unactivated olefins and acetylenes mediated by transition metal complexes has been the subject of several recent investigations.[1] The most common mechanism envisaged is the oxidative coupling via a metallacyclopentene intermediate as illustrated in Scheme 1, path **a**. When terminal alkynes are involved, an alternative mechanism may operate via the successive intermediacy of vinylidene and metallacyclobutane complexes (path **b**). Such a process is not limited to early transition metal complexes,[2] but has also been shown by us[3] to be operative in the reaction of the late transition metal complexes RuTp(COD)Cl (Tp = trispyrazolylborate) and RuTp(κ^1(P),η^2-$Ph_2PCH{=}CH(Ph){=}CH_2$)Cl with terminal acetylenes. The products obtained are η^2-butadiene or, in the presence of base, η^3-butadienyl complexes. Herein, we extend our previous studies on carbon−carbon bond formation between olefins and acetylenes and report on the reaction of [RuCp(κ^1(P),η^2-$Ph_2PCH_2CH_2CH{=}CH_2$)(CH_3CN)]PF_6 with terminal and internal acetylenes. It will be demonstrated that under certain reaction conditions both modes of reaction (path **a** and **b**) occur simultaneously in competition with one another. X-ray structures of representative products are included.

Scheme 1



Results and Discussion

The cationic complex [RuCp(κ^1(P),η^2-$PPh_2CH_2CH_2CH{=}CH_2$)(CH_3CN)]PF_6 (**1**) has been prepared in 83% isolated yield by the reaction of [RuCp(CH_3CN)$_3$]PF_6 with $Ph_2PCH_2CH_2CH{=}CH_2$ in CH_2Cl_2 at room temperature. Characterization was by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies and elemental analysis.

The NMR spectra of **1** bear no unusual features, and it is sufficient to point out that the proton resonances of the terminal $CH_2{=}$ moiety of the $Ph_2PCH_2CH_2CH{=}CH_2$ ligand give rise to two characteristic doublets centered at 4.49 (H^{4anti}, $^3J_{HHcis}$ = 8.5 Hz) and 2.76 ppm (H^{4syn}, $^3J_{HHtrans}$ = 12.6 Hz). As apparent from the ^{31}P{^{1}H} NMR spectra, only one of the two possible isomers is formed.[4] A structural view of **2a**, as determined by X-ray crystallography, is depicted in Figure 1. Important

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(1) (a) Trost, B. M.; Indolese, A. F.; Müller, T. J. J.; Treptow, B. *J. Am. Chem. Soc.* **1995**, *117*, 615. (b) Trost, B. M.; Portnoy, M.; Kurihara, H. *J. Am. Chem. Soc.* **1997**, *119*, 836. (c) Kikuchi, H.; Uno, M.; Takahashi, S. *Chem. Lett.* **1997**, 1273. (d) Derien, S.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2551. (e) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476. (f) Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831. (g) Trost, B. M.; Dyker, G.; Kulawiec, R. *J. Am. Chem. Soc.* **1990**, *112*, 7809. (h) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621. (i) Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 906.

(2) (a) Beckhaus, R. *Angew. Chem.* **1997**, *109*, 695. (b) Beckhaus, R.; Sang, J.; Wagner, T.; Ganter, B. *Organometallics* **1996**, *15*, 1176. (c) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Organomet. Chem.* **1987**, *329*, 61.

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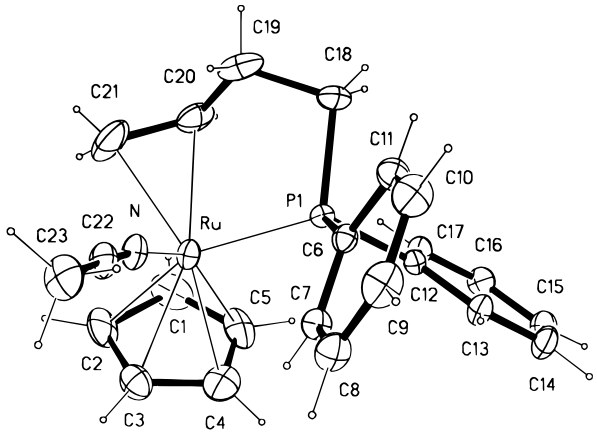

Figure 1. Structural view of **1** (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−P(1) 2.342(1), Ru−N 2.061(4), Ru−C(Cp)$_{av}$ 2.206 (7), Ru−C(20) 2.250(6), Ru−C(21) 2.217(7), C(20)−C(21) 1.421(12), Ru−N−C(22) 172.5(5), C(19)−C(20)−C(21) 119.3(9).

bond distances are reported in the caption. Complex **1** adopts the usual three-legged piano stool structure. The olefin moiety of the $Ph_2PCH_2CH_2CH{=}CH_2$ ligand is bonded almost symmetrically to the metal center, with the Ru−C bonds to the internal and terminal carbon atoms C(20) and C(21) being 2.250(6) and 2.217(7) Å, respectively. The C=C double bond is almost perpendicular to the Ru−N bond. The Ru−N and Ru−P(1) distances are 2.061(4) and 2.342(1) Å, respectively.

Treatment of **1** with HC≡CPh in MeOH in the presence of NaOEt (1 equiv) at 65 °C for 3 h afforded, on workup, the two isomeric η^4-butadiene complexes [RuCp(κ^1(P),η^4-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH{=}CH{-}CH{=}CHPh$)]$PF_6$ (**2a**) and [RuCp(κ^1(P),η^4-(3*Z*)-$PPh_2CH_2CH_2CH{=}CH{-}CPh{=}CH_2$)]$PF_6$ (**2b**) as well as the η^3-butadienyl complex RuCp(κ^1(P),(3,4,5-η)-$PPh_2CH_2CH_2CHCHCCHPh$) (**2c**) in 34, 7, and 39% isolated yields, respectively (Scheme 2).

Characterization of **2** was again by a combination of elemental analysis and ^{1}H and ^{13}C{1H} NMR spectroscopies. The solution ^{1}H NMR spectroscopic data for **2a** include doublets of doublets centered at 6.48 (H^5) and 2.65 ppm (H^{6syn}) with a common coupling constant of $^3J_{HH} = 9.7$ Hz, consistent with an *E*-arrangement of the C5−C6 double bond. The significant upfield shift of the H^{6syn} proton is characteristic of this type of complexes (vide infra). In the ^{1}H NMR spectrum of **2b** the resonances of the terminal $CH_2{=}$ moiety of the $Ph_2PCH_2CH{=}CHCPh{=}CH_2$ show a doublet centered at 3.61 (H^{6anti}, $^2J_{HH} = 4.9$ Hz) and a characteristic doublet of doublets centered at 1.17 ppm (H^{6syn}, $^2J_{HH} = 4.9$ Hz, $^3J_{HP} = 16.4$ Hz). In the ^{13}C{^{1}H} NMR spectrum of **2c**, the characteristic resonance of the C^5 carbon atom is observed at 171.6 ppm, in agreement with those for other η^3-butadienyl complexes.[5] All other resonances are unremarkable and are not discussed here.

In addition to full NMR spectroscopic and analytical characterizations of the products, the solid-state structure of **2a**·CH_2Cl_2 was determined by single-crystal X-ray diffraction. An ORTEP diagram of **2a**·CH_2Cl_2 is depicted in Figure 2, with important bond distances reported in the caption. **2a**·CH_2Cl_2 adopts a three-legged piano stool conformation with P and the two C=C bonds of the $PPh_2CH_2CH_2CH{=}CH{-}C{=}CHPh$ ligand as the legs. The most notable feature, which is consistent with the NMR data, is the *s-cis* structure of the butadiene moiety. The C−C distances within the butadiene fragment are very similar, ranging from 1.426 to 1.431 Å. The Ru−C distances are slightly shorter by about 0.09 Å for C(21) and C(22) than for C(20) and C(23). The Ru−P(1) bond distance is 2.335(1) Å.

When the reaction of **1** with HC≡CPh (3 equiv) is run in the absence of base, complexes **2a** and **2b** are obtained in 56 and 15% isolated yield. However, NMR monitoring of the progress of this reaction indicated complete consumption of **1** after 1 h, giving **2a** and **2b** in 3.3:1.0 ratio, with no evidence found for the formation of **2c** but small amounts of polymeric materials (Table 1).[6] The coupling reaction turned out to be not restricted to terminal alkynes. Thus, in similar fashion, **1** was found to react with 1.5 equiv of internal alkynes $R^1C{\equiv}CR^2$ ($R^1 = R^2 =$ Ph, Et; $R^1 =$ Ph, $R^2 =$ Et) to give the η^4-butadiene complexes [RuCp(κ^1(P),η^4-(3*Z*,5*Z*)-$PPh_2CH_2CH_2CH{=}CH{-}CPh{=}CHPh$)]$PF_6$ (**3**), [RuCp(κ^1(P),η^4-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH{=}CH{-}CEt{=}CHEt$)]$PF_6$ (**4**), and **5** (in the form of the two regioisomers [RuCp(κ^1(P),η^4-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH{=}CH{-}CEt{=}CHPh$)]$PF_6$ (**5a**) and [RuCp(κ^1(P),η^4-(3*Z*,5*Z*)-$PPh_2CH_2CH_2CH{=}CH{-}CPh{=}CHEt$)]$PF_6$ (**5b**)) in high yields (Table 1). The reactions with the internal alkynes are drastically slower than those with HC≡CPh as determined by ^{31}P{^{1}H} NMR spectroscopy (ca. 8 h for PhC≡CPh vs 1 h for HC≡CPh under the same reaction conditions). All complexes have been characterized by elemental analysis and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies. The ^{1}H NMR spectra of all these complexes exhibit resonances for the H^6 proton in the range 2.0−2.4 ppm, indicating that it is *syn* to the metal center. In addition, the molecular structure of the major isomer **5a** determined by X-ray crystallography (Figure 3) confirms that the phenyl substituent is situated on the C^6 carbon atom. Important bond distances and angles are given in the caption. The overall geometry of the complex is very similar to that of **2a**. The bond distances between Ru and the butadiene fragment, which is adopting a *s-cis* conformation, are short for C(21) and C(22), being 2.175(3) and 2.196(3) Å, respectively, and long for C(20) and C(23), being 2.253(3) and 2.304(3) Å, respectively. The C−C bond distances within this moiety are relatively uniform, varying between 1.418 and 1.431 Å, and do not exhibit the typical short−long−short pattern, as is the case for most Ru(II) η^4-diene complexes.[7] The Ru−P(1) bond distance is 2.318(1) Å.

As we have previously shown,[3] the C^5 carbon of the η^3-butadienyl complexes is nucleophilic, which offers the

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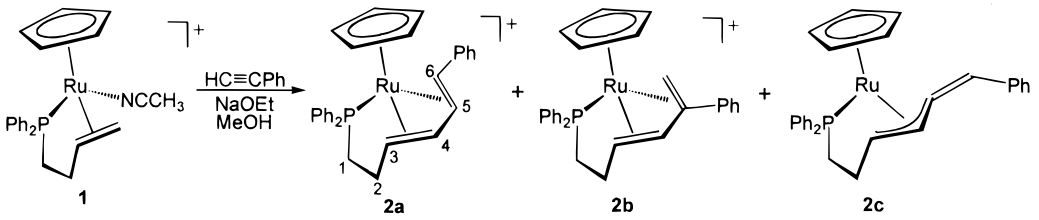
Scheme 2



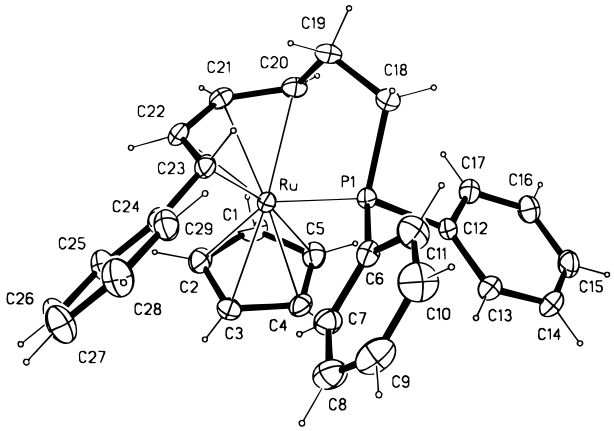
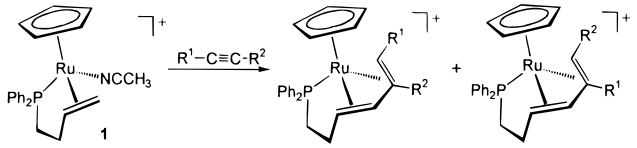


Figure 2. Structural view of **2a**·CH_2Cl_2 (CH_2Cl_2 and PF_6^- omitted for clarity). Selected bond lengths (Å): Ru−P(1) 2.335(1), Ru−$C(Cp)_{av}$ 2.239(4), Ru−C(20) 2.253(3), Ru−C(21) 2.175(3), Ru−C(22) 2.196(3), Ru−C(23) 2.304(3), C(20)−C(21) 1.431(5), C(21)−C(22) 1.426(5), C(22)−C(23) 1.428(5), C(23)−C(24) 1.491(5).

Table 1. Product Distribution of the Reaction of 1 with Alkynes



entry	R^1	R^2	products[a]
1	Ph	H	76% **2a** 23% **2b**
2	Ph	D	78% **2a**^{D} 22% **2b**^{D}
3	Ph	Ph	91% **3**[b]
4	Et	Et	92% **4**[b]
5	Ph	Et	85% **5a** 15% **5b**

[a] Product distribution has been determined by ^{1}H NMR spectroscopy. [b] Isolated yield.

possibility of further functionalizations by treating them with electrophiles. Accordingly, **2c** reacts with CF_3-COOH to yield the new complex [RuCp(κ^1(P),η^4-(3*Z*,5*Z*)-$PPh_2CH_2CH_2CH$═$CH-CH$═$CHPh)]$CF_3COO$ (**2d**) in essentially quantitative yield, as monitored by ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$NMR spectroscopies (Scheme 3). From steric considerations (MM2 calculations indicate unfavorable repulsive interactions between the phenyl substituents of the butadiene and the PPh_2 moieties), **2d** might adopt the 3*Z*,5*Z*-*s*-*trans* conformation,[7a,8] although the alternative *s*-*cis* structure cannot definitely be ruled out. Interestingly, the NMR spectra of **2d** differ significantly

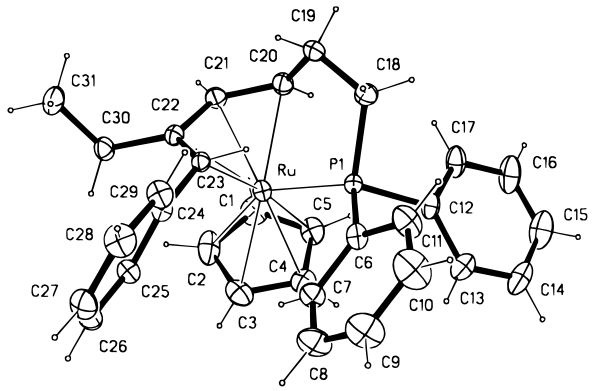


Figure 3. Structural view of **5a**·$^1/_2CH_2Cl_2$ (CH_2Cl_2 and PF_6^- omitted for clarity). Selected bond lengths (Å): Ru−P(1) 2.318(1), Ru−$C(Cp)_{av}$ 2.216(4), Ru−C(20) 2.228(4), Ru−C(21) 2.144(4), Ru−C(22) 2.193(3), Ru−C(23) 2.277-(3), C(20)−C(21) 1.418(5), C(21)−C(22) 1.431(5), C(22)−C(23) 1.423(4), C(23)−C(24) 1.485(4).

from that of **2a**. Thus, the expected upfield resonance of the H^{6syn} proton is no longer present in the ^{1}H NMR spectrum.

Instead, a doublet centered at 5.82 ppm (H^{6anti}) with a coupling constant of $^3J_{HH}$ = 7.6 Hz is observed, further, consistent with a *cis* arrangement of the C^5−C^6 double bond and either a *s*-*cis* or a *s*-*trans* geometry of the butadiene fragment. Unfortunately, attempts to grow suitable crystals for X-ray diffraction study were unsuccessful.

The reaction mechanism shown in Scheme 4 represents our working hypothesis for providing the η^4-butadiene and η^3-butadienyl products. First is the formation of the isomeric η^2-alkyne complexes **A** and **A′**. By analogy with the established coupling mechanisms, proposed by Trost[1a] and Dixneuf,[1d] the oxidative coupling of HC≡CPh with the double bond of the Ph_2PCH_2-CH_2CH═CH_2 ligand leads to the ruthenacyclopentene intermediates **B** and **B′**, which give the complexes **2a** and **2b**, respectively, via a β-elimination/reductive elimination sequence. Parallel to the oxidative coupling process, the cationic vinylidene complex **C** is formed via a 1,2 hydrogen shift.[9] Subsequent [2+2] cycloaddition at the Ru═C bond gives the metallacyclobutane complex **D**. This reaction needs the presence of a strong base

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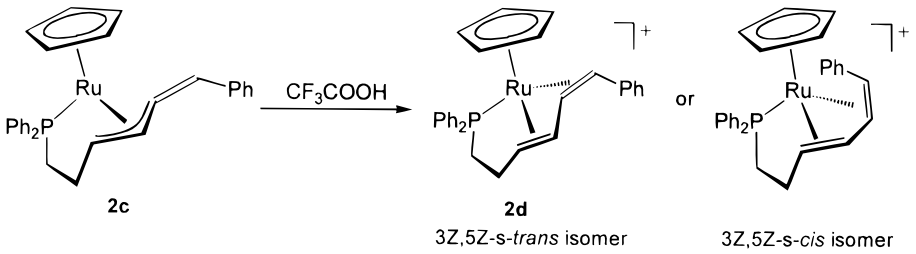
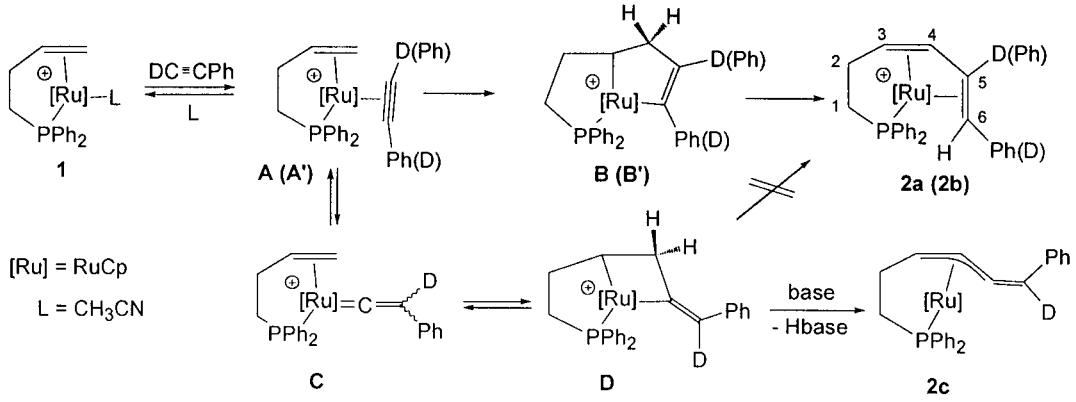
Scheme 3



Scheme 4



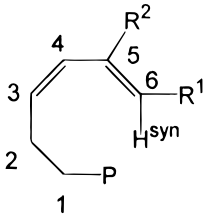
with deprotonation of one of the β-hydrogen atoms, yielding the stable η^3-butadienyl complex **2c**. In the absence of base no evidence of **2c** is found, suggesting that **C** and **D** are in equilibrium with **A** (**A′**) and that alternative rearrangements (e.g., a 1,2-H shift to give either **2a** or the *s-trans* isomer **2d**) are unfavorable or do not take place at all.

The following observations may be taken to support this mechanism. (i) In the absence of base, the reaction of **1** with DC≡CPh gives complexes $\mathbf{2a^D}$ and $\mathbf{2b^D}$, where the deuterium is attached at C^5 and C,[6] respectively, and *anti* to the metal center. This implies that the *syn* hydrogen originates exclusively and in all cases from the olefin. From this labeling experiment and, of course, from the fact that **2a** is actually formed, it is apparent that no vinylidene but a ruthenacyclopentene intermediate is involved in the coupling process. (ii) In the presence of base, on the other hand, the occurrence of a vinylidene intermediate was verified by a labeling experiment. Thus, the η^3-butadienyl product $\mathbf{2c^D}$ (formed together with $\mathbf{2a^D}$ and $\mathbf{2b^D}$) of the reaction of deuterium-labeled phenylacetylene DC≡CPh with **1** contains deuterium exclusively at the olefinic carbon C^6 of the butadienyl moiety, as shown by ^1H and ^{13}C NMR spectroscopy (Scheme 4). The η^3-butadienyl complex **2c** did not incorporate deuterium to give $\mathbf{2c^D}$ under reflux in CD_3OD in the presence of NaOEt. Likewise, also the complexes **2a** and **2b** did not incorporate deuterium to give $\mathbf{2a^D}$ and $\mathbf{2b^D}$ under reflux in CD_3OD.

In summary, we have shown that selective coupling of olefins and acetylenes (internal and terminal) is feasible in the coordination sphere of the RuCp complex $[RuCp(\kappa^1(P),\eta^2\text{-}PPh_2CH_2CH_2CH{=}CH_2)(CH_3CN)]PF_6$. Two different reaction routes have been identified proceeding via either a ruthenacyclopentene complex or the successive intermediacy of a vinylidene and a ruthenacyclobutane complex. The latter mode is restricted to terminal alkynes. It is interesting to note that analogous reactions on RuTp complexes proceed exclusively via the vinylidene pathway.[3]

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[10] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. TLC was performed on Riedel-deHaen TLC-sheets silica gel 60 F 254 (layer thickness 0.2 mm). For column chromatography silica gel grade 60, 70−230 mesh, 60 Å, purchased from Merck, or neutral MN-aluminum oxide, purchased from Macherey-Nagel, was used. $[RuCp(CH_3CN)_3]PF_6$[11] and $Ph_2PCH_2CH_2CH{=}CH_2$[12] were prepared according to the literature. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and H_3PO_4 (85%). Microanalyses were done by Microanalytical Laboratories, University of Vienna.



$[RuCp(\kappa^1(P),\eta^2\text{-}PPh_2CH_2CH_2CH{=}CH_2)(CH_3CN)]PF_6$ (1). To a solution of $[RuCp(CH_3CN)_3]PF_6$ (317 mg, 0.730 mmol) in

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CH_2Cl_2 (6 mL) was slowly added $Ph_2PCH_2CH_2CH{=}CH_2$ (175 mg, 0.730 mmol), and the mixture was stirred at room temperature for 5 h. During that time the color changed from orange to yellow. The solvent was then removed under reduced pressure, and the remaining residue was redissolved in CH_2Cl_2 (1 mL). Upon addition of Et_2O (3 mL) and *n*-hexane (1 mL) a bright yellow precipitate was formed, which was collected on a glass frit, washed with Et_2O (3 × 1 mL) and *n*-hexane (1 × 1 mL), and dried in vacuo. Yield: 360 mg (83%). Anal. Calcd for $C_{23}H_{25}F_6NP_2Ru$: C, 46.63; H, 4.25; N, 2.36. Found: C, 46.78; H, 4.33; N, 2.44. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.69−7.32 (m, 10H, Ph), 5.03−4.88 (m, 1H, H^3), 4.79 (s, 5H, Cp), 4.49 (d, $^3J_{HHcis}$ = 8.5 Hz, 1H, H^{4anti}), 3.21−3.02 (m, 2H, $H^{1,2}$), 2.94−2.62 (m, 1H, $H^{1,2}$), 2.76 (d, $^3J_{HHtrans}$ = 12.6 Hz, 1H, H^{4syn}), 1.90 (s, 3H, N≡C−CH_3), 1.43−1.19 (m, 1H, $H^{1,2}$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 138.1 (d, $^1J_{PC}$ = 45.8 Hz, 1C, Ph^1), 134.0 (d, $^2J_{PC}$ = 9.5 Hz, 2C, $Ph^{2,6}$), 131.7 (d, $^2J_{PC}$ = 10.2 Hz, 2C, $Ph^{2',6'}$), 131.7 (d, $^4J_{PC}$ = 2.5 Hz, 1C, Ph^4), 131.5 (d, $^4J_{PC}$ = 2.5 Hz, 1C, $Ph^{4'}$), 130.2 (d, $^3J_{PC}$ = 1.2 Hz, N≡C−CH_3), 129.9 (d, $^3J_{PC}$ = 10.2 Hz, 2C, $Ph^{3,5}$), 129.6 (d, $^3J_{PC}$ = 10.2 Hz, 2C, $Ph^{3',5'}$), 129.5 (d, $^1J_{PC}$ = 42.6 Hz, 1C, $Ph^{1'}$), 84.0 (d, $^2J_{PC}$ = 1.9 Hz, 5C, Cp), 77.3 (d, J_{PC} = 2.5 Hz, C^3), 52.3 (C^4), 40.9 (d, $^1J_{PC}$ = 30.5 Hz, C^1), 30.6 (d, $^2J_{PC}$ = 9.5 Hz, C^2), 4.1 (N≡C−CH_3). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 76.3 (PPh$_2$), −143.5 ($^1J_{PF}$ = 712.1 Hz, PF$_6$).

[RuCp(κ^1(P),η^4-(3*Z*,5*E*)-$PPh_2CH_2CH_2CH{=}CH{-}CH{=}CHPh$)]$PF_6$ (2a). Method a. A suspension of **1** (202 mg, 0.341 mmol) in MeOH (4 mL) was treated with HC≡CPh (131 μL, 1.19 mmol) and NaOMe (23.2 mg, 0.341 mmol) and was then stirred under reflux for 3 h. After that time the solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (10 mL), and insoluble materials were removed by filtration over Na_2SO_4. The volume of the filtrate was reduced to about 2 mL, and upon addition of Et_2O (15 mL), a white precipitate was formed, which was collected on a glass frit and washed with Et_2O (5 × 2 mL) (the filtrate is used for the isolation of **2c**). The crude product (145 mg) was purified via column chromatography (silica gel). The first yellow band was eluted with CH_2Cl_2/MeOH (v/v = 30:1). Recrystallization from $CHCl_3$ gave **2a** in the form of **2a**·CH_2Cl_2 as pale yellow crystals (the $CHCl_3$ filtrate was used for the isolation of **2b**). Yield: 85 mg of (34%). **Method b.** A solution of **1** (126 mg, 0.213 mmol) and HC≡CPh (70 μL, 0.638 mmol) in $CHCl_3$ (4 mL) was stirred under reflux for 2 h. Upon removal of the solvent the resulting residue was transferred to a glass frit and washed with Et_2O (5 × 1 mL). The crude product was purified by two recrystallizations from $CHCl_3$, yielding yellow crystals of **2a**·CH_2Cl_2 (the $CHCl_3$ solution was used for the isolation of **2b**). Yield: 78 mg (56%). Anal. Calcd for $C_{29}H_{27}F_6P_2Ru$: C, 53.38; H, 4.17. Found: C, 48.99; H, 4.08, which is consistent with $C_{29}H_{27}F_6P_2Ru{\cdot}CH_2Cl_2$. ^{1}H NMR ($\delta$, $MeNO_2$-d_3/$CDCl_3$ (1:3), 20 °C): 7.77−7.33 (m, 10H, PPh_2), 7.21 (t, 1H, Ph^{R4}), 7.08 (t, 2H, $Ph^{R3,5}$), 6.62 (d, 2H, $Ph^{R2,6}$), 6.48 (dd, $^3J_{HHtrans}$ = 9.7 Hz, $^3J_{HHcis}$ = 6.1 Hz, 1H, H^5), 6.03 (dd, $^3J_{HHtcis}$ = 7.9 Hz, $^3J_{HHcis}$ = 6.1 Hz, 1H, H^4), 5.52−5.42 (m, 1H, H^3), 4.95 (s, 5H, Cp), 3.71−3.50 (m, 2H, $H^{1,2}$), 2.68−2.38 (m, 1H, $H^{1,2}$), 2.65 (dd, $^3J_{HHtrans}$ = 9.7 Hz, $^3J_{PH}$ = 12.5 Hz, 1H, H^{6syn}), 1.22−1.05 (m, 1H, $H^{1,2}$). ^{13}C{^{1}H} NMR (δ, CD_3NO_2/$CDCl_3$ (1:3), 20 °C): 140.6 (d, $^1J_{PC}$ = 49.1 Hz, 1C, Ph^1), 139.6 (d, $^3J_{PC}$ = 1.0 Hz, 1C, Ph^{R1}), 134.1 (d, $^2J_{PC}$ = 10.0 Hz, 2C, $Ph^{2,6}$), 132.0 (d, $^4J_{PC}$ = 2.4 Hz, 1C, Ph^4), 131.0 (d, $^4J_{PC}$ = 2.9 Hz, 1C, $Ph^{4'}$), 131.0 (d, $^2J_{PC}$ = 10.0 Hz, 2C, $Ph^{2',6'}$), 129.8 (d, $^1J_{PC}$ = 40.5 Hz, 1C, $Ph^{1'}$), 129.5 (d, $^3J_{PC}$ = 10.5 Hz, 2C, $Ph^{3,5}$), 129.3 (d, $^3J_{PC}$ = 10.5 Hz, 2C, $Ph^{3',5'}$), 128.7 (2C, $Ph^{R3,5}$), 127.7 (1C, Ph^{R4}), 127.4 (2C, $Ph^{R2,6}$), 87.1 (d, $^2J_{PC}$ = 1.0 Hz, 5C, Cp), 83.8 (C^5), 82.1 (C^4), 80.2 (d, $^3J_{PC}$ = 3.8 Hz, C^3), 64.9 (d, $^2J_{PC}$ = 1.9 Hz, C^6), 45.2 (d, $^1J_{PC}$ = 33.9 Hz, C^1), 24.8 (d, $^2J_{PC}$ = 7.6 Hz, C^2). ^{31}P{^{1}H} NMR (δ, CD_3NO_2/$CDCl_3$ (1:3), 20 °C): 90.7 (PPh$_2$), −143.3 ($^1J_{PF}$ = 709.5 Hz, PF$_6$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 89.6 (PPh$_2$), −143.2 ($^1J_{PF}$ = 712.1 Hz, PF$_6$).

[RuCp(κ^1(P),η^4-(3*Z*)-$PPh_2CH_2CH_2CH{=}CH{-}CPh{=}CH_2$)]$PF_6$ (2b). The volume of the $CHCl_3$ filtrate from the recrystallization of **2a** was reduced to about 1 mL. Upon addition of Et_2O, a white precipitate was formed, which was collected on a glass frit, washed with Et_2O (2 × 2 mL), and dried under vacuum. Yields: 16 mg (7%) and 21 mg (15%) from methods a and b, respectively. Anal. Calcd for $C_{29}H_{27}F_6P_2Ru$: C, 53.38; H, 4.17. Found: C, 53.77; H, 4.44. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.90−7.31 (m, 15H, PPh_2, Ph^R), 6.37 (d, $^3J_{HHcis}$ = 8.4 Hz, 1H, H^4), 5.71 (m, 1H, H^3), 4.70 (s, 5H, Cp), 3.61 (d, $^2J_{HH}$ = 4.9 Hz, 1H, H^{6anti}), 3.56−3.27 (m, 2H, $H^{1,2}$), 2.54−2.21 (m, 1H, $H^{1,2}$), 1.17 (dd, $^2J_{HH}$ = 4.9 Hz, $^3J_{PH}$ = 16.4 Hz, 1H, H^{6syn}), 1.05−0.82 (m, 1H, $H^{1,2}$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 140.5 (d, $^1J_{PC}$ = 46.9 Hz, 1C, Ph^1), 138.7 (1C, Ph^{R1}), 134.8 (d, $^2J_{PC}$ = 10.3 Hz, 2C, $Ph^{2,6}$), 132.8 (d, $^4J_{PC}$ = 2.2 Hz, 1C, Ph^4), 132.0 (d, $^1J_{PC}$ = 39.8 Hz, 1C, $Ph^{1'}$), 131.5 (d, $^2J_{PC}$ = 9.8 Hz, 2C, $Ph^{2',6'}$), 131.4 (d, $^4J_{PC}$ = 3.5 Hz, 1C, $Ph^{4'}$), 130.5 (1C, Ph^{R4}), 130.2 (d, $^3J_{PC}$ = 10.9 Hz, 2C, $Ph^{3,5}$), 130.0 (2C, $Ph^{R3,5}$), 129.8 (d, $^3J_{PC}$ = 9.8 Hz, 2C, $Ph^{3',5'}$), 126.8 (2C, $Ph^{R2,6}$), 103.5 (C^5), 89.5 (5C, Cp), 83.6 (C^4), 79.6 (d, $^3J_{PC}$ = 3.3 Hz, C^3), 46.5 (d, $^1J_{PC}$ = 33.2 Hz, C^1), 42.9 (d, $^2J_{PC}$ = 1.0 Hz, C^6), 25.5 (d, $^2J_{PC}$ = 7.8 Hz, C^2). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 91.8 (PPh$_2$), −143.2 ($^1J_{PF}$ = 712.1 Hz, PF$_6$).

RuCp(κ^1(P),(3,4,5-η)−(3*E*,5*E*/*Z*)-$PPh_2CH_2CH_2CHCH{-}CCHPh$) (2c). The volume of the filtrate of **2a** was reduced to about 2 mL, and insoluble materials were removed by filtration. Evaporation of the remaining solvent gave an orange oil (80 mg). The crude product was dissolved in CH_2Cl_2 (1 mL) and purified via column chromatography (neutral Al_2O_3, 5 g). The first yellow band was eluted with CH_2Cl_2 and evaporated to dryness, affording **2c** as an orange oil. Yield: 67 mg (39%). Anal. Calcd for $C_{29}H_{26}PRu$: C, 68.76; H, 5.17. Found: C, 68.91; H, 5.22. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.65−7.01 (m, 13H, PPh_2, H^6, Ph^R), 6.80 (m, 3H, Ph^R), 4.94 (s, 5H, Cp), 4.47 (m, 1H, H^3), 3.57 (m, 1H, H^4), 2.36−2.07 (m, 1H, $H^{1,2}$), 2.01−1.86 (m, 1H, $H^{1,2}$), 1.74−1.57 (m, 1H, $H^{1,2}$), 1.43−0.88 (m, 1H, $H^{1,2}$). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 171.6 (d, $^3J_{PC}$ = 15.8 Hz, 1C, C^5), 140.7 (d, $^4J_{PC}$ = 2.2 Hz, Ph^{R1}), 140.2 (d, $^1J_{PC}$ = 35.4 Hz, 1C, Ph^1), 138.9 (d, $^1J_{PC}$ = 46.3 Hz, 1C, $Ph^{1'}$), 134.4 (d, $^2J_{PC}$ = 11.4 Hz, 2C, $Ph^{2,6}$), 132.0 (d, $^2J_{PC}$ = 9.8 Hz, 2C, $Ph^{2',6'}$), 130.0 (d, $^4J_{PC}$ = 2.2 Hz, 1C, Ph^4), 129.6 (d, $^4J_{PC}$ = 2.7 Hz, 1C, $Ph^{4'}$), 128.3 (d, $^3J_{PC}$ = 9.3 Hz, 2C, $Ph^{3,5}$), 128.8 (d, $^3J_{PC}$ = 9.8 Hz, 2C, $Ph^{3',5'}$), 127.7 (2C, $Ph^{R3,5}$), 125.8 (d, $^5J_{PC}$ = 1.1 Hz, 2C, $Ph^{R2,6}$), 124.7 (Ph^{R4}), 118.3 (d, $^3J_{PC}$ = 4.9 Hz, C^6), 82.1 (d, $^2J_{PC}$ = 2.2 Hz, 5C, Cp), 61.5 (C^4), 40.7 (d, $^2J_{PC}$ = 1.1 Hz, 1C, C^3), 29.4 (d, $^1J_{PC}$ = 32.7 Hz, C^1), 26.8 (d, $^2J_{PC}$ = 14.2 Hz, C^2). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 84.3 (PPh$_2$).

[RuCp(κ^1(P),η^4-(3Z,5E)-$PPh_2CH_2CH_2CH{=}CH{-}CD{=}CHPh$)]$PF_6$ (2a^D). This complex was prepared analogously to **2a** (method a) in MeOH-d_4 (3 mL), with **1** (100 mg, 0.169 mmol) and DC≡CPh (56 μL, 0.507 mmol) as the starting materials. Yield: 40 mg (36%). Anal. Calcd for $C_{29}H_{26}DF_6P_2Ru$: C, 53.30; H, 4.32. Found: C, 53.42; H, 4.29. ^{1}H NMR (δ, $MeNO_2$-d_3/$CDCl_3$ (1:3), 20 °C): 7.77−7.33 (m, 10H, PPh_2), 7.21 (t, 1H, Ph^{R4}), 7.08 (t, 2H, $Ph^{R3,5}$), 6.62 (d, 2H, $Ph^{R2,6}$), 6.03 (d, $^3J_{HHtcis}$ = 7.9 Hz, 1H, H^4), 5.52−5.42 (m, 1H, H^3), 4.95 (s, 5H, Cp), 3.71−3.50 (m, 2H, $H^{1,2}$), 2.68−2.38 (m, 1H, $H^{1,2}$), 2.65 (d, $^3J_{PH}$ = 12.5 Hz, 1H, H^{6syn}), 1.22−1.05 (m, 1H, $H^{1,2}$). ^{13}C{^{1}H} NMR (δ, $MeNO_2$-d_3/$CDCl_3$ (1:3), 20 °C): 140.6 (d, $^1J_{PC}$ = 49.1 Hz, 1C, Ph^1), 139.6 (d, $^3J_{PC}$ = 1.0 Hz, 1C, Ph^{R1}), 134.1 (d, $^2J_{PC}$ = 10.0 Hz, 2C, $Ph^{2,6}$), 132.0 (d, $^4J_{PC}$ = 2.4 Hz, 1C, Ph^4), 131.0 (d, $^4J_{PC}$ = 2.9 Hz, 1C, $Ph^{4'}$), 131.0 (d, $^2J_{PC}$ = 10.0 Hz, 2C, $Ph^{2',6'}$), 129.8 (d, $^1J_{PC}$ = 40.5 Hz, 1C, $Ph^{1'}$), 129.5 (d, $^3J_{PC}$ = 10.5 Hz, 2C, $Ph^{3,5}$), 129.3 (d, $^3J_{PC}$ = 10.5 Hz, 2C, $Ph^{3',5'}$), 128.7 (2C, $Ph^{R3,5}$), 127.7 (1C, Ph^{R4}), 127.4 (2C, $Ph^{R2,6}$), 87.1 (d, $^2J_{PC}$ = 1.0 Hz, 5C, Cp), 83.9 (t, $^1J_{CD}$ = 23 Hz, C^5), 82.3 (C^4), 80.2 (d, $^3J_{PC}$ = 3.8 Hz, C^3), 65.1 (d, $^2J_{PC}$ = 1.8 Hz, C^6), 45.2 (d, $^1J_{PC}$ = 33.9

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Hz, C^1), 24.8 (d, $^2J_{PC}$ = 7.6 Hz, C^2). ^{31}P{^{1}H} NMR (δ, MeNO$_2$-d_3/CDCl$_3$ (1:3), 20 °C): 90.7 (*P*Ph$_2$), −143.3 ($^1J_{PF}$ = 709.5 Hz, *P*F$_6$).

[RuCp(κ^1(P),η^4-(3*Z*,5*E*)-PPh$_2$CH$_2$CH$_2$CH=CH−CD=CHPh)]PF$_6$(2a^D) and [RuCp(κ^1(P),η^4-(3*Z*,5*Z*)-PPh$_2$CH$_2$CH$_2$CH=CH−CPh=CHD)]PF$_6$ (2b^D). A sealed NMR tube, charged with **1** (20 mg, 0.034 mmol) and DC≡CPh (9.6 μL, 0.101 mmol), was heated at 57 °C with CDCl$_3$ as the solvent. The sample was transferred to a NMR probe, and ^{1}H and ^{31}P{^{1}H}NMR spectra were recorded. The conversion was complete after 1 h 10 min, resulting in a mixture of **2a^D** (78%) and **2b^D** (22%). The ^{1}H NMR spectra of these complexes are consistent with those of **2a** and **2b**, respectively, excepting the following signals. **2a^D**: The signal at 6.48 ppm is no longer observed (PhCH=C*D*−CH=CH−CH$_2$), 6.03 (d $^3J_{HHtcis}$ = 7.9 Hz, 1H, PhCH=CD−C*H*=CH−CH$_2$), 2.65 (d, $^3J_{PH}$ = 12.5 Hz, 1H, PhC*H^{syn}*=CD−CH=CH−CH$_2$). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 89.6 (*P*Ph$_2$), −143.2 ($^1J_{PF}$ = 712.1 Hz, *P*F$_6$). **2b^D**: The signal at 3.61 ppm is no longer observed (*D^{anti}*CH=CPh−CH=CH−CH$_2$), 1.17 (d, $^3J_{PH}$ = 16.4 Hz, 1H, DC*H^{syn}*=CPh−CH=CH−CH$_2$). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 91.8 (*P*Ph$_2$), −143.2 ($^1J_{PF}$ = 712.1 Hz, *P*F$_6$).

RuCp(κ^1(P),(3,4,5-η)-PPh$_2$CH$_2$CH$_2$CHCHCCDPh) (2c^D). This complex was prepared analogously to **2a** (method a) in MeOH-d_4 (3 mL), with **1** (100 mg, 0.169 mmol) and DC≡CPh (56 μL, 0.507 mmol) as the starting materials. Yield: 24 mg (28%). Anal. Calcd for C$_{29}$H$_{25}$DPRu: C, 68.62; H, 5.36. Found: C, 68.88; H, 5.44. ^{1}H NMR (δ, CDCl$_3$, 20 °C): 7.65−7.01 (m, 12H, PPh$_2$, Ph^R), 6.80 (m, 3H, Ph^R), 4.94 (s, 5H, Cp), 4.47 (m, 1H, H^3), 3.57 (m, 1H, H^4), 2.36−2.07 (m, 1H, H^{1,2}), 2.01−1.86 (m, 1H, H^{1,2}), 1.74−1.57 (m, 1H, H^{1,2}), 1.43−0.88 (m, 1H, H^{1,2}). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 171.6 (d, $^3J_{PC}$ = 15.8 Hz, 1C, C^5), 140.7 (d, $^4J_{PC}$ = 2.2 Hz, Ph^{R1}), 140.2 (d, $^1J_{PC}$ = 35.4 Hz, 1C, Ph^1), 138.9 (d, $^1J_{PC}$ = 46.3 Hz, 1C, Ph$^{1'}$), 134.4 (d, $^2J_{PC}$ = 11.4 Hz, 2C, Ph^{2,6}), 132.0 (d, $^2J_{PC}$ = 9.8 Hz, 2C, Ph$^{2',6'}$), 130.0 (d, $^4J_{PC}$ = 2.2 Hz, 1C, Ph^4), 129.6 (d, $^4J_{PC}$ = 2.7 Hz, 1C, Ph$^{4'}$), 128.3 (d, $^3J_{PC}$ = 9.3 Hz, 2C, Ph^{3,5}), 128.8 (d, $^3J_{PC}$ = 9.8 Hz, 2C, Ph$^{3',5'}$), 127.7 (2C, Ph^{R3,5}), 125.7 (2C, Ph^{R2,6}), 124.7 (Ph^{R4}), C^6 not observed, 82.1 (d, $^2J_{PC}$ = 2.1 Hz, 5C, Cp), 61.5 (C^4), 40.7 (d, $^2J_{PC}$ = 1.1 Hz, 1C, C^3), 29.4 (d, $^1J_{PC}$ = 32.7 Hz, C^1), 26.8 (d, $^2J_{PC}$ = 14.2 Hz, C^2). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 84.3 (*P*Ph$_2$).

[RuCp(κ^1(P),η^4-(3*Z*,5*E*)-PPh$_2$CH$_2$CH$_2$CH=CH−CH=CHPh)]PF$_6$ (2a) and [RuCp(κ^1(P),η^4-(3*Z*)-PPh$_2$CH$_2$CH$_2$CH=CH−CPh=CH$_2$)]PF$_6$ (2b). A sealed NMR tube, charged with a solution of **1** (20 mg, 0.034 mmol) and HC≡CPh (9.6 μL, 0.101 mmol) in CDCl$_3$ (0.5 mL), was heated at 57 °C. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies, indicating complete conversion after 1 h to give a mixture of **2a** (76%) and **2b** (23%).

[RuCp(κ^1(P),η^4-(3*Z*,5*Z*)-PPh$_2$CH$_2$CH$_2$CH=CH−CH=CHPh)]CF$_3$COO (2d). A 5 mm NMR tube was charged with **1c** (20 mg, 0.039 mmol) and was capped with a septum. A solution of CF$_3$COOH (20 μL) in CDCl$_3$ (0.3 mL) was added by syringe, and the mixture was transferred to the probe head. NMR spectra were immediately recorded, indicating the quantitative formation of **2d**.^{1}H NMR (δ, CDCl$_3$, 20 °C): 7.66−7.24 (m, 15H, PPh$_2$, Ph^R), 5.82 (d, $^3J_{HHcis}$ = 7.6 Hz, 1H, H^6), 5.58 (m, 2H, H^4, H^3), 4.52 (s, 5H, Cp), 3.23−3.08 (m, 3H, H^5, H^{1,2}), 2.86−2.60 (m, 1H, H^{1,2}), 2.38−2.10 (m, 1H, H^{1,2}). ^{13}C-{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 160.7 (q, $^3J_{FC}$ = 38.3 Hz, 1C, *C*F$_3$COO), 138.4 (Ph^{R1}), 136.1 (d, $^1J_{PC}$ = 47.4 Hz, 1C, Ph^1), 132.9 (d, $^2J_{PC}$ = 8.1 Hz, 2C, Ph^{2,6}), 132.6 (d, $^4J_{PC}$ = 2.2 Hz, 1C, Ph^4), 131.5 (d, $^4J_{PC}$ = 2.8 Hz, 1C, Ph$^{4'}$), 130.3 (d, $^3J_{PC}$ = 10.4 Hz, 2C, Ph^{3,5}), 130.2 (d, $^3J_{PC}$ = 9.8 Hz, 2C, Ph$^{3',5'}$), 129.92 (4C, Ph^{R2,3,5,6}), 129.9 (d, $^2J_{PC}$ = 10.4 Hz, 2C, Ph$^{2',6'}$), 127.9 (Ph^{R4}), 127.7 (d, $^1J_{PC}$ = 43.6 Hz, 1C, Ph$^{1'}$), 116.4 (q, $^2J_{FC}$ = 289.6 Hz, 1C, CF$_3$*C*OO), 90.9 (C^5), 90.2 (d, $^2J_{PC}$ = 1.6 Hz, 5C, Cp), 87.9 (C^4), 82.7 (d, $^3J_{PC}$ = 2.7 Hz, C^3), 74.5 (C^6), 41.1 (d, $^1J_{PC}$ = 32.2 Hz, C^1), 25.3 (d, $^2J_{PC}$ = 9.9 Hz, C^2). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 73.4 (*P*Ph$_2$).

[RuCp(κ^1(P),η^4-(3*Z*,5*Z*)-PPh$_2$CH$_2$CH$_2$CH=CH−CPh=CHPh)]PF$_6$ (3). A solution of **1** (108 mg, 0.182 mmol) and PhC≡CPh (48.7 mg, 0.273 mmol) in CHCl$_3$ (4 mL) was heated under reflux for 17 h. The volume of the solution was reduced to 0.5 mL, and upon addition of Et$_2$O (1 mL), a white precipitate was formed, which was collected on a glass frit, washed with Et$_2$O (3 × 2 mL), and dried in vacuo. Yield: 121 mg (91%). Anal. Calcd for C$_{35}$H$_{31}$F$_6$P$_2$Ru: C, 57.69; H, 4.29. Found: C, 57.92; H, 4.42. ^{1}H NMR (δ, CDCl$_3$, 20 °C): 7.48−7.43 (m, 6H, PPh$_2$, Ph$^{R'}$), 7.32−7.20 (m, 9H, PPh$_2$, Ph$^{R'}$), 7.03 (t, 1H, Ph^{R4}), 6.82 (t, 2H, Ph^{R3,5}), 6.37 (d, 2H, Ph^{R2,6}), 6.33 (m, 1H, H^4), 5.61 (m, 1H, H^3), 4.98 (s, 5H, Cp), 3.60−3.41 (m, 2H, H^{1,2}), 2.75−2.43 (m, 1H, H^{1,2}), 2.35 (d, $^3J_{PH}$ = 15.3 Hz, 1H, H^{6syn}), 1.54−1.30 (m, 1H, H^{1,2}). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 141.1 (d, $^1J_{PC}$ = 48.0 Hz, 1C, Ph^1), 139.6 (Ph^{R1}), 137.0 (Ph$^{R'1}$), 134.1 (d, $^2J_{PC}$ = 9.8 Hz, 2C, Ph^{2,6}), 132.1 (d, $^4J_{PC}$ = 2.2 Hz, 1C, Ph^4), 131.6 (2C, Ph$^{R'}$), 131.4 (d, $^4J_{PC}$ = 2.8 Hz, 1C, Ph$^{4'}$), 131.2 (d, $^2J_{PC}$ = 9.8 Hz, 2C, Ph$^{2',6'}$), 130.5 (2C, Ph$^{R'}$), 130.01 (Ph$^{R'4}$), 130.02 (d, $^3J_{PC}$ = 10.4 Hz, 2C, Ph^{3,5}), 130.03 (d, $^1J_{PC}$ = 41.4 Hz, 1C, Ph$^{1'}$), 129.7 (d, $^3J_{PC}$ = 10.4 Hz, 2C, Ph$^{3',5'}$), 129.3 (2C, Ph^{R3,5}), 128.4 (1C, Ph^{R4}), 127.2 (2C, Ph^{R2,6}), 105.5 (C^5), 90.0 (5C, Cp), 84.8 (C^4), 76.8 (d, $^3J_{PC}$ = 3.8 Hz, C^3), 61.7 (d, $^2J_{PC}$ = 1.9 Hz, C^6), 45.5 (d, $^1J_{PC}$ = 34.9 Hz, C^1), 24.9 (d, $^2J_{PC}$ = 8.7 Hz, C^2). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 92.1 (*P*Ph$_2$), −143.4 ($^1J_{PF}$ = 713.4 Hz, *P*F$_6$).

[RuCp(κ^1(P),η^4-(3*Z*,5*Z*)-PPh$_2$CH$_2$CH$_2$CH=CH−CPh=CHPh)]PF$_6$ (3). A sealed NMR tube, charged with a solution of **1** (20 mg, 0.034 mmol) and PhC≡CPh (18.2 mg, 0.102 mmol) in CDCl$_3$ (0.5 mL), was heated at 57 °C. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies, indicating complete conversion after 8 h.

[RuCp(κ^1(P),η^4-(3Z,5E)-PPh$_2$CH$_2$CH$_2$CH=CH−CEt=CHEt)]PF$_6$ (4). A solution of **1** (100 mg, 0.169 mmol) and EtC≡CEt (29.0 μL, 0.254 mmol) in CHCl$_3$ (4 mL) was heated at reflux for 17 h. The solution was reduced to about 0.5 mL, and upon addition of Et$_2$O (1 mL), a bright yellow precipitate was formed, which was collected on a glass frit, washed with Et$_2$O (3 × 2 mL), and dried in a vacuum. Yield: 98 mg (92%). Anal. Calcd for C$_{27}$H$_{31}$F$_6$P$_2$Ru: C, 51.27; H, 4.94. Found: C, 51.44; H, 5.09. ^{1}H NMR (δ, CDCl$_3$/CD$_3$NO$_2$ (4:1), 20 °C): 7.65−7.62 (m, 5H, PPh$_2$), 7.46−7.42 (m, 3H, PPh$_2$), 7.38−7.30 (m, 2H, PPh$_2$), 5.60 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H^4), 5.23 (m, 1H, H^3), 4.83 (s, 5H, Cp.), 3.45−3.02 (m, 2H, H^{1,2}), 2.66−2.04 (m, 3H, C*H*$_2$CH$_3$, H^{1,2}, H^{6syn}), 1.66−1.47 (m, 1H, C*H*$_2$CCH$_3$), 1.36 (m, 4H, H,^{1,2} CH$_2$C*H*$_3$), 1.05−0.85 (m, 2H, C*H*$_2$CH$_3$), 0.60 (VT, 3H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (δ, CDCl$_3$/CD$_3$NO$_2$ (4:1), 20 °C): 140.7 (d, $^1J_{PC}$ = 47.4 Hz, 1C, Ph^1), 133.2 (d, $^2J_{PC}$ = 9.3 Hz, 2C, Ph^{2,6}), 132.3 (d, $^4J_{PC}$ = 2.7 Hz, 1C, Ph^4), 131.4 (d, $^2J_{PC}$ = 10.4 Hz, 2C, Ph$^{2',6'}$), 131.2 (d, $^4J_{PC}$ = 2.7 Hz, 1C, Ph$^{4'}$), 129.9 (d, $^3J_{PC}$ = 10.4 Hz, 2C, Ph^{3,5}), 129.7 (d, $^3J_{PC}$ = 10.4 Hz, 2C, Ph$^{3',5'}$), 129.1 (d, $^1J_{PC}$ = 47.4 Hz, 1C, Ph$^{1'}$), 108.9 (C^5), 87.1 (d, $^2J_{PC}$ = 1.1 Hz, 5C, Cp.), 83.6 (C^4), 77.6 (d, $^3J_{PC}$ = 2.7 Hz, C^3), 65.7 (d, $^2J_{PC}$ = 2.7 Hz, C^6), 44.9 (d, $^1J_{PC}$ = 34.3 Hz, C^1), 29.5 (*C*H$_2$CH$_3$), 25.6 (*C*H$_2$CH$_3$), 24.7 (d, $^2J_{PC}$ = 7.6 Hz, C^2), 18.6 (CH$_2$*C*H$_3$), 16.5 (CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (δ, CDCl$_3$/CD$_3$NO$_2$ (4:1), 20 °C): 86.8 (*P*Ph$_2$), −143.8 ($^1J_{PF}$ = 709.8 Hz, *P*F$_6$).

[RuCp(κ^1(P),η^4-(3Z,5E)-PPh$_2$CH$_2$CH$_2$CH=CH−CEt=CHPh)]PF$_6$(5a) and [RuCp(κ^1(P),η^4-(3Z,5Z)-PPh$_2$CH$_2$CH$_2$CH=CH−CPh=CHEt)]PF$_6$ (5b). A solution of **1** (144 mg, 0.243 mmol) and EtC≡CPh (52 μL, 0.364 mmol) in CHCl$_3$ (4 mL) was heated under reflux for 17 h. The solution was reduced to 0.5 mL, and upon addition of Et$_2$O (1 mL), a white precipitate was formed, which was collected on a glass frit, washed with Et$_2$O (3 × 2 mL), and dried in vaccuo. Yield: 159 mg (96%) as a regioisomeric mixture of **5a** and **5b** in a 7:1 ratio (determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies). **5a** could be obtained in pure form after purification by column chromatography (silica gel). The first yellow band was eluted with CH$_2$Cl$_2$/MeOH (v/v = 30:1). Recrystallization of the crude product from CHCl$_3$ yielded analytically pure **5a** in the form of yellow crystals. Yield: 78 mg (47%). **5b** could not be obtained

Table 2. Crystallographic Data for 1, 2a·CH_2Cl_2, and 5a·$^1/_2CH_2Cl_2$

	1	**2a**·CH_2Cl_2	**5a**·$^1/_2CH_2Cl_2$
formula	$C_{23}H_{25}F_6NP_2Ru$	$C_{30}H_{30}Cl_2F_6P_2Ru$	$C_{31.5}H_{33}ClF_6P_2Ru$
fw	592.45	738.45	724.04
cryst size, mm	0.55 × 0.28 × 0.06	0.65 × 0.12 × 0.12	0.50 × 0.35 × 0.25
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	7.813(2)	10.333(4)	16.349(4)
b, Å	20.403(5)	16.974(6)	17.377(6)
c, Å	15.866(6)	18.054(6)	22.709(8)
β, deg	101.63(2)	106.84(2)	106.72(2)
V, Å^3	2477(1)	3031(1)	6179(3)
Z	4	4	8
ρ_{calc}, g cm^{-3}	1.589	1.618	1.557
T, K	298(2)	298(2)	295(2)
μ, mm^{-1} (Mo Kα)	0.818	0.856	0.755
abs corr	empirical	empirical	multiscan
F(000)	1192	1488	2936
transmiss fact. min/max	0.93−0.84	0.93−0.87	0.80−0.74
θ_{max}, deg	25	25	25
index ranges	$-9 \le h \le 9$ $-24 \le k \le 24$ $-18 \le l \le 18$	$-12 \le h \le 12$ $-20 \le k \le 20$ $-21 \le l \le 21$	$-19 \le h \le 19$ $-20 \le k \le 20$ $-26 \le l \le 27$
no. of rflns measd	24 641	30 458	59 464
no. of unique rflns	4300	5331	10 835
no. of rflns $I > 2\sigma(I)$	3435	4235	8935
no. of params	307	410	812
R_1 ($I > 2\sigma(I)$)[a]	0.048	0.033	0.042
R_1 (all data)	0.063	0.051	0.053
wR_2 (all data)[b]	0.139	0.080	0.109
diff Fourier peaks min/max, e Å^{-3}	−0.56/0.69	−0.31/0.49	−0.56/0.53

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

in pure form. Anal. Calcd for $C_{31}H_{31}F_6P_2Ru$: C, 54.71; H, 4.59. Found: C, 55.00; H, 4.74. **5a**: ^{1}H NMR (δ, $CDCl_3/CD_3NO_2$ (4:1), 20 °C): 7.42−7.40 (m, 4H, PPh_2), 7.29−6.92 (m, 9H, PPh_2, Ph^R), 6.67 (d, 1H, $Ph^{R2,6}$), 5.66 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H^4), 5.27 (m, 1H, H^3), 4.91 (s, 5H, Cp), 3.46−3.35 (m, 3H, CH_2CH_3, $H^{1,2}$), 3.12−2.98 (m, 1H, CH_2CH_3), 2.60−2.47 (m, 1H, $H^{1,2}$), 2.20 (d, $^3J_{PH}$ = 14.4 Hz, 1H, H^{6syn}), 1.38−1.18 (m, 1H, $H^{1,2}$), 1.06 (t, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3/CD_3NO_2$ (4:1), 20 °C): 140.7 (d, $^1J_{PC}$ = 48.0 Hz, 1C, Ph^1), 137.4 (Ph^R), 133.8 (d, $^2J_{PC}$ = 10.4 Hz, 2C, $Ph^{2,6}$), 131.6 (d, $^4J_{PC}$ = 2.7 Hz, 1C, Ph^4), 131.2 (d, $^4J_{PC}$ = 2.7 Hz, 1C, $Ph^{4'}$), 130.9 (d, $^2J_{PC}$ = 9.8 Hz, 2C, $Ph^{2',6'}$), 130.2 (2C, $Ph^{R3,5}$), 129.5 (d, $^3J_{PC}$ = 10.4 Hz, 2C, $Ph^{3,5}$), 128.9 (d, $^3J_{PC}$ = 10.4 Hz, 2C, $Ph^{3',5'}$), 128.5 (2C, $Ph^{R2,6}$), 127.5 (d, $^1J_{PC}$ = 49.6 Hz, 1C, Ph^1), 127.4 (1C, Ph^{R4}), 108.7 (C^5), 87.8 (d, $^2J_{PC}$ = 1.1 Hz, 5C, Cp), 81.1 (C^4), 76.9 (d, $^3J_{PC}$ = 3.3 Hz, C^3), 66.0 (d, $^2J_{PC}$ = 3.3 Hz, C^6), 45.2 (d, $^1J_{PC}$ = 34.9 Hz, C^1), 29.6 (CH_2CH_3), 24.4 (d, $^2J_{PC}$ = 7.6 Hz, C^2), 17.0 (CH_2CH_3). $^{31}P\{^1H\}$ (δ, $CDCl_3/CD_3NO_2$ (4:1), 20 °C): 90.2 (PPh_2), −143.8 ($^1J_{PF}$ = 709.5 Hz, PF_6). NMR spectra of **5b** were taken from the mixture of regioisomers. ^{1}H NMR (δ, $CDCl_3/CD_3NO_2$ (4/1), 20 °C) (resonances in aromatic region could not be assigned): 5.79 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H^4), 5.10 (m, 1H, H^3), 4.82 (s, 5H, Cp), 0.25 (t, 3H, CH_2CH_3); the resonances of all other protons were not assignable. $^{13}C\{^1H\}$ NMR (δ, $CDCl_3/CD_3NO_2$ (4:1), 20 °C): 140.8 (d, $^1J_{PC}$ = 48.0 Hz, 1C, Ph^1), 138.1 (Ph^R), 133.9 (d, $^2J_{PC}$ = 9.8 Hz, 2C, $Ph^{2,6}$), 132.6 (d, $^4J_{PC}$ = 2.7 Hz, 1C, Ph^4), 131.2 (d, $^4J_{PC}$ = 2.7 Hz, 1C, $Ph^{4'}$), 131.0 (d, $^2J_{PC}$ = 9.8 Hz, 2C, $Ph^{2',6'}$), 130.3 (2C, $Ph^{R3,5}$), 129.9 (d, $^3J_{PC}$ = 10.4 Hz, 2C, $Ph^{3,5}$), 129.6 (d, $^3J_{PC}$ = 10.4 Hz, 2C, $Ph^{3',5'}$), 129.0 (d, $^1J_{PC}$ = 36.5 Hz, 1C, Ph^1), 128.9 (2C, $Ph^{R2,6}$) (Ph^{R4} was not observed due to coupling with the deuterium atom), 108.7 (C^5), 88.0 (d, $^2J_{PC}$ = 1.1 Hz, 5C, Cp), 83.3 (C^4) (C^3 was not observed), 66.0 (d, $^2J_{PC}$ = 3.2 Hz, C^6), 44.7 (d, $^1J_{PC}$ = 35.4 Hz, C^1), 25.6 (CH_2CH_3), 24.4 (d, $^2J_{PC}$ = 7.6 Hz, C^2), 15.3 (CH_2CH_3). $^{31}P\{^1H\}$ (δ, $CDCl_3/CD_3NO_2$ (4:1), 20 °C): 90.4 (PPh_2), −143.8 ($^1J_{PF}$ = 709.5 Hz, PF_6).

X-ray Structure Determination for 1, 2a·CH_2Cl_2, and 5a·$^1/_2CH_2Cl_2$. Crystals of **1**, **2a**·CH_2Cl_2, and **5a**·$^1/_2CH_2Cl_2$ were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. Crystal data and experimental details are given in Table 2. X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite monochromated Mo Kα radiation, λ = 0.710 73 Å, a nominal crystal-to-detector distance of 4.45 cm, 0.3° ω-scan frames). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied (multiscan method, program SADABS[13] was used). The structures of **1** and **5a**·$^1/_2CH_2Cl_2$ were solved by direct methods, whereas the structure of **2a**·CH_2Cl_2 was solved by the Patterson method, using the program SHELXS97.[14] Structure refinement on F^2 was carried out with the program SHELXL97.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, bond lengths and angles, and least-squares planes for **1**, **2a**·CH_2Cl_2, and **5a**·$^1/_2CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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