Novel [2+2+1] Cyclotrimerization of Alkynes Mediated by Bidentate Cyclopentadienyl-Phosphine Ruthenium Complexes

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A remarkable change in reactivity of ruthenium cyclopentadienyl phosphine complexes toward alkynes HC≡CR′ (R′ = Ph, C_6H_9, *p*-C_6H_4Me, *p*-C_6H_4OMe, ferrocenyl (Fc)) has been observed when the phosphine ligand is tethered onto the Cp ring via a two-carbon linker. That is, we contrast $[RuCp(PR_3)(CH_3CN)_2]PF_6$, dealt with before, with the bidentate cyclopentadienyl-phosphine complex $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2\text{-}\kappa^1P\text{-}PPh_2)(CH_3CN)_2]PF_6$. While a metallacyclopentatriene complex (**C**) generated via oxidative coupling of two alkynes is a common first key intermediate, the onward reaction of **C** differs greatly. If the phosphine is tethered, a third alkyne molecule can be accommodated, resulting finally in an unusual C−C coupling process involving three alkynes and the tethered phosphine to give the cycloaddition product $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2PH_2\text{-}\kappa^1C\text{-}CH\text{-}\eta^4\text{-}C_5H_5)]^+$. According to DFT/B3LYP calculations this intriguing [2+2+1] alkyne cyclotrimerization proceeds via Ru−P bond dissociation, phosphine attack at the coordinated acetylene to yield a 1-metallacyclopropene, carbene vinyl insertion, and olefin vinyl insertion. On the other hand, for HC≡CR′ (R′ = COOMe, COOEt, COMe) a [2+2+2] cyclotrimerization is favored. In sharp contrast, if the phosphine in **C** is simply unidentate, alkyne attack is prohibited, with alternative internal rearrangements taking place involving phosphine migration or 1,2-hydrogen shift. In these terms tethering may be considered as amounting to a delayed phosphine migration. Thus, the phosphine ligand in ruthenium chemistry is not necessarily just a spectator ligand but can switch over to an actor ligand.

Introduction

Recently we have probed the possibility of utilizing ruthenium complexes for mediating the [2+2+2] cyclotrimerization of alkynes. The metal compound for this purpose should bear, of course, two vacant coordination sites or, equivalently, two substitution-labile ligands. This is the case with RuCp(COD)X and RuCp*(COD)X (X = Cl, Br), which in fact are efficient catalysts for the cyclotrimerization of 1,6-diynes in combination with other alkynes, olefins, and other unsaturated substrates.[1,2] We have used the substitutionally labile complex $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = Me, Ph, Cy), which features the synthetic equivalent for the 14-electron fragment $[RuCp(PR_3)]^+$.[3] This entity is a promising candidate since it enables ligand variations via the phosphine substituents so as to control the regioselectivity of the alkyne coupling process.

Unfortunately, these complexes turned out to be catalytically inactive. Instead, the reaction with alkynes generates a number of unusual compounds such as allyl and butadienyl carbenes.[4] The reaction outcomes were found to vary with the structure of the alkyne and the substituent of the phosphine ligand. Notwithstanding this, there appears to be a common first step given by the formation of a cationic metallacyclopentatriene complex as a result of oxidative coupling. A key feature of these complexes is the remarkable electrophilicity of the α-carbon atoms initiating two types of rearrange-

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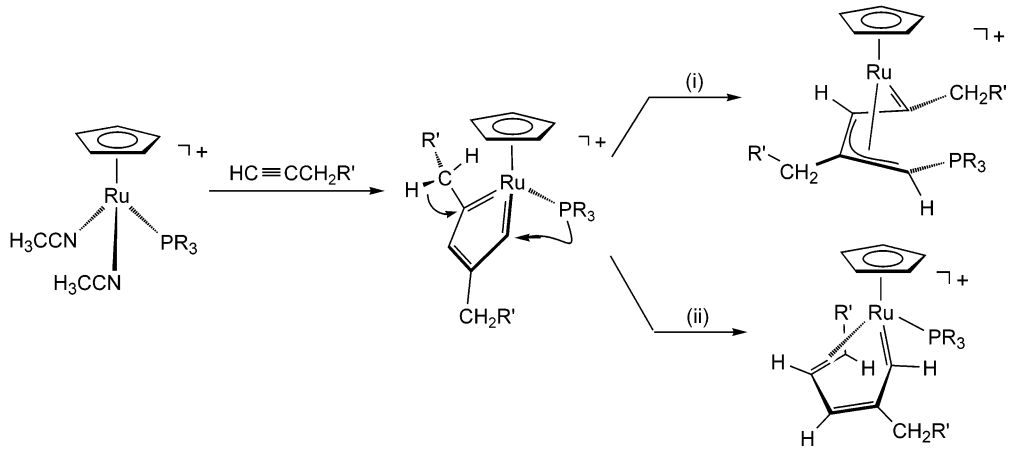
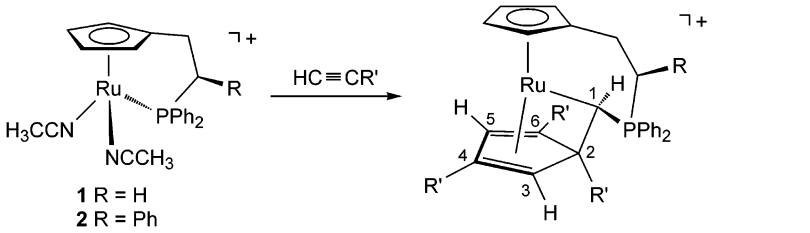
Scheme 1



Scheme 2



1 R = H
2 R = Ph

3a-e R = H; R' = Ph, C_6H_9, *p*-C_6H_4Me, *p*-C_6H_4OMe, Fc
4 R = Ph; R' = *p*-C_6H_4-Me

ment as shown in Scheme 1. Thus, either the phosphine ligand migrates to give allyl carbenes (pathway (i)) or, in the presence of α-substituents with C−H bonds, a 1,2-hydrogen shift results in butadienyl carbenes (pathway (ii)). All these perhaps unexpected and unprecedented reactions, in addition to steric effects imposed by the PR_3 ligand, actually quench the catalytic activity toward cyclotrimerization. For the latter to occur, the addition of a third alkyne to the metal center should be enabled with subsequent C−C bond formation.

It can be expected that nucleophilic attack at the α-carbon of the metallacycle is impeded if in $[RuCp(PR_3)(CH_3CN)_2]^+$ the phosphine ligand is tethered to the Cp unit via a CH_2CH_2 linker. In fact, there are a number of examples known where the introduction of two-carbon tethers in cyclopentadienyl complexes changes dramatically the reactivity pattern relative to the parent cyclopentadienyl system.[5] This scheme is pursued in the present contribution. Thus, we will investigate the reactivity of the bidentate cyclopentadienyl-phosphine ruthenium complex $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2\text{-}\kappa^1P\text{-}PPh_2)(CH_3CN)_2]PF_6$ (**1**) and the chiral derivative $[(S)\text{-}Ru(\eta^5\text{-}C_5H_4CH_2CH(Ph)\text{-}\kappa^1P\text{-}PPh_2)(CH_3CN)_2]PF_6$ (**2**) toward terminal alkynes lacking C−H bonds adjacent to the C−C triple bond. Upon this modification, by anticipation, alkyne cyclotrimerization is unleashed in fact, but in the rather exceptional [2+2+1] mode, instead of the common [2+2+2] type. Here we describe synthetic as well as mechanistic aspects of this intriguing type of conversion supported by DFT/B3LYP calculations.

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Results and Discussion

Synthetic Aspects. Treatment of **1** with 3 equiv of HC≡CR′ (R′ = Ph, C_6H_9, *p*-C_6H_4Me, *p*-C_6H_4OMe, ferrocenyl (Fc)) in CH_2Cl_2 at room temperature for 24 h results in the formation of $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2\text{-}\kappa^1C\text{-}CH\text{-}\eta^4\text{-}C_5R'_3H_2)]PF_6$ (**3a**−**e**) in 72−92% isolated yields (Scheme 2). It should be noted that only trace amounts (<5%) of [2+2+2] cyclotrimerization products were detected. In analogous fashion the chiral complex **2** reacts with HC≡CR′ (R′ = *p*-C_6H_4Me) to give $[Ru(\eta^5\text{-}C_5H_4CH_2CH(Ph)PPh_2\text{-}\kappa^1C\text{-}CH\text{-}\eta^4\text{-}C_5R'_3H_2)]BF_4$ (**4**). These compounds are air-stable both in solution and in the solid state and were characterized by a variety of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic methods as well as elemental analysis. In the course of the overall [2+2+1] cyclotrimerization[6] three new C−C bonds and one P−C bond are formed, thereby converting two C−C triple bonds into C−C double bonds and one C−C triple bond into a C−C single bond. Notwithstanding such a complex course of reaction, the C−C couplings are highly regio- and diastereoselective with the substituents ending up exclusively in the 2, 4, and 6 position, as can be seen from Scheme 2. The ^1H NMR spectroscopic data for **3a** include characteristic resonances at 6.86 (dd, $^4J_{HH}$ = 1.5 Hz, $^4J_{HP}$ = 4.7 Hz), 3.81 (d, 1H, $^4J_{HH}$ = 1.5 Hz), and 1.83 (d, 1H, $^2J_{PH}$ = 13.7 Hz)

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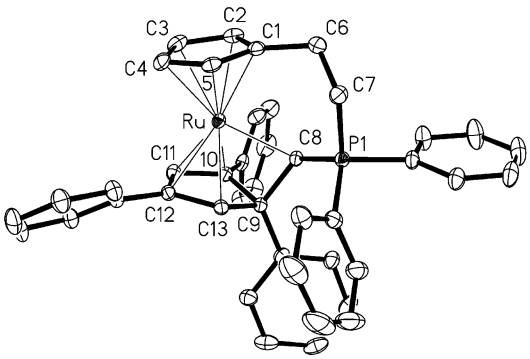

Figure 1. Structural view of [Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1C-CH-η^4-$C_5Ph_3H_2$)]PF_6·$(CH_3)_2CO$ (**3a**·$(CH_3)_2CO$) showing 20% thermal ellipsoids (H atoms, PF_6^-, and $(CH_3)_2CO$ omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ 2.204(2), Ru−C(8) 2.181(2), Ru−C(9) 2.483(2), Ru−C(10) 2.204(2), Ru−C(11) 2.188(2), Ru−C(12) 2.194(2), Ru−C(13) 2.192(2), C(8)−C(9) 1.543(2), C(9)−C(10) 1.558(2), C(10)−C(11) 1.409(2), C(11)−C(12) 1.434(3), C(12)−C(13) 1.416(2), C(13)−C(9) 1.531(2), C(7)−P(1) 1.829(2), C(8)−P(1) 1.782(2), C(8)−C(9)−C(10) 96.7(1), C(8)−C(9)−C(13) 100.5(1).

assignable to the terminal and internal diene protons of the coordinated η^4-cyclopentadiene unit and the Ru−CH-proton. In the $^{13}C\{^1H\}$ NMR spectrum the resonance of the sp^3 carbon C^1 is diagnostic, giving rise to an unusually high-field-shifted doublet centered at −37.1 ppm with a coupling constant $^1J_{PC}$ of 52.9 Hz. The coordinated sp^2 carbon atoms C^3, C,^{4} C,^{5} and C^6 of the cyclopentadiene moiety exhibit resonances at 57.4 (d, $^3J_{PC}$ = 4.6 Hz), 101.0, 82.5, and 62.6 ppm, respectively, while the noncoordinated quaternary sp^3 carbon C^2 gives rise to a doublet centered at 85.7 ppm ($^2J_{PC}$ = 17.6 Hz). In the $^{31}P\{^1H\}$ NMR spectrum the phosphonium moiety exhibits a singlet at 20.3 ppm. Concurrent NMR spectra are observed for **3b**−**e** and **4**.

In addition, the reaction of **1** with HC≡C-*p*-C_6H_4Me was also studied at −30 °C in acetone-d_6 by means of a ^1H, ^{31}P-HMBC (heteronuclear multiple bond correlation) experiment, revealing the formation of an intermediate with a ^{31}P resonance at 16.3 ppm correlated to a hydrogen atom at 4.76 ppm (J_{PH} = 17.8 Hz). Furthermore, this proton exhibits a long-range coupling with a coupling constant of J_{HH} = 2.0 Hz. These data point to the presence of a $-PPh_2-CH{=}CR'-CH-$ unit with the phosphine moiety already attached to a carbon atom bearing a hydrogen atom.

The structural identity of **3a** was established by X-ray crystallography. The ORTEP diagram of **3a**·$(CH_3)_2CO$ depicted in Figure 1 displays an overall three-legged piano stool geometry with the C atom of the $-CHPPh_2-$ moiety and the two C=C bonds of the cyclopentadiene unit as the legs. All Ru−C distances of the cyclopentadiene moiety are rather uniform, ranging from 2.188(2) to 2.204(2) Å. The Ru−C(8) bond is 2.181(2) Å, typical of a Ru−C(sp^3) single bond in Ru(II) complexes. For comparison, in [RuCp(η^4-CH(C_6H_9)CHC(C_6H_9)CHPCy_2-(η^1-C_6H_{10}))]PF_6 and [Ru(η^6-$MeC_6H_4Pr^i$)(κ^2S,S'-$(SPPh_2)_2$-η^1-CMe)]PF_6 the Ru−C σ-bond distance amounts to 2.214(2) and 2.239(10) Å, respectively.[7,8] The butadiene C−C bonds C(10)−C(11), C(11)−C(12), and C(12)−C(13) reveal slightly alternating bond distances in terms of a short−long−short pattern (1.409(2), 1.434(3), and 1.416(2) Å). The C−C bond distances about the quaternary carbon C(9) are 1.543(2) Å to C(8), 1.558(2) Å to C(10), and 1.531(2) Å to C(13).

It should be emphasized that depending on the substituents of the alkyne also other conversions are feasible. Thus, upon treatment of **1** with an excess of HC≡CR′ (R′ = COOMe, COOEt, COMe) at room temperature in CD_3NO_2 as the solvent only small amounts (<10%) of a [2+2+1] cycloaddition product of the type **3** and **4** could be detected by ^{31}P NMR spectroscopy (characteristic resonances were observed at about 20 ppm). The major products turned out to be isomeric mixtures of 1,2,4- and 1,3,5-substituted benzenes (ca 60% conversion after 5 days) apparently from catalytic [2+2+2] cyclotrimerization. Actually, treatment of HC≡CR′ with catalytic amounts of **1** (5 mol %) in CD_3NO_2 at 90 °C for 14 h afforded quantitatively the corresponding trisubstituted benzenes in a 3:1 ratio. Similar results have been obtained with the chiral complex **2** as catalyst. The organic products were readily identified by comparison with the literature.[9]

Mechanistic Aspects

A mechanistic proposal for the conversions of **1** and **2** with alkynes to the products **3** and **4** is presented in Scheme 3. Support for this scheme comes from DFT/B3LYP calculations using Gaussian98 for the reaction of the model complex [Ru(η^5-$C_5H_4CH_2CH_2$-κ^1P-PH_2)-$(HCN)_2]^+$ (**A**) with HC≡CH used as model substrate. Energy profiles for the conversion of **A** to the [2+2+1] cycloaddition product [Ru(η^5-$C_5H_4CH_2CH_2PH_2$-κ^1C-CH-η^4-C_5H_5)]$^+$ (**H**) are shown in Figures 2−4 (energies in kcal/mol). The reliability of the computational method (details in Experimental Section) is supported by the good agreement between the calculated geometries of **A** and **H** with the X-ray structures of **1**, **2**,[10] and **3a**.

In the initial step the acetonitrile ligands are replaced by acetylene, leading to the bis-acetylene complex **B**. In line with analogous reactions of monophosphine complexes reported recently,[4] complex **B** undergoes a regioselective and symmetry-allowed head-to-tail coupling to afford the metallacyclopentatriene intermediate **C** with the substituents ending up in the 1 and 3 position. Location of the transition state $\mathbf{TS_{BC}}$ revealed a moderate activation barrier of 9.6 kcal/mol. The formation of **C** is strongly exothermic, releasing 27.1 kcal/mol. The calculated structure of **C** compares well with the X-ray structures of related species containing the CpRuBr and RuCp*Cl fragments[11] as well as recent calculations performed on similar systems.[9,12,13]

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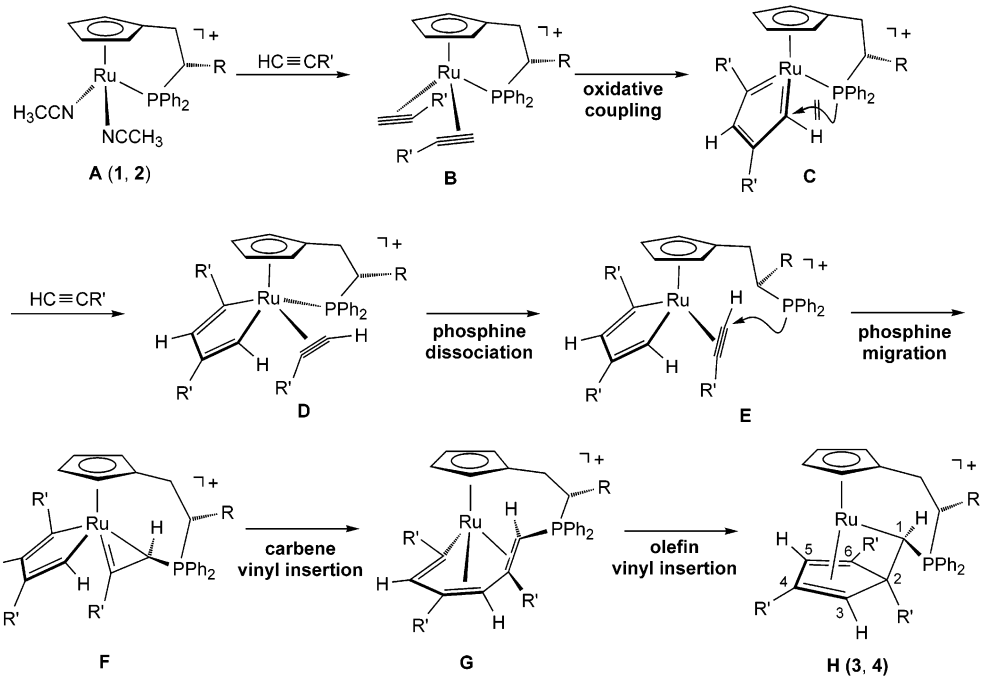
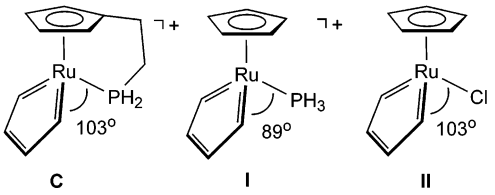
Scheme 3



Scheme 4



The reactivity of **C** is guided by the availability of the attack of an additional ligand. This is prohibited particularly in the presence of bulky monodentate PR_3 (or SbR_3) co-ligands,[4] whereupon the concurrent pathway (i) in Scheme 1 is followed, giving an allyl carbene complex via phosphine migration. Tethering of the phosphine ligand, on the other hand, opens the interligand space between the metallacycle plane and the Ru−P vector, as may be seen by comparing $[RuCp(PH_3)]^+$ (**I**) and **C** in Scheme 4. It may be relevant to note that the corresponding angle of 103° in **C** is similar to that in the RuCpCl complex (**II**), which has been proposed as an intermediate in the catalyzed cyclotrimerization of alkynes.[13]

Along these lines, **C** is able to accommodate a third alkyne to afford the metallacyclopendiene acetylene complex **D**. In the crowded construction of the latter, the Ru−P bond is labilized, giving, in an endothermic reaction, a free phosphine arm in **E**. The effect of ring strain introduced by a two-carbon tether has been demonstrated recently by Casey et al.[5a] The subsequent reaction steps are quite straightforward: Nucleophilic attack of the pendant phosphine ligand at the coordinated acetylene results in the formation of the novel metallacyclopentadiene 1-metallacyclopropene complex **F**. The activation energy for this intramolecular process is 11.2 kcal/mol. It should be noted that related coupling reactions between a coordinated alkyne and a coordinated phosphine to yield 1-metallacyclopropenes and vinyl complexes have been reported in the literature.[14,15] Also intermolecular nucleophilic additions of phosphines and phosphites to alkyne ligands are feasible.[16] Complex **F** is prone to C−C coupling between the carbene carbon atom of the 1-metallacyclopropene moiety and the α-carbon of the metallacyclopentadiene unit bearing no substituent, yielding **G**. This reaction requires merely 2.5 kcal/mol activation energy and is energetically very favorable, releasing 35.0 kcal/mol. Intermediate **G** features a $-PPh_2-CH{=}CR'-CH-$ unit, in line with the intermediate observed in low-temperature $^1H-^{31}P$-HMBC experiments. The final and rate-determining step is the insertion of the vinyl moiety into the η^2-olefin unit, giving **H**, thus completing the [2+2+1] cyclotrimerization. The overall reaction from **A** to **H** is strongly exothermic by −82.0 kcal/mol.

The [2+2+2] cyclotrimerization encountered with the C−C coupling between the metallacyclopentadiene moiety and the η^2-coordinated acetylene molecule can in principle occur either in **D** and/or in **E** (Scheme 5). However, since the C−C coupling is not regioselective, with mixtures of the two possible isomers obtained, it is more likely that **E** is the key intermediate rather than **D**. In **E** (Figure 3), steric effects do not appear to play a significant role, and C−C coupling between either of the two α-carbon atoms of the metallacyclopentadiene moiety and the acetylene might be equally facile. In **D** (Figure 3), on the other hand, steric restraints should be more relevant favoring the coupling between the unsubstituted α-carbon atom of the metallacycle and the alkyne. Mechanistic details of both coupling modes based on DFT calculations on related RuCp systems have been reported elswhere.[12,13]

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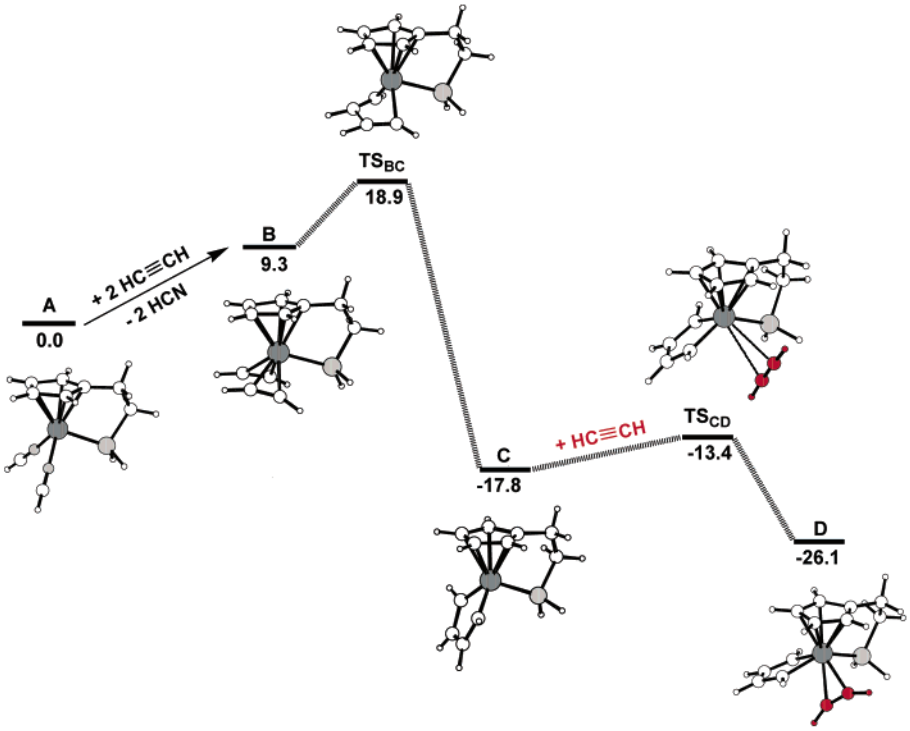


Figure 2. Energy profile for the reaction of **A** with acetylene to give **D** (in kcal/mol, relative to **A**).

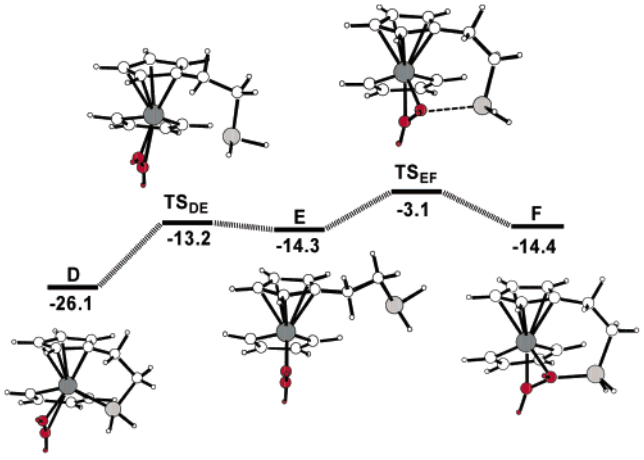


Figure 3. Energy profile for the reaction of **D** to **F** (in kcal/mol, relative to **A**).

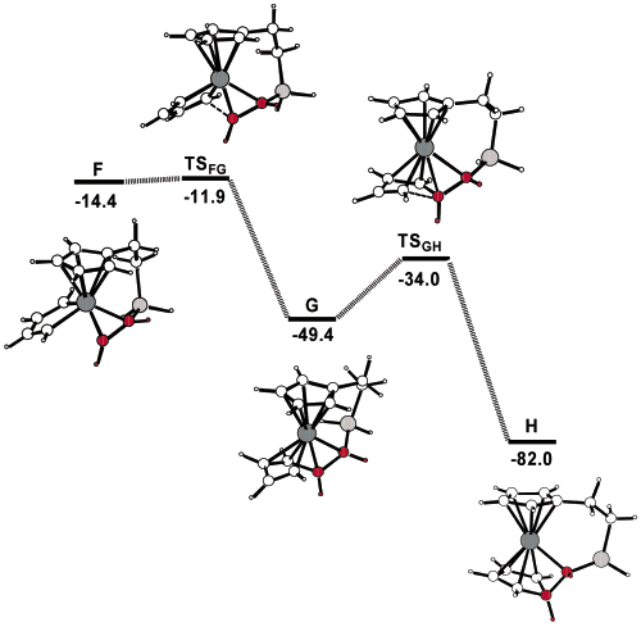
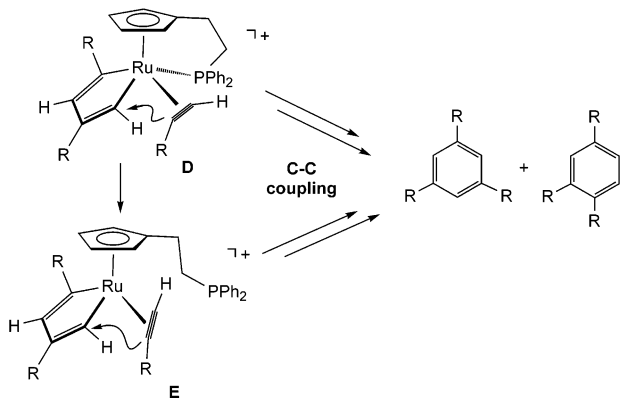


Figure 4. Energy profile for the reaction of **F** to **H** (in kcal/mol, relative to **A**).

Scheme 5

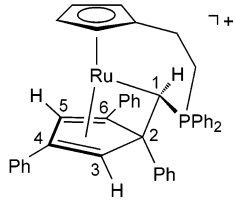


In conclusion, we have shown a way by which tethering of a phosphine ligand onto the Cp ring via a two-carbon linker changes the reactivity of ruthenium cyclopentadienyl phosphine complexes. The unusual C−C coupling process initiated involves three alkynes and a tethered phosphine. In the course of this formally [2+2+1] cycloadditon, two C−C triple bonds are converted into C−C double bonds and one C−C triple bond is transformed into a C−C single bond, with an additional phosphine carbon bond being formed as well. Despite such complexity, the reactions are both regio- and diastereoselective. This is another example of the finding that a phosphine ligand in ruthenium chemistry need not necessarily be just a spectator ligand but can switch over to an actor ligand, undergoing facile migration onto coordinated alkynes.

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.[17] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. Complexes [Ru(η^5-$C_5H_4CH_2CH_2$-κ^1P-PPh_2)$(CH_3CN)_2$]PF_6 (**1**) and [(S)-Ru(η^5-$C_5H_4CH_2CH$(Ph)-κ^1P-PPh_2)$(CH_3CN)_2$]BF_4 (**2**) have been prepared according to the literature.[10] ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AVANCE-250 and AVANCE-300 spectrometers equipped with BB-inverse probeheads and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively. ^{1}H and ^{13}C{^{1}H} NMR signal assignments were confirmed by ^{1}H, ^{1}H-COSY, DEPT-135, ^{1}H−^{13}C-HSQC, ^{1}H−^{13}C-HMBC, and ^{1}H−^{31}P-HMBC experiments.

[Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1C-CH-η^4-$C_5Ph_3H_2$)]PF_6 (3a). A solution of [Ru(η^5-$C_5H_4CH_2CH_2$-κ^1P-PPh_2)$(CH_3CN)_2$]PF_6 (**1**) (200 mg, 0.330 mmol) and phenylacetylene (116.1 μL, 1.057 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 24 h, whereupon the color of the solution changed from yellow to dark red. After reduction of the volume of the solution to about 1 mL, addition of Et_2O afforded a red solid, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 251 mg (92%). Anal. Calcd for $C_{43}H_{36}F_6P_2Ru$: C, 62.24; H, 4.37. Found: C, 62.31; H, 4.49. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.11−6.98 (m, 23H, Ph), 6.86 (dd, J_{HH} = 1.5 Hz, J_{HP} = 4.7 Hz, 1H, CH^5), 6.75−6.64 (m, 2H, Ph), 5.50 (dt, J_{HH} = 2.5 Hz, J_{HP} = 1.1 Hz, 1H, Cp), 5.32−5.23 (m, 2H, Cp), 3.81 (d, J_{HH} = 1.5 Hz, 1H, CH^3), 3.75−3.66 (m, 1H, Cp), 3.67−3.55 (m, 1H, P−CH$_2$), 3.40−3.26 (m, 1H, P−CH$_2$), 2.89−2.38 (m, 2H, Cp-CH$_2$), 1.83 (d, J_{HP} = 13.7 Hz, CH^1). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 147.3 (1C, Ph^1), 134.7−124.0 (28C, Ph), 120.7 (d, J_{CP} = 78.2 Hz, 1C, C^2−Ph^1), 102.5 (d, J_{CP} = 3.1 Hz, 1C, Cp^1), 101.0 (1C, C^4), 86.0 (1C, Cp), 85.7 (d, J_{CP} = 17.6 Hz, 1C,C^2), 83.2 (1C, Cp), 82.5 (1C,C^5), 80.9 (1C, Cp), 78.4 (1C, Cp), 62.6 (1C, C^6), 57.4 (d, J_{CP} = 4.6 Hz, 1C,C^3), 34.6 (d, J_{CP} = 68.2 Hz, 1C, P−CH$_2$), 18.3 (d, J_{CP} = 5.4 Hz, 1C, Cp-CH$_2$), −37.1 (d, J_{CP} = 52.9 Hz, 1C, C^1). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 20.3 (PPh$_2$), −144.1 (J_{PF} = 712.0 Hz, PF_6).



[Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1C-CH-η^4-$C_5(C_6H_9)_3H_2$)]PF_6 (3b). A solution of [Ru(η^5-$C_5H_4CH_2CH_2$-κ^1P-PPh_2)$(CH_3CN)_2$]-PF_6 (**1**) (100 mg, 0.165 mmol) and 1-ethynylcyclohexene (62.1 μL, 0,528 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 24 h. The solvent was then evaporated to dryness, and the crude product was purified by column chromatography (neutral Al_2O_3, CH_2Cl_2/CH_3CN, 1:1). Yield: 126 mg (91%). Anal. Calcd for $C_{43}H_{48}F_6P_2Ru$: C, 61.35; H, 5.75. Found: C, 61.43; H, 5.69. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.14−7.63 (m, 10H, Ph), 6.36−6.32 (m, 1H, Cy^2), 6.31 (dd, J_{HH} = 1.3 Hz, J_{HP} = 4.6 Hz, 1H, CH^5), 6.11−6.04 (m, 1H, Cy^2), 5.54−5.49 (m, 1H, Cp), 5.43−5.37(m, 1H, Cy^2), 5.27 (dt, J_{HH} = 2.5 Hz, J_{HP} = 1.0 Hz, 1H, Cp), 4.95−4.90 (m, 1H, Cp), 3.99−3.95 (m, 1H, Cp), 3.59−3.39 (m, 1H, P−CH$_2$), 3.27−3.10 (m, 2H, CH$_2$), 2.82 (d, J_{HH} = 1.1 Hz, 1H, CH^3), 2.71−2.51 (m, 1H, Cp−CH$_2$), 2.15−0.90 (m, 24H, CH$_2^{Cy}$), 1.18 (d, J_{HP} = 14.8 Hz, CH^1). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 142.8 (1C, Cy^1), 135.4 (d, J_{CP} = 9.2 Hz, 2C, Ph^{2,6}), 134.0 (d, J_{CP} = 2.3 Hz, 1C, Ph^4), 133.3 (d, J_{CP} = 2.3 Hz, 1C, Ph$^{4'}$), 132.6 (d, J_{CP} = 7.7 Hz, 2C, Ph$^{2',6'}$), 131.8 (1C, Cy^1), 130.7 (1C, Cy^1), 129.7 (d, J_{CP} = 10.7 Hz, 2C, Ph^{3,5}), 129.1 (d, J_{CP} = 11.5 Hz, 2C, Ph$^{3',5'}$), 125.4 (1C, Cy^2), 124.6 (1C, Cy^2), 121.8 (d, J_{CP} = 78.2 Hz, 2C, Ph^1), 120.1 (1C, Cy^2), 104.1 (1C, C^4), 101.4 (d, J_{CP} = 3.1 Hz, 1C, Cp^1), 83.3 (1C, Cp), 83.0 (d, J_{CP} = 17.6 Hz, 1C, C^2), 80.7 (1C, Cp), 78.0 (1C, Cp), 77.9 (1C, C^5), 76.1 (1C, Cp), 62.9 (d, J_{CP} = 3.8 Hz, 1C, C^6), 56.9 (d, J_{CP} = 4.6 Hz, 1C,C^3), 34.9 (d, J_{CP} = 67.5 Hz, 1C, P−CH$_2$), 27.4 (1C, CH$_2$), 25.9 (2C, CH$_2$), 25.3 (1C, CH$_2$), 23.8 (1C, CH$_2$), 22.6 (1C, CH$_2$), 22.3 (1C, CH$_2$), 22.2 (1C, CH$_2$), 22.0 (3C, CH$_2$), 21.6 (1C, CH$_2$), 18.5 (d, J_{CP} = 5.4 Hz, 1C, Cp−CH$_2$), −33.4 (d, J_{CP} = 52.9 Hz, 1C, C^1). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 21.4 (PPh$_2$), −144.2 (J_{PF} = 719.5 Hz, PF_6).

[Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1C-CH-η^4-C_5(p-$C_6H_4Me)_3H_2$)]-PF_6 (3c). This compound was prepared analogously to **3b** with **1** (200 mg, 0.330 mmol) and *p*-tolylacetylene (133.9 μL, 1.057 mmol) as the starting materials. The crude product was purified by column chromatography (neutral Al_2O_3, acetone/CH_2Cl_2, 1:1). Yield: 255 mg (87%). Anal. Calcd for $C_{46}H_{42}F_6P_2$-Ru: C, 63.37; H, 4.86. Found: C, 63.43; H, 4.69. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.06−6.99 (m, 18H, Ph), 6.85−6.80 (m, 1H, CH^5), 6.85 (d, J_{HH} = 8.1 Hz, 2H, C^6−Tolyl), 6.57 (d, J_{HH} = 8.1 Hz, 2H, C^6−Tolyl), 5.46 (dt, J_{HH} = 2.5 Hz, J_{HH} = 1.0 Hz, 1H, Cp), 5.23 (t, J_{HH} = 1.3 Hz, 1H, Cp), 5.16 (t, J_{HH} = 1.3 Hz, 1H, Cp), 3.70 (d, J_{HH} = 1.2 Hz, 1H, CH^3), 3.65 (dt, J_{HH} = 2.5 Hz, J_{HH} = 1.1 Hz, 1H, Cp, 3.44−3.08 (m, 2H, P−CH$_2$), 2.91−2.21 (m, 2H, Cp−CH$_2$), 2.34 (s, 3H, CH$_3$), 2.27 (s, 3H, CH$_3$), 2.16 (s, 3H, CH$_3$), 1.75 (d, J_{HP} = 13.9 Hz, CH^1). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 144.9 (1C, Tol^1), 138.6−124.0 (28C, Ph), 120.8 (d, J_{CP} = 77.4 Hz, 1C, C^2−Tol^1), 102.0 (d, J_{CP} = 3.8 Hz, 1C, Cp^1), 101.2 (1C, C^4), 85.7 (1C, Cp), 85.5 (d, J_{CP} = 17.6 Hz, 1C,C^2), 83.1 (1C, Cp), 82.1 (1C,C^5), 80.7 (1C, Cp), 78.1 (1C, Cp), 62.2 (d, J_{CP} = 2.3 Hz, 1C, C^6), 57.7 (d, J_{CP} = 5.4 Hz, 1C,C^3), 34.5 (d, J_{CP} = 68.2 Hz, 1C, P−CH$_2$), 20.5, 20.4, 20.3 (3C, CH$_3$), 18.5 (d, J_{CP} = 5.4 Hz, 1C, Cp−CH$_2$), −36.6 (d, J_{CP} = 52.9 Hz, 1C, C^1). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20°C): 20.1 (PPh$_2$), −144.1 (J_{PF} = 719.5 Hz, PF_6).

[Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1C-CH-η^4-C_5(p-$C_6H_4OMe)_3H_2$)]-PF_6 (3d). This compound was prepared analogously to **3a** with **1** (200 mg, 0.330 mmol) and *p*-methoxyphenylacetylene (139.6 μL, 1.057 mmol) as the starting materials. Yield: 274 mg (90%). Anal. Calcd for $C_{46}H_{42}F_6O_3P_2Ru$: C, 60.07; H, 4.60. Found: C, 59.91; H, 4.77. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.20−7.33 (m, 20H, Ar), 7.28 (dd, J_{HH} = 2.5 Hz, J_{HP} = 8.8 Hz, 1H, CH^5), 7.05 (d, J_{HH} = 8.8 Hz, 2H, C^6−Ar), 5.46 (m, 1H, Cp),5.22 (t, J_{HP} = 1.0 Hz, 1H, Cp), 5.15 (t, J_{HP} = 1.0 Hz, 1H, Cp), 3.82 (s, 3H, OCH$_3$), 3.78 (s, 3H, OCH$_3$), 3.74 (d, J_{HH} = 2.5 Hz, 1H, CH^3), 3.71−3.68 (m, 1H, Cp), 3.66 (s, 3H, OCH$_3$), 3.37−3.25 (m, 2H, P−CH$_2$), 2.77−2.65 (m, 2H, Cp−CH$_2$), 1.68 (d, J_{HP} = 14.0 Hz, 1H, CH^1). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 160.1, 159.2, 159.0 (3C, Ar^4), 140.1 (1C, Ph^1), 135.0−123.6 (25C, Ph), 120.4 (1C, C^2−Ph^1), 101.7 (d, J_{CP} = 3.8 Hz, 1C, Cp^1), 101.4 (1C, C^4), 86.2 (1C, Cp), 85.9 (1C, C^2), 82.8 (1C, Cp), 81.7 (1C,C^5), 80.6 (1C, Cp), 77.9 (1C, Cp), 61.8 (1C, C^6), 57.0 (d, J_{CP} = 5.4 Hz, 1C, C^3), 54.8, 54.7, 54,6 (3C, OCH$_3$), 34.6 (d, J_{CP} = 68.4 Hz, 1C, P−CH$_2$), 18.5 (d, J_{CP} = 5.4 Hz, 1C, Cp−CH$_2$), −36.7 (d, J_{CP} = 52.9 Hz, 1C, C^1). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 20.2 (PPh$_2$), −144.2 (J_{PF} = 719.5 Hz, PF_6).

[Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1C-CH-η^4-$C_5(Fc)_3H_2$)]PF_6 (3e). This compound was prepared analogously to **3b** with **1** (200 mg, 0.330 mmol) and ethynylferrocene (222 mg, 1.057 mmol) as the starting materials. Reaction time was 48 h. The crude product was purified by column chromatography (neutral Al_2O_3). Unreacted ethynyl ferrocene was first eluated with Et_2O. The second red band containing the product was eluated with CH_2Cl_2. Yield: 273 mg (72%). Anal. Calcd for $C_{55}H_{48}F_6$-Fe_3P_2Ru: C, 57.27; H, 4.19. Found: C, 57.41; H, 4.43. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.05−7.75 (m, 10H, Ph), 6.88 (d, J_{HP} = 4.6 Hz, 1H, CH^5), 5.52−5.47 (m, 1H, Cp), 5.43−5.38 (m, 1H, Cp), 4.93−4.89 (m, 1H, Cp^{Fc}), 4.82−4.77 (m, 1H, Cp), 4.55−4.10 (m, 11H,Fc), 4.33 (s, 10H, Cp^{Fc}), 4.32 (s, 5H, Cp^{Fc}), 3.86−3.83 (m, 1H, Cp) 3.42−3.28 (m, 3H, P−CH$_2$, CH^3), 2.73−2.52 (m, 2H, Cp−CH$_2$), 1.20 (d, J_{HP} = 12.1 Hz, 1H, CH^1). ^{13}C{^{1}H}

NMR (δ, acetone-d_6, 20 °C): 135.9 (d, J_{CP} = 9.2 Hz, 2C, $Ph^{2,6}$), 134.1 (d, J_{CP} = 3.0 Hz, 1C, Ph^{4}), 134.0 (d, J_{CP} = 8.4 Hz, 2C, $Ph^{2',6'}$), 133.5 (d, J_{CP} = 2.3 Hz, 1C, $Ph^{4'}$), 129.4 (d, J_{CP} = 11.5 Hz, 2C, $Ph^{3,5}$), 129.3 (d, J_{CP} = 10.7 Hz, 2C, $Ph^{3',5'}$), 125.4 (d, J_{CP} = 74.4 Hz, 1C, Ph^{1}), 122.9 (d, J_{CP} = 75.9 Hz, 1C, $Ph^{1'}$), 101.9 (d, J_{CP} = 3.0 Hz, 1C, Cp^{1}), 100.9 (1C, C^{4}), 86.1 (1C, Cp), 85.8 (1C, C^{2}), 82.4 (1C, Cp), 81.9 (1C, C^{5}), 79.7 (1C, Cp), 79.4 (1C, Cp), 71.3−66.4 (15C, Fc), 69.6 (5C, Cp^{Fc}), 69.5 (5C, Cp^{Fc}), 68.4 (5C, Cp^{Fc}), 62.7 (d, J_{CP} = 4.6 Hz, 1C, C^{3}), 57.8 (d, J_{CP} = 3.8 Hz, 1C, C^{6}), 34.8 (d, J_{CP} = 67.5 Hz, 1C, P−CH_2), 18.8 (d, J_{CP} = 5.4 Hz, 1C, Cp-CH_2), −31.5 (d, J_{CP} = 51.4 Hz, 1C, C^{1}). $^{31}P\{^{1}H\}$ NMR (δ, acetone-d_6, 20 °C): 20.8 (PPh_2), −144.4 (J_{PF} = 719.5 Hz, PF_6).

[Ru(η^5-$C_5H_4CH_2CH(Ph)PPh_2$-κ^1C-CH-η^4-C_5(p-$C_6H_4Me)_3$-H_2)]BF_4 (4). This compound was prepared analogously to **3a** with **2** (200 mg, 0.321 mmol) and *p*-tolylacetylene (130.2 μL, 1.027 mmol) as the starting materials. Yield: 251 mg (88%). Anal. Calcd for $C_{52}H_{46}BF_4PRu$: C, 70.19; H, 5.21. Found: C, 70.12; H, 5.33. ^1H NMR (δ, acetone-d_6, 20 °C): 8.14−6.73 (m, 25H, Ar), 6.88 (dd, J_{HH} = 1.5 Hz, J_{HP} = 4.7 Hz, 1H, CH^{5}), 6.52 (d, J_{HH} = 8.1 Hz, 2H, C^{6}−Tolyl), 6.00 (dd, J_{HH} = 1.5 Hz, J_{HP} = 0.9 Hz, 1H, Cp), 5.64 (dt, J_{HH} = 2.4 Hz, J_{HH} = 1.0 Hz, 1H, Cp), 5.20 (dt, J_{HH} = 1.7 Hz, J_{HP} = 13.5 Hz, 1H, P−CHPh), 4.91 (t, J_{HH} = 1.2 Hz, 1H, Cp), 3.69−3.49 (m, 1H, Cp−CH_2), 3.52−3.47 (m, 1H, Cp), 3.35−3.13 (m, 1H, Cp−CH_2), 3.15 (d, J_{HH} = 1.4 Hz, 1H, CH^{3}), 2.35 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 1.95 (d, J_{HP} = 15.4 Hz, CH^{1}). $^{13}C\{^{1}H\}$ NMR (δ, acetone-d_6, 20 °C): 145.3 (1C, Tol^{1}), 138.5−124.1 (34C, Ar), 118.3 (d, J_{CP} = 79.0 Hz, 1C, C^{2}−Tol^{1}), 101.6 (1C, Cp^{1}), 101.4 (1C, C^{4}), 88.0 (1C, Cp), 84.3 (d, J_{CP} = 17.6 Hz, 1C, C^{2}), 81.7 (1C, C^{5}), 80.7 (1C, Cp), 78.9 (1C, Cp), 76.3 (1C, Cp), 65.2 (1C, C^{6}), 58.7 (d, J_{CP} = 5.4 Hz, 1C, C^{3}), 47.1 (d, J_{CP} = 55.2 Hz, 1C, P−CHPh), 20.5, 20.3, 20.0 (3C, CH_3), 25.5 (1C, Cp−CH_2), −33.2 (d, J_{CP} = 47.8 Hz, 1C, C^{1}). $^{31}P\{^{1}H\}$ NMR (δ, acetone-d_6, 20 °C): 29.5 (PPh_2).

Reactions of 1 and 2 with HC≡CR′ (R′ = COOMe, COOEt, COMe). In a typical procedure, a 5 mm NMR tube was charged with a solution of **1** (30 mg, 0.049 mmol) in CD_3NO_2 (0.5 mL) and was capped with a septum. The alkynes HC≡CR′ (0.987 mmol) were added by syringe, and the tube was kept at 90 °C for 14 h. The sample was transferred to a NMR probe, and ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded. The same protocol was performed with complex **2** as catalyst.

Computational Details. All calculations were performed using the Gaussian98 software package on the Silicon Graphics Origin 2000 of the Vienna University of Technology.[18] The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level[19] with the Stuttgart/Dresden ECP (SDD) basis set[20] to describe the electrons of the Ru atom. For all other atoms the 6-31g** basis set was employed.[21] Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the reaction energy profile. All geometries were optimized without constraints (C_1 symmetry), and the energies were zero-point corrected. Relative energies were compared taking into account the total number of molecules present.

X-ray Structure Determination for 3a·$(CH_3)_2CO$. Crystals of **3a**·$(CH_3)_2CO$ were obtained by diffusion of Et_2O into an acetone solution. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, 0.3° ω-scan frames). Data processing included a correction for absorption.[22] The structure was solved with direct methods using the program SHELXS97.[23] Structure refinement on F^2 was carried out with the program SHELXL97.[23] 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. The PF_6 anion showed disorder by adopting two complementary orientations.

3a·$(CH_3)_2CO$): $C_{46}H_{42}F_6OP_2Ru$, M_r = 887.81, monoclinic, space group $P2_1/c$, T = 150(2) K, a = 13.927(2) Å, b = 15.616(3) Å, c = 19.552(3) Å, β = 105.74(1)°, V = 4093(1) Å^3, Z = 4, $F(000)$ = 1816, ρ_{calcd} = 1.441 g cm^{-3}, μ = 0.523 mm^{-1}. Of 32 693 reflections collected with θ_{max} = 30°, 11 547 were independent; R_{int} = 0.026; final R indices: R_1 = 0.046 (all data), wR_1 = 0.081 (all data).

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, and bond lengths and angles for **3a**·$(CH_3)_2CO$ with two structural views showing complete labeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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