

Addition of Carbon Nucleophiles to the Allenylidene Ligand of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$: Synthesis of New Organic Ligands by Formal C–C Coupling between Mutually Inert Fragments

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EHT-MO Calculations on the model cation $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CH}_2)(\text{CO})(\text{PH}_3)]^+$ (**1a**) suggest that 23% and 31% of the LUMO and 26% of the HOMO of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**1**) are located on C_α , C_γ , and C_β of the allenylidene ligand, respectively. On the basis of these results, we report a new synthetic strategy for the preparation of compounds resulting from the formal addition of phenylacetylene, acetone, and methane to the allenylidene of **1**. Treatment of **1** with $\text{LiC}\equiv\text{CPh}$ leads to the allenyl complex $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{C}\equiv\text{CPh})=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**2**) and the alkynyl derivative $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}\equiv\text{C}-\text{C}(\text{Ph})_2\text{C}\equiv\text{CPh}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**3**). The reaction of **2** with HBF_4 affords the substituted carbene compound $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{C}\equiv\text{CPh})\text{CH}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**4**), which is a result from the formal addition of phenylacetylene to the $\text{C}_\alpha\text{--C}_\beta$ double bond of the allenylidene of **1**. The molecular structure of **4** has been determined by X-ray crystallography. The geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face. The $\text{Ru}=\text{C}$ bond length is 2.004(5) Å. In the presence of KOH , complex **1** reacts with acetone to give $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}\equiv\text{C}-\text{C}(\text{Ph})_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**5**). The reaction of **5** with HBF_4 leads to the unsaturated cyclic carbene complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{CCH}_2\text{C}(\text{Ph})_2\text{CH}=\text{C}(\text{CH}_3)\text{O}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**6**). Complex **5** also reacts with 2 equiv of $\text{CF}_3\text{CO}_2\text{D}$ to give $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{CCD}_2\text{C}(\text{Ph})_2\text{CH}=\text{C}(\text{CH}_3)\text{O}\}(\text{CO})(\text{P}^i\text{Pr}_3)](\text{CF}_3\text{CO}_2)$ (**6-d**) and $\text{CF}_3\text{CO}_2\text{H}$, and the reaction of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}\equiv\text{C}-\text{C}(\text{Ph})_2\text{CD}_2\text{C}(\text{O})\text{CD}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**5-d**) with 2 equiv of HBF_4 affords $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{CCH}_2\text{C}(\text{Ph})_2\text{CD}=\text{C}(\text{CD}_3)\text{O}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**6-d**) and DBF_4 . On the basis of these isotope labeling experiments, the mechanism for the addition of acetone to the allenylidene ligand of **1** is discussed. Complex **1** also reacts with $\text{Na}(\text{acac})$ and CH_3Li . The reaction with $\text{Na}(\text{acac})$ leads to $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}\equiv\text{C}-\text{C}(\text{Ph})_2\text{CH}[\text{C}(\text{O})\text{CH}_3]_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**7**), while the treatment of **1** with CH_3Li gives a mixture of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}_3)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**8**) and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}\equiv\text{C}-\text{C}(\text{Ph})_2\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**9**). Complex **9** reacts with HBF_4 to afford $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{CHC}(\text{Ph})_2\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**10**), which is a result of the formal addition of a C–H bond of methane to the $\text{C}_\beta\text{--C}_\gamma$ double bond of the allenylidene of **1**.

Introduction

Owing to the increasing demand for new organic products, the development of highly efficient selective synthetic methods is one of the most urgent tasks for chemical science. In this respect, the formation of carbon–carbon bonds mediated by transition metal compounds has emerged in its own right over the last few years as an important step in organic synthesis, which has general interest.¹

In this context, it should be mentioned that Werner has recently proved that in the series carbene–vinylidene–allenylidene not only carbene and vinylidene complexes but also allenylidene compounds can be used as starting materials for C–C coupling reactions.² In agreement with this, Gimeno *et al.* had observed that the ruthenium–allenylidene derivative $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)$

$(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2]\text{PF}_6$ underwent regioselective nucleophilic attacks at C_γ by the anionic species $[(\text{CO})_5\text{M}=\text{C}(\text{OMe})\text{CH}_2]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) to yield the binuclear alkynyl–carbene complexes $(\text{PPh}_3)_2(\eta^5\text{-C}_9\text{H}_7)\text{Ru}-\text{C}\equiv\text{C}-\text{CPh}_2-\text{CH}_2-\text{C}(\text{OMe})=\text{M}(\text{CO})_5$.³ Along this line, Kolobova *et al.* have shown that the allenylidene

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ligand of the complex Mn(η^5 -C₅H₅)(C=C=CPh₂)(CO)₂ can be coupled with *tert*-butyl isocyanide to form a cumulenylidene derivative,⁴ and Fisher *et al.* have reported on the formation of binuclear cyclobutenylidene complexes by cycloaddition of the carbon–carbon triple bond of alkynyl complexes to the C_α–C_β double bond of allenylidene compounds.⁵

Most recently, we have reported the synthesis of the less basic compound [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ which, in contrast to the Gimeno's complex, adds water, alcohols, thiols, and benzophenone imine at the C_α–C_β double bond of the allenylidene group to afford α,β -unsaturated hydroxycarbene, alkoxycarbene, (alkylthio)carbene, and 2-azaallenyl compounds, respectively.⁶ After observing this, we asked ourselves whether products formally resulting from the addition to the allenylidene group of kinetically inert molecules in the presence of [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ could be also obtained.

In this paper, we prove that, in fact, the products resulting from the formal addition of phenylacetylene (PhC $\equiv$ C[−] and H⁺), acetone (CH₃COCH₂[−] and H⁺), and methane (CH₃[−] and H⁺) to the C_α–C_β or C_β–C_γ double bonds of the allenylidene of [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ can be obtained by an easy method.

Results and Discussion

EHT-MO Calculations for [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)] BF₄. In order to design a synthetic strategy to prepare the resultant compounds from the formal addition of phenylacetylene, acetone, and methane to the allenylidene ligand of [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ (**1**), we carried out an analysis of the electronic structure of this complex. The study has been performed using EHT-MO calculations⁷ on the model cation [Ru(η^5 -C₅H₅)(C=C=CH₂)(CO)(PH₃)]⁺ (**1a**).⁸

The molecular orbital diagram of **1a** is shown in Figure 1. Its orbital scheme is related to the interaction of the electronic structures of the fragments [Ru(η^5 -C₅H₅)(CO)(PH₃)]⁺ and allenylidene (C=C=CH₂), which are well-known.⁹ The allenylidene coordinates to the metal center as a σ -donor and π -acceptor ligand. The σ -donor component of the bond, which takes place between the HOMO of the allenylidene and the LUMO of the metallic fragment, produces a charge transfer of 0.44 e from the ligand to the metallic fragment. However, the interaction between the HOMO of the metallic fragment and the LUMO of the allenylidene—the π -acceptor component of the metal–allenylidene bond—leads to a charge transfer of 0.93 e, from the metallic moiety to the η^1 -carbon ligand. So, from the point of view of

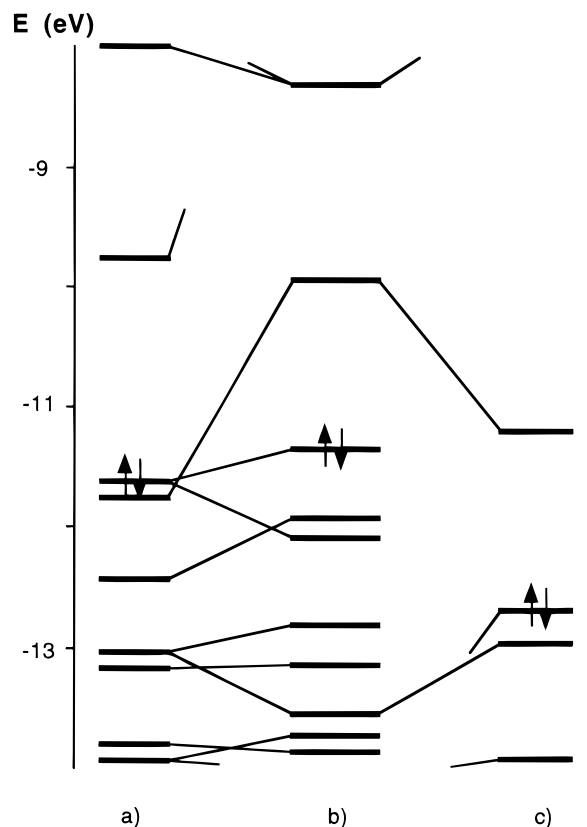


Figure 1. (b) Molecular orbital diagram of model complex [Ru(η^5 -C₅H₅)(C=C=CH₂)(CO)(PH₃)]⁺, and interaction diagram between fragments (a) [Ru(η^5 -C₅H₅)(CO)(PH₃)]⁺ and (c) (C=C=CH₂).

the charge, the π -acceptor component of the bond is stronger than the σ -donor one, and the resultant bond, including all contributions, produces a total charge transfer of 0.45 e from the metallic fragment to the carbon atoms of the allenylidene.

According to a Mulliken population analysis, 60% of the LUMO of **1a** is located on the allenylidene ligand, with a distribution on the carbon atoms of 23% (C_α), 6% (C_β), and 31% (C_γ) (Figure 2). From the same analysis, it is inferred that the net charges on each carbon atom are −0.36 (C_α), −0.13 (C_β), and −0.05 (C_γ).

Nucleophilic attack reactions can be orbital and charge directed and strongly depend on the characteristic of the LUMO of the electrophile.¹⁰ So, the orbital-controlled nucleophilic attacks to **1** should indistinctly lead to addition products on the C_α or C_γ atoms of the allenylidene ligand.

The 26% of the HOMO of **1a** is also located on the allenylidene ligand, mainly on the β -carbon atom (20%) (Figure 2). This implies that the allenylidene ligand of **1** should not only undergo attacks of nucleophiles at C_α and C_γ but also of electrophiles at C_β.

Addition of Phenylacetylene. In agreement with the theoretical results, the treatment of a tetrahydrofuran solution of **1** with 1.1 equiv of lithium phenylacetylide, between −40 and 10 °C, leads to a mixture of the allenyl derivative Ru(η^5 -C₅H₅){C(C $\equiv$ CPh)=C=CPh₂}(CO)(PⁱPr₃) (**2**) and its alkynyl isomer Ru(η^5 -

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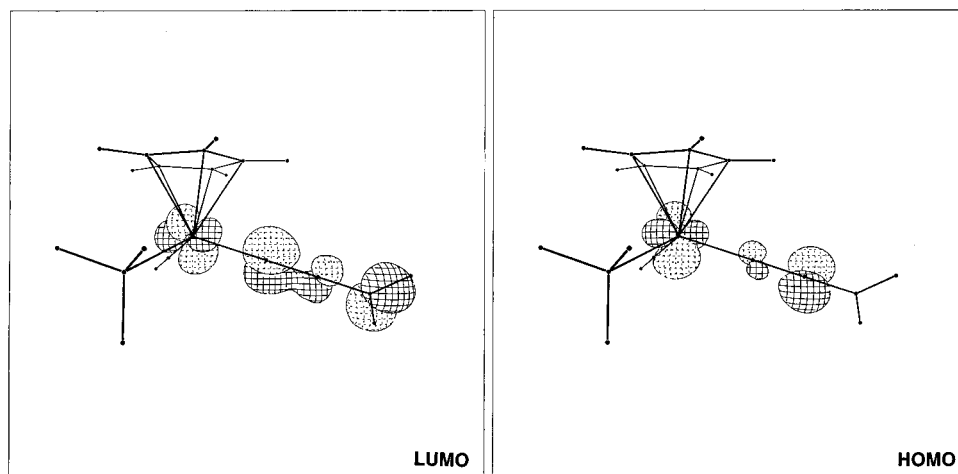
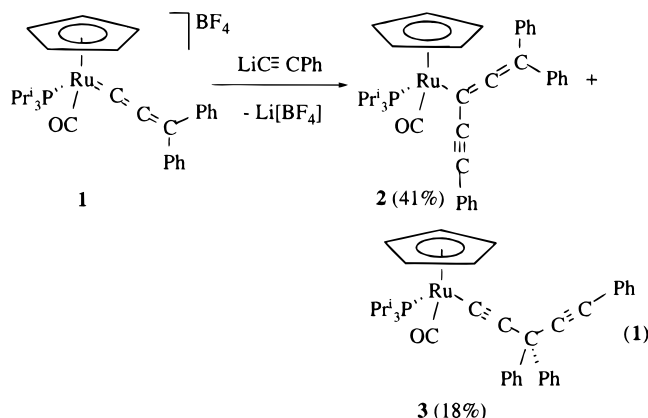


Figure 2. Partial view of the frontier molecular orbitals of the model complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{C}=\text{CH}_2)(\text{CO})(\text{PH}_3)]^+$ showing the Ru and allenylidene contributions.

$\text{C}_5\text{H}_5\{\text{C}\equiv\text{C}-\text{C}(\text{Ph})_2\text{C}\equiv\text{CPh}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**3**, eq 1). The



allenyl complex **2**, which is a result of the attack of the acetylide group at the α -carbon atom of the allenylidene ligand of **1**, is the main product from the reaction and was isolated as a yellow solid in 41% yield. The isomer **3**, which is a result of the attack of the acetylide group at the γ -carbon atom of the allenylidene unit, is obtained in 18% yield and was isolated as a white solid.

The formation of **2** according to eq 1 is noteworthy, firstly, because transition metal compounds containing (alkynyl)allenyl ligands have not previously been reported and, secondly, because the formation of allenyl complexes by attack of anionic nucleophiles to allenylidene ligands has no precedent. We note that the reactions of $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{C}\equiv\text{C}=\text{CPh}_2)(\text{PPh}_3)_2]\text{PF}_6$ with $\text{LiC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$, $n\text{-C}_3\text{H}_7$) have been previously studied.¹¹ In contrast to the reaction shown in eq 1, the acetylide groups attack solely at the γ -carbon atom of the allenylidene ligand of this indenyl complex. The formation of related compounds to **2** is not observed. In addition, it should be mentioned that rhodium compounds containing γ -functionalized alkynyl groups have been recently prepared by migratory insertion of an allenylidene unit into $\text{Rh}-\text{OR}$ ($\text{R} = \text{Ph}$, CH_3CO) bonds.¹²

η^1 -Allenyl transition metal compounds are rare, most of them have been prepared by oxidative addition of

propargyl or allenyl halides to electron-rich metal precursors.¹³ Recently, it has been also reported that the alkynyl(hydrido) osmium complexes $\text{OsHCl}\{\text{C}\equiv\text{CC}(\text{OH})\text{-Ph}_2\}(\text{NO})(\text{PR}_3)_2$ react with acidic alumina to afford the allenyl osmium(II) derivatives $\text{OsCl}_2\{\text{CH}=\text{C}=\text{CPh}_2\}(\text{NO})\text{-}(\text{PR}_3)_2$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$, PPh^iPr_2).¹⁴ We have described that both the deprotonation of α,β -unsaturated alkoxy carbene, (alkylthio)carbene, and 2-azaallenyl complexes as well as the dehydration of alkoxyalkenyl yield allenyl derivatives.^{6,15}

In addition, $[(\text{PR}_3)\text{-allenyl}]^+$ complexes have been synthesized. PMe_3 adds regioselectively to the γ -carbon atom of the allenylidene ligand of $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{C}\equiv\text{C}=\text{CPh}_2)(\text{dppm})]\text{PF}_6$ to give the alkynyl derivative $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)\{\text{C}\equiv\text{CC}(\text{PMe}_3)\text{Ph}_2\}(\text{dppm})]\text{PF}_6$, which isomerizes into $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)\{\text{C}(\text{PMe}_3)=\text{C}=\text{CPh}_2\}(\text{dppm})]\text{PF}_6$.¹¹ Fischer has reported that the allenylidene complex $\text{Cr}(\text{CO})_5\{\text{C}=\text{C}=\text{C}(\text{C}_6\text{H}_4\text{NMe}_2\text{-}p)_2\}$ adds phosphines at the α -carbon atom to give ylides complexes $\text{Cr}(\text{CO})_5\{\text{C}(\text{PR}_3)=\text{C}=\text{C}(\text{C}_6\text{H}_4\text{NMe}_2\text{-}p)_2\}$ ($\text{PR}_3 = \text{PMe}_3$, PPh_2 , PH_2Mes). At room temperature, the complex $\text{Cr}(\text{CO})_5\{\text{C}(\text{PPh}_2)=\text{C}=\text{C}(\text{C}_6\text{H}_4\text{NMe}_2\text{-}p)_2\}$ rearranges to $\text{Cr}(\text{CO})_5\{\text{PPh}_2[\text{CH}=\text{C}=\text{C}(\text{C}_6\text{H}_4\text{NMe}_2\text{-}p)_2]\}$.¹⁶ The complexes $\text{M}(\text{CO})_5\{\text{C}(\text{PPh}_3)=\text{C}=\text{C}(\text{CHMe}_2)_2\}$ ($\text{M} = \text{Cr}$, W) have been prepared by addition of PPh_3 to the corresponding allenylidene precursors.¹⁷

Complexes **2** and **3** were characterized by elemental analysis and IR and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies. The IR spectrum of **2** in Nujol shows the characteristic $\text{C}=\text{C}=\text{C}$ stretching frequency at 1927 cm^{-1} , along with two bands at 2168 and 1934 cm^{-1} corresponding to the $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{CO})$ vibrations, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum contains the

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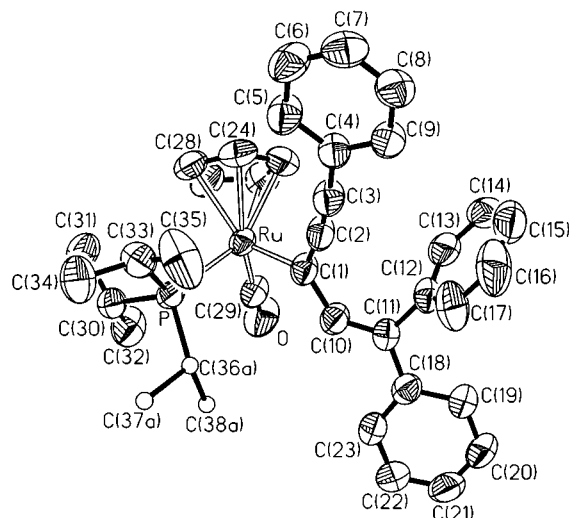
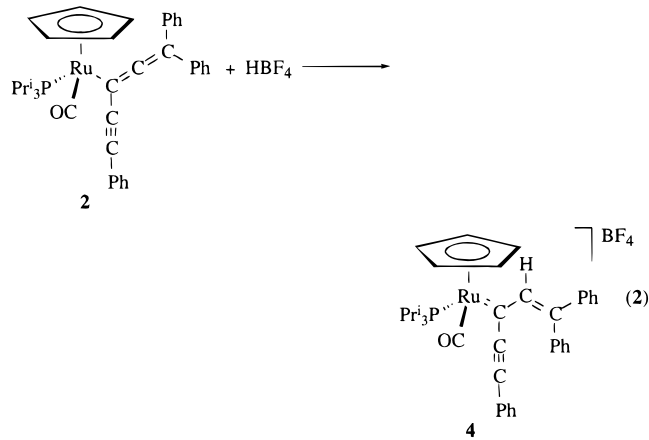


Figure 3. Molecular diagram of complex [Ru(η^5 -C₅H₅)-{C(C≡CPh)CH=CPh₂}(CO)(PⁱPr₃)]BF₄ (**4**). Thermal ellipsoids are shown at 50% probability.

resonances due to the sp²-carbon atoms of the allenyl unit at 209.7 (C_β), 98.3 (C_γ), and 74.3 (C_α) ppm. The first and third resonances appear as doublets with P–C coupling constants of 1.5 and 11.9 Hz, respectively, while the second one is observed as a singlet. In addition, two singlets at 94.7 and 91.3 should be mentioned, corresponding to the sp-carbon atoms of the acetylide group. In the IR spectrum of **3** in Nujol, the most noticeable features are two ν (C≡C) bands at 2109 and 2096 cm^{−1}. In the ¹³C{¹H} NMR spectrum, the resonance of the Ru–C≡ carbon atom appears at 90.9 ppm as a doublet with a P–C coupling constant of 22.2 Hz, while the C_β and C_γ carbon atoms of the alkynyl group display singlets at 106.8 and 48.2 ppm. The resonance of the sp-carbon atoms of the –C≡CPh unit are observed as singlets at 95.1 and 83.1 ppm.

Complex **2** reacts with 1 equiv of HBF₄ in dichloromethane at room temperature to give the unusual carbene complex [Ru(η^5 -C₅H₅){C(C≡CPh)CH=CPh₂}(CO)(PⁱPr₃)]BF₄ (**4**, eq 2), where the substituted carbene ligand has two unsaturated groups, the acetylide PhC≡C– and the alkenyl–CH=CPh₂.



We have previously mentioned that complex **1** adds water, alcohols, and thiols at the C_α–C_β double bond of the allenylidene to give the corresponding α,β -unsaturated (functionalized)carbene derivatives. The α,β -unsaturated (acetylide)carbene complex **4** is a result

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Ru(η^5 -C₅H₅){C(C≡CPh)CH=CPh₂}(CO)(PⁱPr₃)]BF₄ (**4**)

Bond Lengths			
Ru–C(24)	2.276(5)	Ru–C(1)	2.004(5)
Ru–C(25)	2.242(5)	C(1)–C(2)	1.401(7)
Ru–C(26)	2.239(5)	C(2)–C(3)	1.212(7)
Ru–C(27)	2.285(5)	C(3)–C(4)	1.432(6)
Ru–C(28)	2.310(5)	C(1)–C(10)	1.441(6)
Ru–C(29)	1.834(5)	C(10)–C(11)	1.350(6)
C(29)–O	1.150(6)	C(11)–C(12)	1.485(7)
Ru–P	2.381(1)	C(11)–C(18)	1.481(6)
Bond Angles			
P–Ru–C(1)	96.5(1)	C(1)–C(2)–C(3)	172.7(5)
P–Ru–C(29)	92.3(2)	C(2)–C(3)–C(4)	174.5(6)
P–Ru–G(1) ^a	124.0(2)	C(2)–C(1)–C(10)	120.3(4)
C(1)–Ru–C(29)	92.4(2)	C(1)–C(10)–C(11)	130.7(5)
C(1)–Ru–G(1) ^a	121.9(2)	C(10)–C(11)–C(12)	121.6(4)
C(29)–Ru–G(1) ^a	121.7(2)	C(10)–C(11)–C(18)	120.6(4)
Ru–C(1)–C(10)	125.5(3)	C(12)–C(11)–C(18)	117.5(4)
Ru–C(1)–C(2)	114.1(3)		

^aG(1) is the midpoint of the C(24)–C(28) Cp ligand.

that one should expect if, in the presence of complex **1**, the phenylacetylene molecule had shown the same behavior as the above-mentioned molecules. This suggests that the inertia of the alkyne is kinetic in origin and is connected with the transition state of the addition to the C_α–C_β double bond of the allenylidene. Because the α - and β -carbon atoms of the allenylidene are electrophilic and nucleophilic centers, respectively, and the H–X (X = O, S) hydrogen atom of the RXH molecules is electrophilic, the transition state for the RX–H addition most probably requires a heteroatom–C_α interaction, which labilizes the H–X bond, favoring the migration of the H–X hydrogen atom to the β -carbon atom of the allenylidene. Thus, the lower nucleophilic character of the terminal carbon atom of the alkyne can explain why the addition of phenylacetylene to the allenylidene is kinetically disfavored.

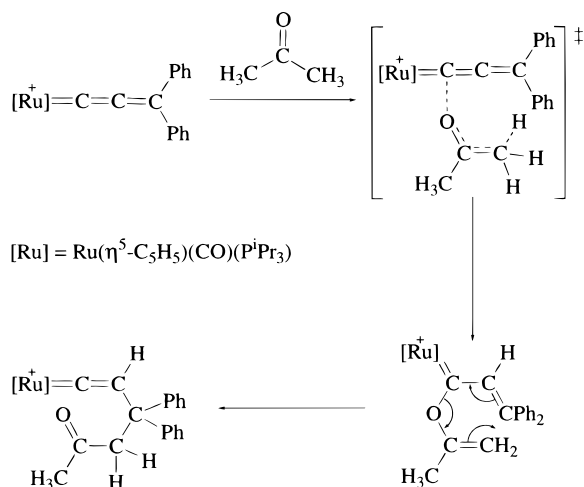
Complex **4** was isolated as a dark brown solid in 89% yield and characterized by elemental analysis, IR and ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectroscopies, and X-ray diffraction. A view of the molecular geometry is shown in Figure 3. Selected bond distances and angles are listed in Table 1.

The geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face, and the angles formed by the triisopropylphosphine, the carbonyl group, and the unsaturated η^1 -carbon ligand are close to 90°.

The most conspicuous features of this structure are firstly the Ru–C(1) bond length (2.004(5) Å), which is consistent with a Ru–C(1) double bond formulation, and secondly the bond angles around C(1) (between 114.1–(3)° and 125.5(3)°) which clearly indicate sp² hybridization for the C(1) carbon atom. Similar values have been reported for other ruthenium–carbene complexes.¹⁸ The bond lengths and angles within the alkylidene ligand are consistent with the α,β -alkenyl–(acetylide)carbene proposal; e.g., C(1) and C(10) are separated by 1.441(6) Å and C(10) and C(11) by 1.350(6) Å, and the bond angles around C(11) are about 120°, while the C(2)–C(3) bond length is 1.212(7) Å and the angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4) are 172.7(5)° and 174.5–(6)°, respectively.

In agreement with the presence of an acetylide group in the carbene ligand, the IR spectrum of **4** in Nujol

Scheme 1

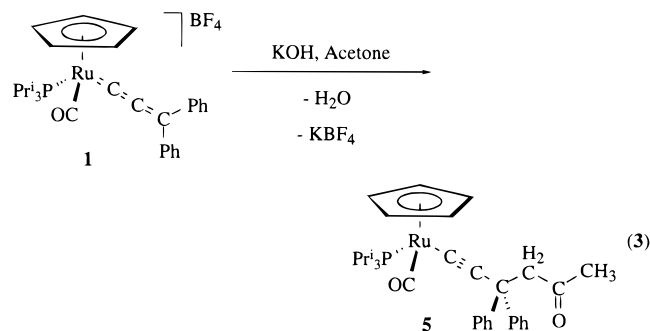


contains a $\nu(\text{C}\equiv\text{C})$ band at 2123 cm^{-1} . In the ^1H NMR spectrum, the most noticeable resonance is a singlet at 8.31 ppm, which was assigned to the $=\text{CH}-$ proton of the alkenyl group of the unsaturated η^1 -carbon ligand. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonance of the $\text{Ru}=\text{C}$ carbon atom appears at 283.0 ppm whereas the olefinic resonances of the alkenyl group are observed at 148.7 ($\text{CH}=\text{}$) and 122.5 ($=\text{CPh}_2$) ppm and those of the acetylide unit at 106.9 and 77.3 ppm.

Addition of Acetone. The previous results from the reactions of **1** with water, alcohols, thiols, and phenylacetylene seem to suggest that addition of neutral molecules to the allenylidene of **1** requires a transition state, which favors the transfer of an electrophilic hydrogen atom from the substrate to the β -carbon atom of the allenylidene by means of an heteroatom- C_α interaction. The hydrogen atom of the carbon contiguous to the carbonyl group of a ketone is lightly acidic, and the oxygen atom has nucleophilic character. So, at first glance, one should expect a reaction between the allenylidene ligand of **1** and acetone. The expected reaction product should be a functionalized vinylidene derivative, as a result of a Claysen-type rearrangement (Scheme 1). However, the allenylidene complex **1** is stable in acetone solution, and apparently, a reaction is not observed.

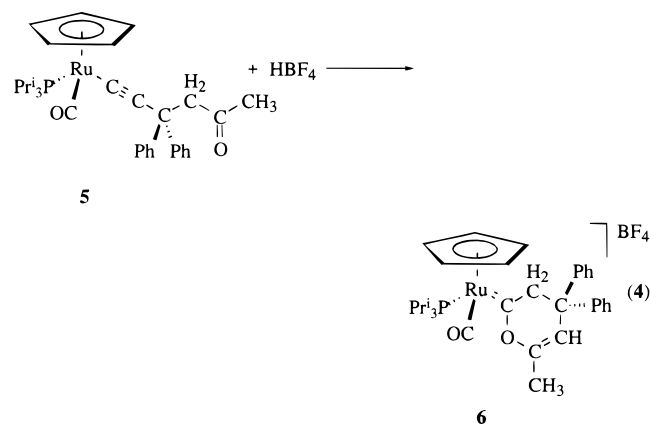
If we assume that the allenylidene complex **1** is thermodynamically more stable than the functionalized vinylidene and that in acetone solution complex **1** is in equilibrium with no detectable concentrations of this vinylidene, the addition of base to the acetone solutions of **1** should lead to a functionalized alkynyl complex, as a result of the deprotonation of the β -hydrogen atom of the vinylidene. The fair acidic character of this atom

in vinylidene compounds is well-known.¹⁹ This prompted us to add potassium hydroxide to the acetone solutions of **1**, and as expected, the functionalized alkynyl complex $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}\equiv\text{C}-\text{C}(\text{Ph})_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**5**) was formed (eq 3).



Complex **5** was isolated as a white solid, only in 25% yield due to the partial decomposition of the starting complex **1** in the basic medium. The presence of the functionalized alkynyl ligand in **5** is mainly supported by the IR and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the compound. The IR spectrum in Nujol shows the $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{O})$ bands at 2108 and 1702 cm^{-1} , respectively. In the ^1H NMR spectrum, the most noticeable resonances are two singlets at 3.36 and 2.01 ppm, with a 2:3 intensity ratio, which were assigned to the $-\text{CH}_2-$ and $-\text{CH}_3$ protons of the alkynyl ligand. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the α -carbon atom of this ligand displays a doublet at 90.9 ppm, with a $\text{P}-\text{C}$ coupling of 21.1 Hz, while the resonance of the β -carbon atom is observed as a singlet at 110.2 ppm.

Because the allenylidene complex **1** is thermodynamically more stable than the vinylidene intermediate shown in Scheme 1, protonation of the alkynyl complex **5** should regenerate **1**. However, we have observed that the treatment of a diethyl ether solution of **5** with HBF_4 in ca. 1:2 molar ratio does not lead to **1** but affords the unsaturated cyclic carbene complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{CCH}_2\text{C}(\text{Ph})_2\text{CH}=\text{C}(\text{CH}_3)\text{O}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**6**), which was isolated as a pink solid in 86% yield (eq 4).



(18) (a) Clark, G. R.; Hodgson, D. J.; Ng, M. M. P.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1552. (b) Adams, H.; Bailey, N. A.; Ridgway, C.; Taylor, B. F.; Walters, S. J.; Winter, M. J. *J. Organomet. Chem.* **1990**, 394, 349. (c) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, 11, 809. (d) Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1992**, 114, 8733. (e) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, 13, 4258. (f) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, 117, 5503. (g) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2039. (h) Nombel, P.; Luga, N.; Mathieu, R. *J. Organomet. Chem.* **1995**, 503, C22. (i) Morran, P. D.; Mawby, R. J.; Wilson, G. D.; Moore, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 261. (j) Grunwald, C.; Gevert, O.; Wolf, J.; Gonzalez-Herrero, P.; Werner, H. *Organometallics* **1996**, 15, 1960.

From a methodological point of view, it should be noted that the formation of an unsaturated cyclic carbene from an allenylidene and a ketone has no precedent. Previously, heteroatom-containing cyclic metal-carbene complexes have been conveniently prepared *via*

(19) Bruce, M. I. *Chem. Rev.* **1991**, 91, 197.

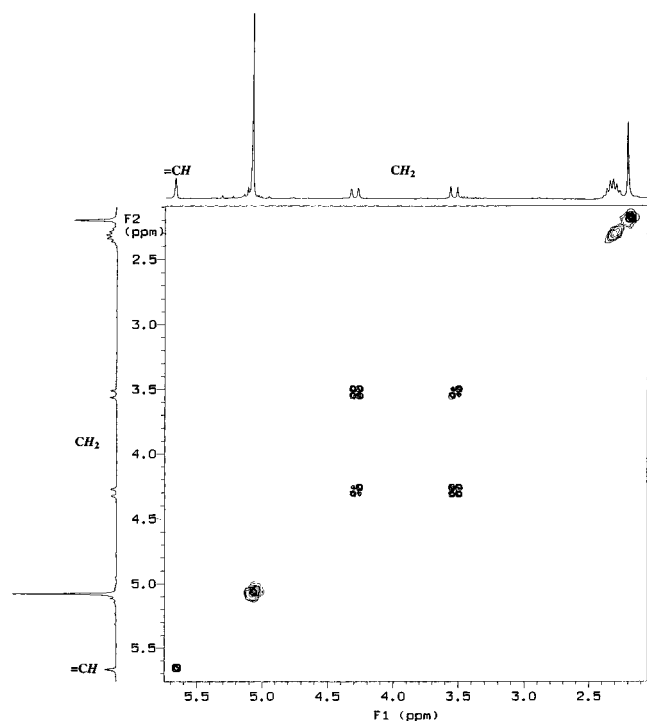


Figure 4. ^1H , ^1H -COSY NMR spectrum of complex [Ru(η^5 -C₅H₅){CCH₂C(Ph)₂CH=C(CH₃)O}(CO)(PⁱPr₃)]BF₄ (**6**), showing the resonances of the =CH- and -CH₂ protons of the unsaturated cyclic carbene ligand.

metal ω -haloacyl, carbamoyl, alkoxy carbonyl, or imido intermediates,²⁰ opening of epoxides by deprotonated Fischer-type carbene complexes,²¹ and activation of homopropargylic alcohols with low-valent d⁶ complexes,²² including ruthenium(II) derivatives.²³ In general, the preparation of unsaturated cyclic carbene complexes requires the previous preparation of functional carbenes to react with β -dicarbonyl derivatives, acrylates, and enol ethers.²⁴

Complex **6** was characterized by elemental analysis and IR and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies. In the ^1H NMR spectrum, the most noticeable resonances are a singlet at 5.67 ppm and two doublets at 4.35 and 3.52 ppm with a H-H coupling constant of 16.0 Hz. On the basis of the ^1H -COSY NMR spectrum shown in Figure 4, the first resonance was assigned to the =CH- proton of the unsaturated cyclic carbene ligand and the other two resonances to the -CH₂- protons of the same ligand. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonance corresponding to the Ru=C carbon atom appears at 308.1 ppm as a doublet with a P-C coupling constant of 9.6 Hz. In addition,

(20) (a) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1922. (b) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 3554. (c) Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343. (d) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 93.

(21) (a) Casey, C. P.; Brunsvold, W. R.; Scheck, D. M. *Inorg. Chem.* **1977**, *16*, 3059. (b) Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807. (c) Baldoli, C.; Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *Organometallics* **1993**, *12*, 2994.

(22) (a) Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514. (b) Dötz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424. (c) Quayle, P.; Rahman, S.; Ward, E. L. M.; Herbert, J. *Tetrahedron Lett.* **1994**, *35*, 3801.

(23) (a) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. (b) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768. (c) Ruiz, N.; Péron, D.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 1095.

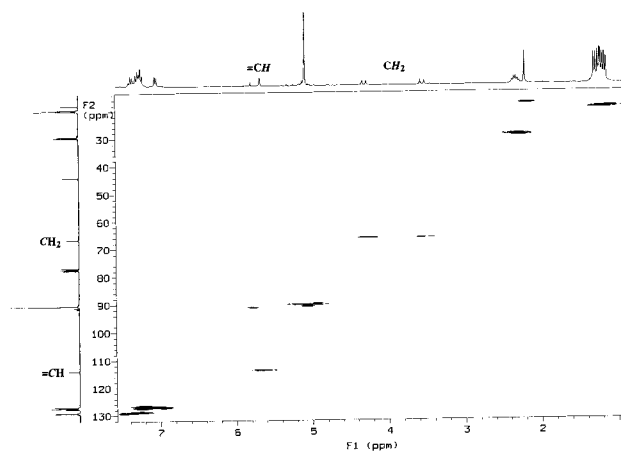
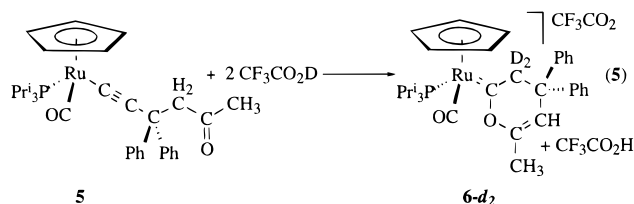


Figure 5. ^1H , ^{13}C -HETCOR NMR spectrum of complex [Ru(η^5 -C₅H₅){CCH₂C(Ph)₂CH=C(CH₃)O}(CO)(PⁱPr₃)]BF₄ (**6**).

five singlets at 149.9, 113.8, 66.4, 43.8, and 17.8 ppm should be mentioned, which were assigned to the carbon atoms -C=, =CH, CH₂, -CPh₂, and CH₃, respectively, on the basis of the $^{13}\text{C}\{^1\text{H}\}$ -DEPT and ^1H , ^{13}C -HETCOR (Figure 5) spectra.

In order to rationalize the unexpected finding of **6**, we carried out the protonation of **5** with deuterated trifluoroacetic acid. The addition of 2 equiv of deuterated trifluoroacetic acid to an NMR tube containing a chloroform-*d* solution of **5** produces the formation of ca. 1 equiv of trifluoroacetic acid and 1 equiv of complex [Ru(η^5 -C₅H₅){CCD₂C(Ph)₂CH=C(CH₃)O}(CO)(PⁱPr₃)]⁺ (**6-d₂**) (eq 5), only traces of [Ru(η^5 -C₅H₅){CCHDC(Ph)₂-CH=C(CH₃)O}(CO)(PⁱPr₃)]⁺ (**6-d₁**) and **6** are detected.

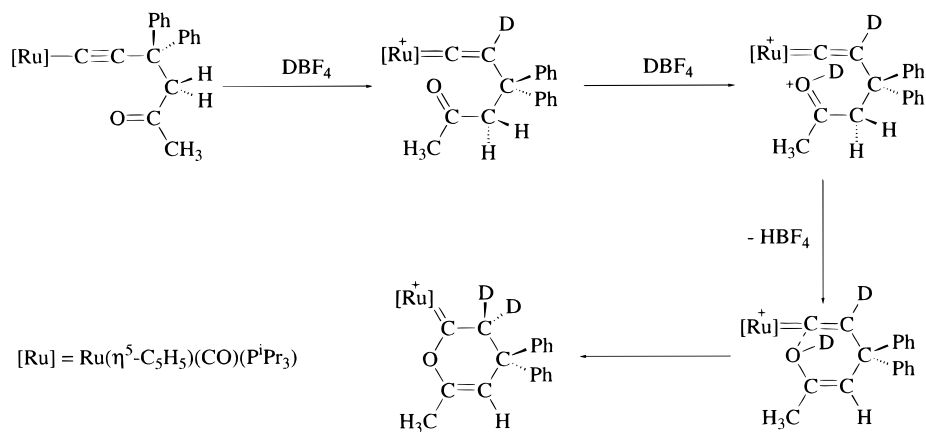


The presence of two deuterium atoms in **6-d₂** is strongly supported by the ^2H NMR spectrum of the complex, which contains two broad signals at 3.97 and 3.55 ppm. In this spectrum, no other resonances were detected.

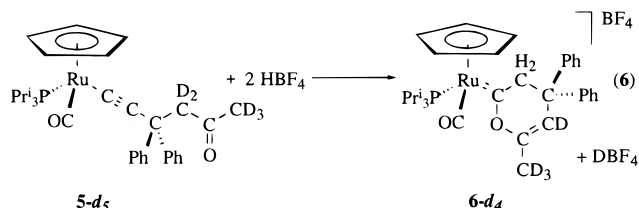
To preclude some substantial kinetic isotope effects at the CH₂ group of the unsaturated cyclic carbene, we also studied the protonation with HBF₄ of Ru(η^5 -C₅H₅){C=C-C(Ph)₂CD₂C(O)CD₃}(CO)(PⁱPr₃) (**5-d₅**), which was prepared similarly to **5** but starting from **1** and deuterated acetone. In this case, under the same experimental conditions as those used for the formation of **6-d₂**, the main organometallic product is [Ru(η^5 -C₅H₅){CCH₂C(Ph)₂CD=C(CD₃)O}(CO)(PⁱPr₃)]BF₄ (**6-d₄**)

(24) (a) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravittles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. (b) Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762. (c) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. (d) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419. (e) Segundo, A.; Moreto, J. M.; Viñas, J. M.; Ricart, S.; Molins, E. *Organometallics* **1994**, *13*, 2467.

Scheme 2



in addition to ca. 1 equiv of DBF₄ (eq 6). The position

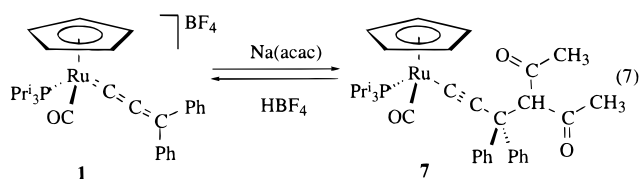


of the deuterium atoms in **6-d₄** is supported by the ²H NMR spectrum, which shows two singlets at 5.90 (=CD-) and 2.30 (-CD₃) ppm.

The formation of **6-d₂** and **6-d₄** can be rationalized according to Scheme 2. One equivalent of acid protonates the alkynyl group to afford a vinylidene intermediate, whereas the other equivalent catalyzes the keto-enol conversion. Finally, the addition of the enol to the C-C double bond of the vinylidene intermediate yields the unsaturated cyclic carbene ligand.

The formation of **6** appears to be possible because the keto-enol conversion is faster than the elimination of acetone from the vinylidene intermediate. In contrast to simple carbonyl compounds, the 1,3-dicarbonyl compounds exist in their enol form in appreciable concentration. For instance, acetylacetone has an enol content of about 80%. Furthermore, it has two nucleophilic leading groups (the carbonyls) and an electrophilic hydrogen atom. So, at first glance, this diketone should be an adequate substrate to give a related compound to **6**, by simple addition to complex **1**. However, all our attempts were unsuccessful.

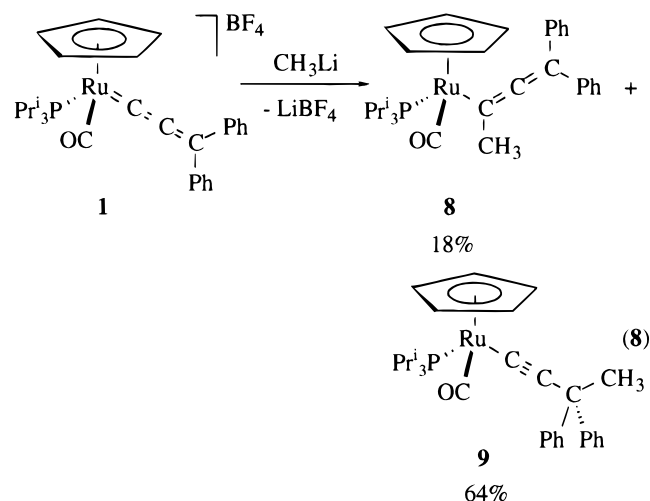
Although complex **1** was recovered unchanged from its acetylacetone solutions, it reacts with sodium acetylacetonate to give the alkynyl derivative Ru(η⁵-C₅H₅){C≡C-C(Ph)₂CH[C(O)CH₃]₂}(CO)(PⁱPr₃) (**7**), related to **5**. On the other hand, in contrast to **5**, the reaction of **7** with HBF₄ regenerates **1**, with the formation of acetylacetone (eq 7). This suggests that the inertia of



the acetylacetone is thermodynamic in origin and it seems to be associated to the low stability of a vinylidene intermediate, similar to that shown in Scheme 2.

The reaction of **1** with sodium acetylacetonate was carried out with tetrahydrofuran as the solvent, and complex **7** was isolated as a white solid in 79% yield. The presence of the alkynyl ligand in **7** is supported by the IR and ¹H and ¹³C{¹H} NMR spectra. The IR spectrum in Nujol shows the ν(C≡C) band at 2105 cm⁻¹ along with two ν(C=O) absorptions at 1710 and 1699 cm⁻¹. In the ¹H NMR spectrum, the most noticeable resonances of the alkynyl ligand are three singlets with a 1:3:3 intensity ratio at 4.90, 2.11, and 2.07 ppm which were assigned to the CH proton and both methyl groups. In the ¹³C{¹H} NMR spectrum, the α-carbon atom of the alkynyl group appears at 94.8 ppm as a doublet with a P-C coupling constant of 19.5 Hz, while the resonance of the β-carbon atom is observed as a singlet at 108.0 ppm.

Addition of Methane. Complex **1** does not react with methane. However, the product resulting from the formal addition of this unreactive molecule to the C_β-C_γ double bond of the allenylidene ligand of **1** can be obtained by means of a synthetic strategy similar to that previously described for the carbene complex **4**. Similar to the reaction shown in eq 1, treatment of the allenylidene compound **1** with ca. 1 equiv of methyllithium with tetrahydrofuran as the solvent leads to a mixture of the allenyl complex Ru(η⁵-C₅H₅){C(C≡C-CH₃)=C(Ph)₂}(CO)(PⁱPr₃) (**8**) and the alkynyl isomer Ru(η⁵-C₅H₅){C≡C-C(Ph)₂CH₃}(CO)(PⁱPr₃) (**9**), according to eq 8.

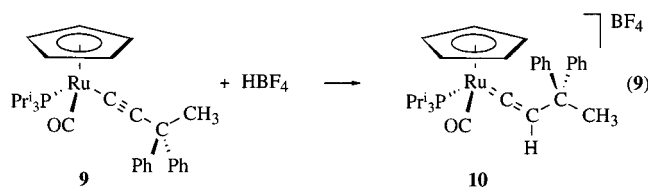


The isomers were separated by fractional recrystallization in *n*-hexane. Complex **8** (the minor product of

the reaction) was obtained in 18% yield as a yellow solid, whereas the alkynyl isomer **9** (the main product of the reaction) was obtained in 64% yield as a white solid. In addition, the different selectivity between the reaction shown in eq 8 and that observed for the reaction summarized in eq 1 should be noted. While the addition of the acetylide is favored in a 2.3:1 ratio toward the α -carbon atom of the allenylidene, the addition of the methyl group is favored in a 1:3.5 ratio toward the γ -carbon atom of the unsaturated η^1 -carbon ligand.

Complexes **8** and **9** were characterized by elemental analysis and IR and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopies. Similar to the allenyl complex **2**, the most characteristic spectroscopic features of **8** are the C=C=C stretching frequency in the IR spectrum, which is observed at 1889 cm⁻¹, and the three resonances in the ¹³C{¹H} NMR spectrum at 200.0 (d, *J*(PC) = 2.3 Hz), 97.7 (s), and 88.3 (d, *J*(PC) = 10.1 Hz) ppm for the C_β, C_γ, and C_α allenyl carbon atoms, respectively. In the IR spectrum of **9**, the most noticeable absorption is that corresponding to the ν (C≡C) vibration, which is observed at 2114 cm⁻¹. In the ¹³C{¹H} NMR spectrum, the resonance of the α -carbon atom of the alkynyl ligand appears at 85.6 ppm as a doublet, with a P-C coupling constant of 21.8 Hz. In addition, the singlets at 113.2, 47.3 and 32.4, corresponding to C_β, CPh₂, and CH₃ carbon atoms of the alkynyl ligand, should be mentioned.

The alkynyl complex **9** reacts with 1 equiv of HBF₄ in diethyl ether to afford the vinylidene derivative [Ru(η^5 -C₅H₅){C=CHC(Ph)₂CH₃}(CO)(PⁱPr₃)]BF₄ (**10**, eq 9), which is a result of the formal addition of a H-C bond of methane to the C_β-C_γ double bond of the allenylidene group of **1**.



Complex **10** was isolated as an orange solid in 97% yield. The presence of a vinylidene ligand in this complex is mainly supported by the ¹H and ¹³C{¹H} NMR spectra. The ¹H NMR spectrum contains the characteristic =CH- resonance, which appears at 5.75 ppm as a doublet with a P-H coupling constant of 1.4 Hz, whereas the ¹³C{¹H} NMR spectrum shows a doublet at 356.0 ppm with a P-C coupling constant of 11.3 Hz for the α -carbon atom of the vinylidene group.

Concluding Remarks

Previously, we have reported that the allenylidene complex **1** reacts with water, alcohols, thiols, and benzophenone imine to afford α,β -unsaturated hydroxycarbene, alkoxy carbene, (alkylthio)carbene, and 2-azaallenyl compounds, which are a result of the addition of the H-X bond of the above-mentioned RXH molecules to the C_α-C_β double bond of the allenylidene ligand of **1**. This study has revealed that although phenylacetylene, acetone, and methane do not react with **1**, the products resulting from the formal addition of H-C bonds of these molecules to the C_α-C_β or C_β-C_γ bonds of the allenylidene ligand of **1** can be easily obtained.

Because in the allenylidene ligand of **1**, the α - and γ -carbon atoms are electrophilic centers and the β -carbon atom is nucleophilic; the general synthetic strategy involves the initial nucleophilic attack of a carbanion at the α - or γ -atom of the allenylidene group and the subsequent protonation of the resulting allenyl or alkynyl derivatives.

In conclusion, we report a new synthetic strategy that allows the formation of products, which are a result of the formal C-C coupling between mutually inert fragments.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ (**1**) was prepared by the published method.⁶

NMR spectra were recorded on either a Varian Unity 300, a Varian GEMINI 2000 300 MHz or a Bruker 300 ARX spectrometer. Chemical shifts are expressed in ppm upfield from Me₄Si (¹H and ¹³C) and 85% H₃PO₄ (³¹P). Coupling constants, *J*, are given in Hertz. IR spectra were run on a Nicolet 550 spectrophotometer (Nujol mulls on polyethylene sheets). Elemental analyses were carried out on a Perkin-Elmer 2400 CHNS/O analyzer. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the standard Cs⁺ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Preparation of Ru(η^5 -C₅H₅){C(C≡CPh)=C=CPh₂}(CO)-(PⁱPr₃) (2**) and Ru(η^5 -C₅H₅){C≡CC(Ph)₂C≡CPh}(CO)-(PⁱPr₃) (**3**).** A solution of **1** (310 mg, 0.49 mmol) in 10 mL of tetrahydrofuran at 233 K was treated with lithium phenylacetylide (58 mg, 0.54 mmol), and the mixture was stirred for 1 h while the temperature was slowly increased to 263 K. The color turned from dark red to orange, and the solvent was removed in vacuo. Toluene (12 mL) was added, and the mixture was filtered to eliminate LiBF₄. The solvent was evaporated at room temperature, and the residue was washed with *n*-hexane, dried in vacuo, and washed with methanol to afford **2** as a yellow solid. Yield: 130 mg (41%). Anal. Calcd for C₃₈H₄₁OPRu: C, 70.67; H, 6.40. Found: C, 70.23; H, 6.66. IR (Nujol, cm⁻¹): ν (C≡C) 2168 (m); ν (CO) 1934 (vs); ν (C=C=C) 1927 (s); ν (Ph) 1594 (m). ¹H NMR (300 MHz, 293 K, C₆D₆): δ 7.70–6.80 (15H, Ph), 4.95 (s, 5H, Cp), 1.97 (m, 3H, PCHCH₃), 0.94 (dd, 9H, *J*(HH) = 6.8, *J*(PH) = 13.5, PCHCH₃), 0.86 (dd, 9H, *J*(HH) = 7.0, *J*(PH) = 12.8, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, C₆D₆): δ 70.2 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, C₆D₆): δ 209.7 (d, *J*(PC) = 1.5, =C=), 207.0 (d, *J*(PC) = 19.6, CO), 140.1, 139.9 (both s, C_{ipso}), 131.6–125.9 (Ph), 98.3 (s, =CPh₂), 94.7, 91.3 (s, C≡C), 86.4 (s, Cp), 74.3 (d, *J*(PC) = 11.9, Ru-C=), 27.7 (d, *J*(PC) = 22.4, PCHCH₃), 20.0, 19.5 (both s, PCHCH₃). The orange *n*-hexane solution was concentrated to ca. 3 mL, and **3** precipitated as a white solid, which was washed with cold *n*-hexane. Yield: 56 mg (18%). Anal. Calcd for C₃₈H₄₁OPRu: C, 70.67; H, 6.40. Found: C, 70.18; H, 6.38. IR (Nujol, cm⁻¹): ν (C≡C) 2109, 2096 (both m); ν (CO) 1931 (vs); ν (Ph) 1598 (m). ¹H NMR (300 MHz, 293 K, C₆D₆): δ 8.20–6.90 (15H, Ph), 4.80 (s, 5H, Cp), 2.03 (m, 3H, PCHCH₃), 1.10 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, PCHCH₃), 0.84 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 12.7, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, C₆D₆): δ 74.8 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, C₆D₆): δ 206.4 (d, *J*(PC) = 19.0, CO), 147.7, 147.4 (both s, C_{ipso}), 131.9–124.8 (Ph), 106.8 (s, C_β), 95.1, 83.1 (both s, PhC≡C), 90.9 (d, *J*(PC) = 22.2, C_α), 85.6 (s, Cp), 48.2 (s, C_γ), 27.3 (d, *J*(PC) = 23.7, PCHCH₃), 20.3, 19.5 (both s, PCHCH₃).

Preparation of [Ru(η^5 -C₅H₅){C(C≡CPh)CH=CPh₂}(CO)-(PⁱPr₃)]BF₄ (4**).** A solution of **2** (119 mg, 0.18 mmol) in 5 mL of dichloromethane was treated with tetrafluoroboric acid

(26 μ L, 0.18 mmol, 54% in diethyl ether). Immediately, the color turned from yellow to dark brown, and the solution was concentrated almost to dryness. By slow addition of diethyl ether, **4** was obtained as a dark brown solid. Yield: 120 mg (89%). Anal. Calcd for $C_{38}H_{42}BF_4OPRu$: C, 62.21; H, 5.77. Found: C, 62.32; H, 5.45. IR (Nujol, cm^{-1}): $\nu(C\equiv C)$ 2123 (m); $\nu(CO)$ 1950 (vs); $\nu(Ph)$ 1590 (w); $\nu(C=C)$ 1502 (m); $\nu(BF_4)$ 1053 (vs, br). 1H NMR (300 MHz, 293 K, $(CD_3)_2CO$): δ 8.31 (br s, 1H, HC=), 7.54–6.96 (15H, Ph), 5.71 (s, 5H, Cp), 2.55 (m, 3H, $PCHCH_3$), 1.36, 1.24 (both dd, 18H, $J(HH) = 7.4$, $J(Ph) = 14.8$, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $(CD_3)_2CO$): δ 68.2 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $(CD_3)_2CO$): δ 283.0 (br, Ru=C), 202.7 (d, $J(PC) = 16.2$, CO), 148.7 (br s, 1H, HC=), 141.3, 138.9 (both s, C_{ipso}), 131.8, 131.7, 131.4, 131.3, 130.4, 130.2, 129.2, 128.8, 128.7 (all s, Ph), 122.5 (s, $=CPh_2$), 106.9 (br s, $C=CPh$), 93.3 (br, Cp), 77.3 (s, $C=CPh$), 29.8 (br d, $J(PC) = 23.9$, $PCHCH_3$), 19.8, 19.6 (both s, $PCHCH_3$).

Preparation of $Ru(\eta^5-C_5H_5)\{C\equiv CC(Ph)_2CH_2C(O)CH_3\}(CO)(P^iPr_3)$ (5**).** **1** (350 mg, 0.55 mmol) was added in small amounts to a stirred suspension of potassium hydroxide (69 mg, 85%, 1.05 mmol) in 10 mL of acetone at 303 K, and the mixture was stirred for 10 min. The solvent was removed in vacuo from the yellow solution, 12 mL of toluene was added, and the mixture was filtered to eliminate $NaBF_4$ and excess of potassium hydroxide. The solvent was removed in vacuo, and the residue was extracted with 6 fractions of 10 mL of *n*-hexane each at 203 K. The yellow *n*-hexane solution was concentrated to ca. 2 mL, and **5** precipitated as a white solid. The solid was washed with cold *n*-hexane. Yield: 85 mg (25%). Anal. Calcd for $C_{33}H_{41}O_2PRu$: C, 65.87; H, 6.87. Found: C, 65.26; H, 7.04. IR (Nujol, cm^{-1}): $\nu(C\equiv C)$ 2108 (m); $\nu(CO)$ 1931 (vs); $\nu(C=O)$ 1702 (s); $\nu(Ph)$ 1595 (m). 1H NMR (300 MHz, 293 K, C_6D_6): δ 7.72–7.70 (10H, Ph), 4.87 (s, 5H, Cp), 3.36 (s, 2H, CH_2), 2.01 (s, 3H, CH_3), 1.92 (m, 3H, $PCHCH_3$), 1.04 (dd, 9H, $J(HH) = 7.1$, $J(Ph) = 14.5$, $PCHCH_3$), 0.81 (dd, 9H, $J(HH) = 7.1$, $J(Ph) = 12.9$, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 75.1 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6): δ 206.5 (d, $J(PC) = 18.1$, CO), 205.7 (s, $C=O$), 148.7, 148.5 (both s, C_{ipso}), 128.0–125.9 (Ph), 110.2 (s, C_β), 90.9 (d, $J(PC) = 21.1$, C_α), 85.6 (d, $J(PC) = 0.9$, Cp), 57.3, 49.5 (both s, $CH_2 + C_\gamma$), 31.4 (s, CH_3), 27.2 (d, $J(PC) = 23.9$, $PCHCH_3$), 20.2, 19.4 (both s, $PCHCH_3$).

Preparation of $Ru(\eta^5-C_5H_5)\{C\equiv CC(Ph)_2CD_2C(O)CD_3\}(CO)(P^iPr_3)$ (5-d₅**).** To a stirred solution of diisopropylamine (55 μ L, 0.40 mmol) in 10 mL of tetrahydrofuran at 195 K was added butyllithium (247 μ L, 0.40 mmol, 1.6 M in *n*-hexane). The mixture was stirred for 1.5 h and then was treated with acetone- d_6 (29 μ L, 0.40 mmol) and stirred for 30 min. The temperature was slowly increased to 243 K, and then **1** (250 mg, 0.40 mmol) was added. The mixture was stirred for 1 h while the temperature slowly increased to room temperature, and the color changed from dark red to yellow. The solvent was evaporated, 40 mL of *n*-hexane was added, and the mixture was filtered to eliminate $LiBF_4$. The solution was concentrated to ca. 2 mL, and **5-d₅** precipitated as a white solid. Yield: 58 mg (24%). 1H NMR (300 MHz, 293 K, C_6D_6): δ 7.72–7.70 (10H, Ph), 4.87 (s, 5H, Cp), 1.92 (m, 3H, $PCHCH_3$), 1.04 (dd, 9H, $J(HH) = 7.1$, $J(Ph) = 14.5$, $PCHCH_3$), 0.81 (dd, 9H, $J(HH) = 7.1$, $J(Ph) = 12.9$, $PCHCH_3$). $^2D\{^1H\}$ NMR (46.07 MHz, 293 K, C_6D_6): δ 3.29 (br s, CD_2), 1.93 (s, CD_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 75.1 (s).

Preparation of $[Ru(\eta^5-C_5H_5)\{CCH_2C(Ph)_2CH=C(CH_3)O\}(CO)(P^iPr_3)]BF_4$ (6**).** A solution of **5** (80 mg, 0.13 mmol) in 5 mL of diethyl ether was treated with tetrafluoroboric acid (38 μ L, 0.26 mmol, 54% in diethyl ether). Immediately, **6** precipitated as a pink solid. Yield: 79 mg (86%). Anal. Calcd for $C_{33}H_{42}BF_4O_2PRu$: C, 57.48; H, 6.14. Found: C, 56.94; H, 5.84. IR (Nujol, cm^{-1}): $\nu(CO)$ 1985 (vs); $\nu(C=C-O)$ 1701 (m); $\nu(Ph)$ 1599 (m); $\nu(BF_4)$ 1045 (vs, br). 1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.41–7.02 (10H, Ph), 5.67 (br s, 1H, $C=CH$), 5.09 (s, 5H, Cp), 4.35, 3.52 (both d, 2H, $J_{gem} = 16.0$, CH_2), 2.35 (m,

3H, $PCHCH_3$), 2.20 (s, 3H, CH_3), 1.27 (dd, 9H, $J(HH) = 7.4$, $J(Ph) = 16.4$, $PCHCH_3$), 1.18 (dd, 9H, $J(HH) = 7.4$, $J(Ph) = 14.8$, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$): δ 68.7 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$, plus DEPT): δ 308.1 (C_{quat} , d, $J(PC) = 9.6$, Ru=C), 201.5 (C_{quat} , d, $J(PC) = 15.6$, CO), 149.9 (C_{quat} , s, $CH_3-C=$), 143.6, 143.2 (C_{quat} , both s, C_{ipso}), 129.0, 128.9, 127.4, 127.3, 127.1, 126.8 (–, all s, Ph), 113.8 (–, s, $=CH$), 90.4 (–, s, Cp), 66.4 (+, s, CH_2), 43.8 (C_{quat} , s, CPh_2), 29.3 (–, d, $J(PC) = 24.9$, $PCHCH_3$), 19.7, 19.5 (–, both s, $PCHCH_3$), 17.8 (–, s, CH_3). MS (FAB⁺): $m/z = 603$ (M^+).

Reaction of **5** with Deuterated Trifluoroacetic Acid:

Preparation of $[Ru(\eta^5-C_5H_5)\{CDD_2C(Ph)_2CH=C(CH_3)O\}(CO)(P^iPr_3)]BF_4$ (6-d₂**).** A solution of **5** (11.5 mg, 0.019 mmol) in 0.5 mL of $CDCl_3$ in an NMR tube was treated with deuterated trifluoroacetic acid (3.0 μ L, 0.038 mmol). The NMR tube was sealed under argon, and measurements were made immediately. 1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.41–7.02 (10H, Ph), 5.68 (br s, 1H, $C=CH$), 5.00 (s, 5H, Cp), 2.35 (m, 3H, $PCHCH_3$), 2.20 (s, 3H, CH_3), 1.27 (dd, 9H, $J(HH) = 7.4$, $J(Ph) = 16.4$, $PCHCH_3$), 1.18 (dd, 9H, $J(HH) = 7.4$, $J(Ph) = 14.8$, $PCHCH_3$). $^2D\{^1H\}$ NMR (46.07 MHz, 293 K, CH_2Cl_2): δ 3.97, 3.55 (both br, CD_2). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$): δ 68.7 (s).

Reaction of **5-d₅** with Tetrafluoroboric Acid: Prepara-

tion of $[Ru(\eta^5-C_5H_5)\{CCH_2C(Ph)_2CD=C(CD_3)O\}(CO)(P^iPr_3)]BF_4$ (6-d₄**).** A solution of **5-d₅** (10.4 mg, 0.017 mmol) in 0.5 mL of $CDCl_3$ in an NMR tube was treated with tetrafluoroboric acid (4.6 μ L, 0.034 mmol). The NMR tube was sealed under argon, and measurements were made immediately. 1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.41–7.02 (10H, Ph), 5.09 (s, 5H, Cp), 4.34, 3.49 (both d, 2H, $J_{gem} = 16.0$, CH_2), 2.35 (m, 3H, $PCHCH_3$), 1.27 (dd, 9H, $J(HH) = 7.4$, $J(Ph) = 16.4$, $PCHCH_3$), 1.18 (dd, 9H, $J(HH) = 7.4$, $J(Ph) = 14.8$, $PCHCH_3$). $^2D\{^1H\}$ NMR (46.07 MHz, 293 K, CH_2Cl_2): δ 5.90 (br, $C=CD$), 2.30 (s, CD_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$): δ 68.7 (s).

Preparation of $Ru(\eta^5-C_5H_5)\{C\equiv CC(Ph)_2CH[C(O)CH_3\}_2(CO)(P^iPr_3)$ (7**).** A solution of **1** (250 mg, 0.40 mmol) was treated with sodium acetylacetonate (49 mg, 0.40 mmol) in 10 mL of tetrahydrofuran, and the mixture was stirred for 2 min. The color turned from dark red to pale yellow and the solvent was removed in vacuo. Toluene (12 mL) was added, and the mixture was filtered to eliminate $NaBF_4$. The solvent was removed in vacuo, and the residue was washed with *n*-pentane to afford **7** as a white solid. Yield: 200 mg (79%). Anal. Calcd for $C_{35}H_{43}O_3PRu$: C, 65.30; H, 6.73. Found: C, 65.02; H, 6.54. IR (Nujol, cm^{-1}): $\nu(C\equiv C)$ 2105 (m); $\nu(CO)$ 1938 (vs); $\nu(C=O)$ 1710, 1699 (both s); $\nu(Ph)$ 1595 (w). 1H NMR (300 MHz, 293 K, C_6D_6): δ 7.99–6.89 (10H, Ph), 4.93 (s, 5H, Cp), 4.90 (s, 1H, CH), 2.11, 2.07 (both s, 6H, $2CH_3$), 1.92 (m, 3H, $PCHCH_3$), 1.11 (dd, 9H, $J(HH) = 7.1$, $J(Ph) = 14.5$, $PCHCH_3$), 0.90 (dd, 9H, $J(HH) = 7.1$, $J(Ph) = 13.0$, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 75.5 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6): δ 206.3 (d, $J(PC) = 18.0$, CO), 205.7, 205.4 (both s, $C=O$), 147.5, 147.4 (both s, C_{ipso}), 128.0–126.4 (Ph), 108.0 (s, C_β), 94.8 (d, $J(PC) = 19.5$, C_α), 85.6 (s, Cp), 77.3 (s, CH), 52.9 (s, C_γ), 31.4, 31.3 (both s, CH_3), 27.5 (d, $J(PC) = 23.4$, $PCHCH_3$), 20.3 (s, $PCHCH_3$), 19.5 (d, $J(PC) = 1.4$, $PCHCH_3$).

Preparation of $Ru(\eta^5-C_5H_5)\{C(CH_3)=C=CPh_2\}(CO)(P^iPr_3)$ (8**) and $Ru(\eta^5-C_5H_5)\{C\equiv CC(Ph)_2CH_3\}(CO)(P^iPr_3)$ (**9**).** A solution of **1** (300 mg, 0.48 mmol) in 5 mL of tetrahydrofuran at 195 K was treated with methyllithium (300 μ L, 0.48 mmol, 1.6 M in diethyl ether), and immediately the color turned from dark red to yellow. The temperature was increased to room temperature, and the solvent was evaporated. Toluene (12 mL) was added, and the mixture was filtered to eliminate $LiBF_4$. The solvent was removed in vacuo, and the residue was extracted with *n*-hexane to afford **9** as a white solid. Yield: 170 mg (64%). Anal. Calcd for $C_{31}H_{39}$ -

OPRu: C, 66.52; H, 7.02. Found: C, 66.67; H, 6.82. IR (Nujol, cm⁻¹): ν (C≡C) 2114 (m); ν (CO) 1930 (vs); ν (Ph) 1597 (m). ¹H NMR (300 MHz, 293 K, C₆D₆): δ 7.60–6.80 (10H, Ph), 4.86 (s, 5H, Cp), 2.11 (s, 3H, CH₃), 1.90 (m, 3H, PCHCH₃), 1.88 (dd, 9H, J(HH) = 7.2, J(PH) = 14.4, PCHCH₃), 0.86 (dd, 9H, J(HH) = 7.2, J(PH) = 13.2, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, C₆D₆): δ 75.0 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, C₆D₆): δ 206.6 (d, J(PC) = 18.9, CO), 150.7, 150.5 (both s, C_{ipso}), 128.2–125.6 (Ph), 113.2 (s, C_β), 85.6 (d, J(PC) = 1.3, Cp), 85.6 (d, J(PC) = 21.8, C_α), 47.3 (s, C_γ), 32.4 (s, CH₃), 27.2 (d, J(PC) = 23.5, PCHCH₃), 20.2 (s, PCHCH₃), 19.4 (d, J(PC) = 1.6, PCHCH₃). The solvent from the yellow *n*-hexane solution was evaporated, and the residue was washed with methanol to afford **8** as a yellow solid. Yield: 49 mg (18%). Anal. Calcd for C₃₁H₃₉OPRu: C, 66.52; H, 7.02. Found: C, 66.40; H, 7.14. IR (Nujol, cm⁻¹): ν (CO) 1914 (vs); ν (C=C) 1889 (s); ν (Ph) 1596 (m). ¹H NMR (300 MHz, 293 K, C₆D₆): δ 7.70–7.10 (10H, Ph), 4.93 (s, 5H, Cp), 2.49 (s, CH₃), 1.89 (m, 3H, PCHCH₃), 0.97 (dd, 9H, J(HH) = 7.4, J(PH) = 14.2, PCHCH₃), 0.73 (dd, 9H, J(HH) = 7.1, J(PH) = 12.8, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, C₆D₆): δ 72.6 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, C₆D₆): δ 208.3 (d, J(PC) = 20.7, CO), 200.0 (d, J(PC) = 2.3, =C=), 141.9, 141.8 (both s, C_{ipso}), 129.3–125.0 (Ph), 97.7 (s, =CPh₂), 88.3 (d, J(PC) = 10.1, Ru–C=), 85.9 (d, J(PC) = 0.9, Cp), 32.9 (s, CH₃), 27.1 (d, J(PC) = 22.0, PCHCH₃), 20.1, 19.08 (both s, PCHCH₃).

Preparation of [Ru(η^5 -C₅H₅){C=CHC(Ph)₂CH₃}(CO)-(PⁱPr₃)]BF₄ (10**).** A solution of **9** (68.5 mg, 0.12 mmol) in 5 mL of diethyl ether was treated with tetrafluoroboric acid (17 μ L, 0.12 mmol, 54% in diethyl ether). Immediately, **10** precipitated as an orange solid. Yield: 77 mg (97%). Anal. Calcd for C₃₁H₄₀BF₄OPRu: C, 57.50; H, 6.23. Found: C, 57.16; H, 6.31. IR (Nujol, cm⁻¹): ν (CO) 2010 (vs); ν (C=C) 1673 (m); ν (Ph) 1599 (w); ν (BF₄) 1049 (vs, br). ¹H NMR (300 MHz, 293 K, (CD₃)₂CO): δ 7.37–7.17 (10H, Ph), 5.75 (d, 1H, J(PH) = 1.4, HC=), 5.50 (s, 5H, Cp), 2.39 (m, 3H, PCHCH₃), 1.92 (s, 3H, CH₃), 1.28 (dd, 9H, J(HH) = 7.1, J(PH) = 10.5, PCHCH₃), 1.23 (dd, 9H, J(HH) = 7.1, J(PH) = 9.8, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, (CD₃)₂CO): δ 79.1 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, (CD₃)₂CO): δ 356.0 (d, J(PC) = 11.3, C_α), 198.1 (d, J(PC) = 15.1, CO), 147.5, 146.6 (both s, C_{ipso}), 128.6, 128.4, 127.4, 127.1, 127.0, 126.9 (all s, Ph + C_β), 92.5 (s, Cp), 47.9 (s, C_γ), 31.0 (s, CH₃), 28.9 (d, J(PC) = 25.6, PCHCH₃), 20.0, 19.6 (both s, PCHCH₃).

X-ray Structure Analysis of Complex [Ru(η^5 -C₅H₅)-{C(C≡CPh)CH=CPh₂}(CO)(PⁱPr₃)]BF₄ (4**).** Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of **4** in CH₂Cl₂. A summary of the crystal data and refinement parameters is reported in Table 2. The yellow, prismatic crystal, of approximate dimensions 0.32 × 0.22 × 0.27 mm, was glued on a glass fiber and mounted on a Siemens-STOE AED-2 diffractometer. A group of 57 reflections in the range 20° ≤ 2θ ≤ 35° was carefully centered at 298 K and used to obtain the unit cell dimensions by least-squares methods. Three standard reflections were monitored at periodic intervals throughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.²⁵ The structure was solved by Patterson (Ru atom, SHELXTL-PLUS²⁶) and conventional Fourier techniques and refined by full-matrix least-squares on F² (SHELXL93²⁷). An isopropyl group of a phosphine ligand (C(36)–C(38)) was observed to be disordered. The disordered group was modeled by including two different isopropyl groups with a complementary occupancy factor refined to a final value

Table 2. Crystal Data and Data Collection and Refinement for [Ru(η^5 -C₅H₅){C(C≡CPh)-CH=CPh₂}(CO)(PⁱPr₃)]BF₄ (4**)**

Crystal Data	
formula	C ₃₈ H ₄₂ BF ₄ OPRu
mol wt	733.57
color and habit	yellow, prismatic block
cryst size, mm	0.32 × 0.22 × 0.27
symmetry	monoclinic
space group	P2 ₁ /n
<i>a</i> , Å	9.687(1)
<i>b</i> , Å	18.539(3)
<i>c</i> , Å	19.785(2)
β , deg	99.88(1)
<i>V</i> , Å ³	3500.4(8)
<i>Z</i>	4
<i>D</i> _{calcd} , g cm ⁻³	1.392
Data Collection and Refinement	
diffractometer	four-circle Siemens-STOE AED
λ (Mo K α), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ , mm ⁻¹	0.54
scan type	$\omega/2\theta$
2 θ range, deg	3° ≤ 2θ ≤ 50°
temp, K	298
no. of data collect	6337
no. of unique data	6149 (<i>R</i> _{int} = 0.0498)
no. of params refined	456
<i>R</i> ₁ ^a (<i>F</i> ² > 2 σ (<i>F</i> ²))	0.0530
<i>wR</i> ₂ ^b (all data (<i>F</i> _o ≥ 0))	0.1472
<i>S</i> ^c (all data)	1.066

^a *R*₁(*F*) = $\sum||F_o| - |F_c||/\sum|F_o|$. ^b *wR*₂(*F*²) = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^c Goof = *S* = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

of 0.67(3) for the *a*-labeled atoms and 0.33(3) for the *b*-labeled ones. Both, *a*- and *b*-labeled groups were refined with a common restrained C(36)–C(37) and C(36)–C(38) distance (1.54(1) Å). The BF₄[−] anion was also observed to be disordered. It was modeled on the basis of two different moieties sharing the central boron atom with complementary occupancy factors refined to a final values of 0.59(3) and 0.41(3). Both groups were refined with a common restrained B–F distance (1.33-(1) Å). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms, except those of the isopropyl group involved in the disorder. The hydrogen atoms were calculated and refined riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Ru and P, were implemented by the program. The refinement converged to *R*₁ = 0.0530 (*F*² > 2 σ (*F*²)) and *wR*₂ = 0.1472 (all data *F*_o ≥ 0), with weighting parameters *x* = 0.0799 and *y* = 4.85.

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Appendix: The extended Hückel calculations have been carried out on model complex [Ru(η^5 -C₅H₅)-(C=C=CH₂)(CO)(PH₃)]⁺ using standard geometrical parameters. The calculations have been performed using the program CACAO²⁸ with the supplied atomic *H*_{ii} parameters.

Supporting Information Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, experimental details of the X-ray study, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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