Reactivity of the Electron-Rich Allenylidene−Ruthenium Complexes [Cp*Ru{=C=C=C(R)Ph}(dippe)][BPh_4] (R = H, Ph). X-Ray Crystal Structure of a Novel Dicationic Ruthenium Carbyne (Cp* = C_5Me_5; dippe = 1,2-bis(diisopropylphosphine)ethane)

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The reactions of the allenylidene complexes [Cp*Ru{=C=C=C(R)Ph}(dippe)][BPh_4] (R = H (**1**), Ph (**2**)) with different substrates have been studied, providing a new form of allenylidene−ruthenium reactivity. The observed reactivity pattern depends strongly on the substituents on the γ-carbon. The *secondary* allenylidene **1** undergoes addition of weakly nucleophilic reagents such as pyrazole, 3,5-dimethylpyrazole, or thiophenol to the $C_\beta-C_\gamma$ double bond, yielding substituted vinylidene compounds [Cp*Ru{=C=CHCH(L)Ph}(dippe)][BPh_4] (L = pyrazolyl (**3**), 3,5-dimethylpyrazolyl (**4**), phenylsulfanyl (**5**)). The reaction of **1** with pyrrole or 2-methylfuran to afford analogous complexes [Cp*Ru{=C=CH−CH(L)Ph}(dippe)][BF_4] (L = 2-pyrrolyl (**6**), 5-methyl-2-furanyl (**7**)) takes place only in the presence of acid. This suggests that an initial protonation at the β-carbon of the allenylidene occurs, enhancing the electrophilic character of the γ-carbon atom. This mechanism involves the formation of dicationic carbyne ruthenium complexes [Cp*Ru{≡C−CH=C(R)Ph}(dippe)]$^{2+}$ (R = H (**8**), Ph (**9**)), which have been isolated and characterized as [$B(Ar_F)_4$] (Ar_F = 3,5-$(CF_3)_2C_6H_3$) salts, by protonation of the cationic allenylidenes with [$H(Et_2O)_2$][$B(Ar_F)_4$]. The X-ray crystal structure of the carbyne compound **9** is reported. A series of neutral functionalized alkynyl compounds [Cp*Ru{C≡CCR(L)Ph}(dippe)] (L = CH_3COCH_2, R = H (**10**), R = Ph (**11**); L = pyrazolyl, R = H (**12**); R = Ph (**13**)) have also been synthesized by regioselective addition of anionic nucleophiles such as potassium acetonate or potassium pyrazolate. The structures of **11** and **13** in the solid state have been determined by X-ray diffraction analysis. Protonation of **10** and **11** with HBF_4·Et_2O yields the vinylidene compounds [Cp*Ru{=C=CH−CR(CH_2COCH_3)Ph}(dippe)][BF_4] (R = H (**14**), Ph (**15**)).

Introduction

Allenylidene chemistry has been rapidly and largely developed in recent years, being a subject of extensive reviews.[1−5] In 1982, a simple method for the preparation of cationic ruthenium−allenylidene complexes by activation of alkynols with the electron-rich complex [CpRuCl(PMe_3)$_2$] was reported by Selegue.[6] By this general method, a wide range of allenylidene species have been synthesized and characterized with a variety of metals. Among them, allenylidene−ruthenium(II) complexes constitute the most extended group.[3] Although in recent years their applications as catalyst are being increased,[7] it is in the field of stoichiometric processes where these complexes have shown a diverse and frequently unusual behavior due to the unsaturated character of the carbon chain.[3,8] The allenylidene reactivity greatly depends on the electron richness of the in situ generated 16-electron species.[4] According to this, electrophilic ruthenium complexes such as [$RuCl_2(PMe_3)$(arene)][9,10] or [CpRuCl(CO)(PR_3)] (R = Ph,[10] ^iPr[11]) lead to highly reactive allenylidenes, which are seldom isolated. They typically undergo addition of alcohols to give α,β-unsaturated

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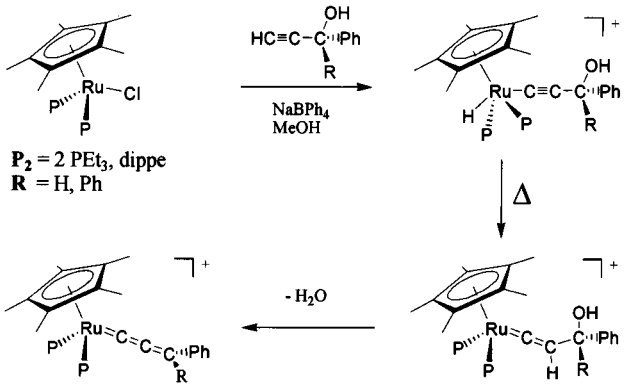
Scheme 1



alkoxycarbenes. The bulkiness and electron-releasing properties of the auxiliary ligands allow the stabilization of allenylidenes with a variety of metallic fragments such as $[RuCl(L)_2]^+$ (L = chelating diphosphine or phosphinoether),[12] $RuCl_2(np_3)$ ($np_3 = (PPh_2C_2H_4)_3N$),[13] $[Ru(L_2)(indenyl)]^+$ (L_2 = 2 PPh_3, dppe, dppm),[5] or $[CpRu(L)_2]^+$ (L = PMe_3,[6] PPh_3,[14] dippe[15]). Their reactivity is mostly focused on the electrophilic γ-carbon. Neutral allenylidenes do not exhibit an electrophilic behavior. On the contrary, protonation of [CpOsCl(=C=C=CPh_2)(P^iPr_3)] at the β-carbon forms a cationic carbyne complex.[16] The nucleophilic character of the β-carbon of allenylidene−ruthenium complexes has also been suggested by theoretical calculations.[17] In the course of our studies on the activation of the 1-phenyl- and 1,1-diphenylpropynol derivatives by $[Cp^*RuCl(L_2)]$ (L_2 = 2 PEt_3,[18] dippe[19]), we have described the sequence of species involved. In both cases, the η^5-C_5Me_5 ligand plays a key role in the isolation of the Ru(IV) intermediate $[Cp^*RuH\{C{\equiv}CC(OH)RR'\}(L_2)]^+$ since it provides the necessary electron density at the metal center. Isomerization to 3-hydroxyvinylidene $[Cp^*Ru\{=C=CHC(OH)RR'\}(L_2)]^+$ and further dehydration led to stable allenylidene products $[Cp^*Ru\{=C=C=C(R)Ph\}(L_2)][BPh_4]$ (R = H, Ph). Their reactivity is expected to be intermediate between those observed for neutral nucleophilic and cationic γ-electrophilic allenylidene derivatives, as it has been recently described for the analogous osmium complex $[CpOs(=C=C=CPh_2)(P^iPr_3)_2][PF_6]$.[20]

In the present paper we explore the reactivity of the electron-rich allenylidenes $[Cp^*Ru\{=C=C=C(R)Ph\}(dippe)][BPh_4]$ (R = H (**1**), Ph (**2**)). It is noteworthy that the study of a *secondary* allenylidene such as **1** introduces a new factor to consider since the loss of one phenyl group at the γ-carbon might enhance its reactivity due to a lesser stabilization of the partial positive charge on this carbon atom and likely due to a lesser steric protection as well.

Results and Discussion

As a consequence of the steric hindrance and electron-releasing capability of the $\{[Cp^*Ru(dippe)]^+\}$ moiety, the allenylidene complexes **1** and **2** are less electrophilic and therefore stable toward addition of alcohols. In fact, both compounds are obtained by activation of the alkynol using methanol as solvent.[19] Although both complexes can be regarded as electron-rich allenylidenes, their behavior depends strongly on the γ-carbon substituents. Thus, whereas the diphenylallenylidene complex **2** does not react with weakly nucleophilic reagents, the *secondary* allenylidene complex **1** undergoes addition of neutral nucleophiles bearing weakly acidic protons such as pyrazole, 3,5-dimethylpyrazole, or thiophenol, at the $C_\beta-C_\gamma$ double bond of the unsaturated chain. The resulting cationic vinylidenes $[Cp^*Ru\{=C=CHCH(L)Ph\}(dippe)][BPh_4]$ (L = pyrazolyl (**3**), 3,5-dimethylpyrazolyl (**4**), phenylsulfanyl (**5**)) have been characterized by elemental analysis and IR and NMR spectroscopy. The ^1H NMR spectrum shows in all cases a characteristic pair of doublets in the range δ 4.37−6.08 ppm, corresponding to the hydrogens on β- and γ-carbons. All vinylidene α-carbons appear as triplets around δ 335 ppm with coupling constants of 14−16 Hz in the $^{13}C\{^1H\}$ NMR spectra. The $^{31}P\{^1H\}$ NMR spectra of **3**−**5** at 25 °C consist of an AB spin pattern with a coupling constant of 17−18 Hz, which is common to all vinylidene complexes derived from **1** due to the effect of the chiral center on the γ-carbon.[19]

Previously, there have been reported direct additions to the $C_\alpha-C_\beta$ double bond of electrophilic ruthenium complexes such as $[CpRu(=C=C=CPh_2)(CO)(P^iPr_3)][BF_4]$, which adds alcohols, water, or benzophenone imine and, in particular, thiols[11] or pyrazole.[21] A nucleophilic attack on the α-carbon is postulated as the

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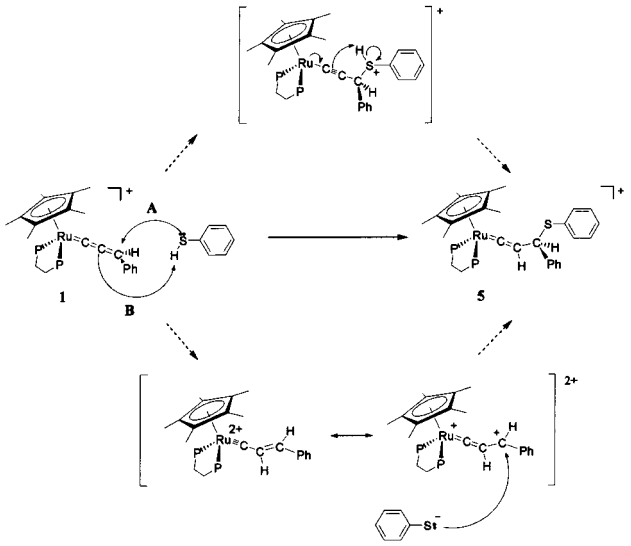
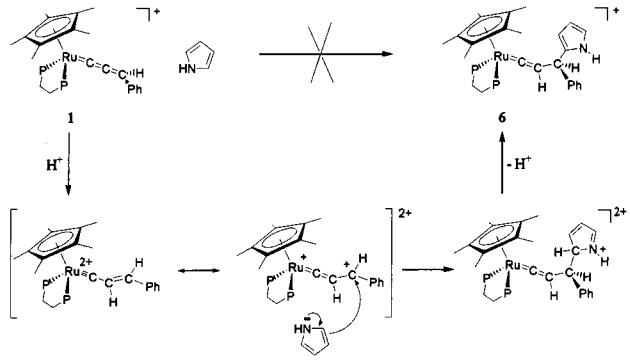
Scheme 2



Scheme 3



first step of the addition mechanism. In our case, the α-carbon is less electrophilic and any possible attack is hindered by the effective steric protection provided by the η^5-C_5Me_5 and phosphine ligands.

In view of this, a nucleophilic attack on the γ-carbon and subsequent protonation of the β-carbon can be proposed (see Scheme 2, A). However, an alternative pathway may operate in the case of electron-rich allenylidenes. When the β-carbon is nucleophilic enough, an initial protonation of the allenylidene β-carbon would enhance the electrophilic character of the γ-carbon, causing the nucleophilic attack (see Scheme 2, B). This possibility has been probed by the reaction of **1** with pyrrole, a weak nucleophilic reagent bearing a slightly acidic proton, and with 2-methylfuran, which has no acidic protons. In both cases there was no reaction until HBF_4·Et_2O was added to the solution. After workup, orange solids were obtained and identified as γ-substituted vinylidene compounds, with the corresponding heterocycle bonded through the 2-position: $[Cp^*Ru\{=C=CHCH(L)Ph\}(dippe)]^+$ (L = 2-pyrrolyl (**6**), 5-methyl-2-furanyl (**7**)). The IR spectrum of **6** shows the ν(N−H) absorption at 3374 cm^{-1}. The N−H proton appears at δ 8.77 ppm in the ^1H NMR spectrum, besides three signals for the C−H protons of the ring. In the case of **7**, two correlated doublets appear at δ 5.67 and 5.83 ppm for protons at the 3- and 4-positions of the ring and a singlet at δ 2.23 ppm corresponding to the methyl group at the 5-position. Hydrogens on β- and γ-carbons of the vinylidene ligand appear as doublets in the range δ 4.45−4.87 ppm in both cases. In the $^{13}C\{^1H\}$ NMR spectra of **6** and **7**, the vinylidene α-carbons appear around δ 338 ppm. The formation of such complexes can be explained by initial protonation on the β-carbon of the allenylidene, nucleophilic attack of the heterocycle through its 2-position (which is induced by the so-called "heteroatom effect"), and final deprotonation (see Scheme 3).

The proposed mechanism for this process postulates a dicationic vinyl−carbyne complex as intermediate. To the best of our knowledge, such a dicationic species has never been described in the chemistry of ruthenium. Moreover, even monocationic or neutral ruthenium−carbynes are very scarce. The only crystallographically characterized ruthenium−carbynes have been recently reported by Werner et al., as a result of the protonation on the β-carbon atom of the neutral vinylidenes $[RuCl_2(=C=CHPh)(P^iPr_3)_2]$ and $[RuCl(\kappa^2\text{-}O_2CCF_3)(=C=CHPh)(P^iPr_3)_2]$.[22] Neutral carbyne complexes such as $[Ru(\equiv CR)Cl(CO)(PPh_3)_2]$ have also been described.[23] At variance with this, osmium−carbynes are well-known species[24,25] due to the remarkable preference of osmium (versus ruthenium) for higher oxidation state and formation of new metal−ligand bonds.[26]

Nevertheless, the dicationic carbyne ruthenium complexes $[Cp^*Ru\{\equiv C-CH=C(R)Ph\}(dippe)]^{2+}$ (R = H (**8**), Ph (**9**)) have been isolated and characterized as $[B(Ar_F)_4]$ (Ar_F = 3,5-$(CF_3)_2C_6H_3$) salts, by protonation of the corresponding cationic allenylidene with $[H(Et_2O)_2]$-$[B(Ar_F)_4]$. Their synthesis in good yields (80−90%) is particularly remarkable. Both complexes are moderately stable in air when handled as solids. The hydrogen on the β-carbon atom is relatively acidic, and they revert partially to allenylidene in the presence of weak bases such as methanol or acetone, preventing the isolation of the carbyne complex in pure form. Recrystallization by slow diffusion of petroleum ether into a Et_2O solution of **9** afforded appropriate red crystals for an X-ray diffraction study. An ORTEP[27] view of the dicationic complex **9** is depicted in Figure 1. Selected bond lengths and angles are listed in Tables 1 and 2.

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Table 1. Selected Bond Lengths (Å) for Compounds 9, 11, and 13, with Estimated Standard Deviations in Parentheses

9			11			13		
Ru(1)	P(1)	2.393(1)	Ru(1)	P(1)	2.304(1)	Ru(1)	P(1)	2.313(1)
Ru(1)	P(2)	2.380(1)	Ru(1	P(2)	2.311(1)	Ru(1)	P(2)	2.314(1)
Ru(1)	C(1)	2.384(3)	Ru(1)	C(1)	2.310(2)	Ru(1)	C(1)	2.319(3)
Ru(1)	C(2)	2.385(3)	Ru(1)	C(2)	2.278(2)	Ru(1)	C(2)	2.280(3)
Ru(1)	C(3)	2.294(3)	Ru(1)	C(3)	2.234(2)	Ru(1)	C(3)	2.236(3)
Ru(1)	C(4)	2.261(3)	Ru(1)	C(4)	2.236(2)	Ru(1)	C(4)	2.234(3)
Ru(1)	C(5)	2.299(3)	Ru(1)	C(5)	2.275(2)	Ru(1)	C(5)	2.282(3)
Ru(1)	C(25)	1.766(3)	Ru(1)	C(25)	2.006(2)	Ru(1)	C(25)	2.004(2)
C(25)	C(26)	1.388(4)	C(25)	C(26)	1.215(3)	C(25)	C(26)	1.214(3)
C(26)	C(27)	1.384(4)	C(26)	C(27)	1.485(3)	C(26)	C(27)	1.481(3)
C(27)	C(28)	1.468(5)	C(27)	C(28)	1.549(3)	C(27)	C(28)	1.540(4)
C(27)	C(34)	1.466(4)	C(27)	C(34)	1.542(3)	C(27	C(34)	1.535(4)
			C(27)	C(40)	1.565(3)	C(27)	N(1)	1.501(4)

Table 2. Selected Angles (deg) for Compounds 9, 11, and 13, with Estimated Standard Deviations in Parentheses

9		11		13	
P(1)Ru(1)P(2)	81.80(4)	P(1)Ru(1)P(2)	83.71(2)	P(1)Ru(1)P(2)	83.07(3)
P(1)Ru(1)C(25)	91.9(1)	P(1)Ru(1)C(25)	84.4(1)	P(1)Ru(1)C(25)	83.6(1)
P(2)Ru(1)C(25)	89.3(1)	P(2)Ru(1)C(25)	87.6(1)	P(2)Ru(1)C(25)	87.5 (1)
Ru(1)C(25)C(26)	171.0(2)	Ru(1)C(25)C(26)	173.9(2)	Ru(1)C(25)C(26)	176.8(2)
C(25)C(26)C(27)	129.8(3)	C(25)C(26)C(27)	173.1(2)	C(25)C(26)C(27)	169.9(3)
C(26)C(27)C(28)	122.8(3)	C(26)C(27)C(40)	107.9(2)	C(26)C(27)N(1)	107.8(2)
C(26)C(27)C(34)	118.6(3)	C(26)C(27)C(28)	107.7(2)	C(26)C(27)C(28)	106.4(2)
C(25)C(26)H(26)	115.1	C(26)C(27)C(34)	112.4(2)	C(26)C(27)C(34)	113.4(2)

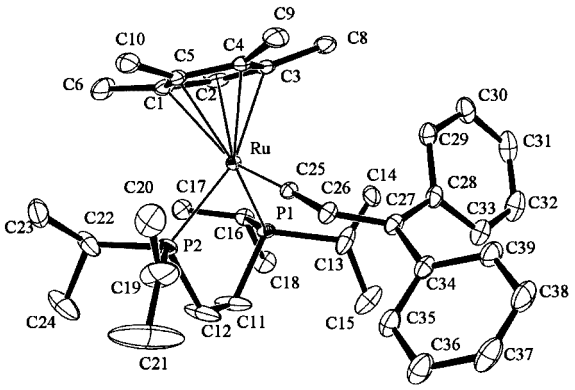
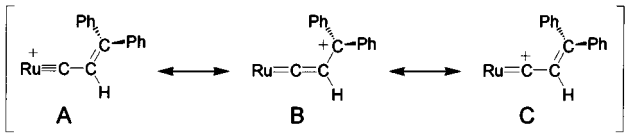


Figure 1. ORTEP drawing (20% thermal ellipsoids) of the cation $[Cp^*Ru(dippe)(\equiv C-CH=CPh_2)]^{2+}$ (**9**). Hydrogen atoms and the two $[B(Ar_F)_4]^-$ anions have been omitted.

The coordination geometry around the ruthenium center corresponds to that of a three-legged piano stool, with the Cp* ligand occupying three sites. The angle Ru(1)−C(25)−C(26) of 171.0(2)° is slightly bent, similarly to other carbyne−metal compounds.[28] The Ru(1)−C(25) bond length of 1.766(3) Å is longer than those of Werner's ruthenium−carbyne structures (1.660 Å)[22] and shorter than that observed in the vinylidene complex $[Cp^*Ru(=C=CHCOOMe)(dippe)][BPh_4]$ (1.807 Å).[29] The angles around C(26) and C(27) are close to 120°, as expected for sp^2-hybridized carbon atoms, and the bond lengths corresponding to C(25)−C(26) and C(26)−C(27) are almost identical (1.388(4) and 1.384(4) Å), which indicates a high contribution of the canonical forms B and C (Scheme 4).

The IR spectra of **8** and **9** lack the characteristic allenylidene band, and the $^{31}P\{^1H\}$ NMR spectra show a singlet slightly shifted to lower field compared to the allenylidene signals. The ^1H NMR spectrum of **8** displays a pair of doublets at δ 6.53 and 8.11 ppm attributable to the hydrogens on the β- and γ-carbons. The coupling constant of 16 Hz is consistent with a *trans* arrangement around the double bond. In the case of **9**, the observed singlet at δ 6.31 ppm compares well with that reported for the complex $[CpOs(\equiv C-CH=CPh_2)(P^iPr_3)_2][PF_6]_2$ at δ 6.66 ppm, attributed to the proton on the β-carbon.[20] The $^{13}C\{^1H\}$ NMR spectra show the resonance corresponding to the α-carbon atom of the carbyne ligand at δ 332.4 ppm for **8** and 327.5 ppm for **9**, as triplets with coupling constants of 13.1 and 12.5 Hz, respectively. The β-carbon signals are singlets at δ 141.0 and 138.3 ppm, whereas the more electrophilic γ-carbons appear at δ 167.9 and 180.1 ppm, respectively. The relation $\delta(C_\gamma) > \delta(C_\beta)$ is also found for other osmium vinyl−carbyne species.[24]

Scheme 4



The isolation of the carbyne species **8**, along with the observed reactivity pattern of **1** against weakly nucleophilic reagents (with or without acidic protons), allows us to propose the existence of an alternative pathway for $C_\beta-C_\gamma$ additions in electron-rich allenylidenes, carbyne species being intermediates in this process. Therefore, when pyrazole is added to a solution of **8** in CH_2Cl_2, a fast color change is observed. The formation of the substituted vinylidene **3** is inferred from the NMR data. However, the carbyne complex **9** and its parent diphenylallenylidene **2** do not show analogous behavior, being inert toward any of the described nucleophilic reagents.On the other hand, compounds **1** and **2** can behave as γ-electrophiles when exposed to anionic nucleophiles undergoing regioselective additions. Thus, a series of

(28) Schubert, U. Solid-state Structures of Carbyne Complexes. In *Carbyne Complexes*; Fischer, H., Hofmann, P., Kreissl, F. R., Schrock, R. R., Schubert, U., Weiss, K., Eds.; VCH Verlagsgesellschaft mbH: Weinheim, Germany, 1988.

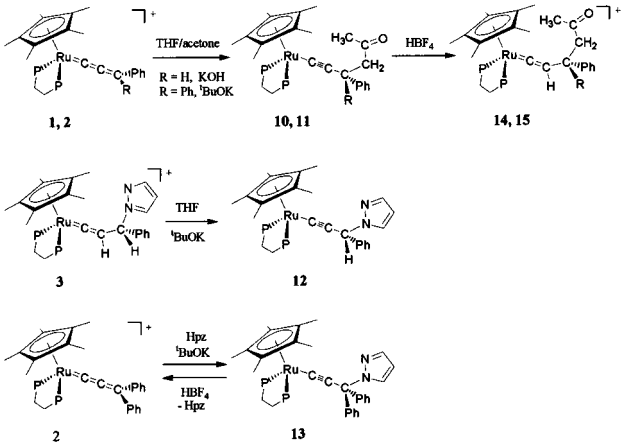
(29) De los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529.

Table 3. Summary of Crystallographic Data for Compounds 9, 11, and 13

	9	11	13
formula	$C_{103}H_{82}B_2F_{48}P_2Ru$	$C_{42}H_{62}OP_2Ru$	$C_{42}H_{60}N_2P_2Ru$
fw	2416.32	745.93	755.93
T (K)	208(2)	223(2)	223(2)
cryst size (mm)	0.60 × 0.50 × 0.42	0.64 × 0.60 × 0.35	0.80 × 0.62 × 0.22
cryst color, habit	dark red, oval	yellow, block	yellow, block
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
cell params	a = 13.878(5) Å	a = 12.771(3) Å	a = 9.851(3) Å
	b = 14.199(5) Å	b = 15.094(3) Å	b = 10.557(3) Å
	c = 27.619(9) Å	c = 20.385(4) Å	c = 37.831(9) Å
	α = 97.97(2)°		
	β = 98.67(2)°	β = 97.16(1)°	β = 95.42(1)°
	γ = 102.12(2)°		
volume (Å^3)	5178(3)	3899(1)	3917(2)
Z	2	4	4
ρ_{calc} (g cm^{-3})	1.550	1.271	1.282
μ(Mo Kα) (mm^{-1})	0.316	0.514	0.513
F(000)	2432	1584	1600
max. and min. transmn factors	1.000−0.903	1.000−0.925	1.000−0.868
θ range for data collection	1.5 to 27.0°	1.6 to 30.0°	2.2 to 30.0°
no. of reflns collected	62 368	54 602	49 626
no. of unique reflns	22 443 (R_{int} = 0.024)	11 215 (R_{int} = 0.020)	10 958 (R_{int} = 0.026)
no. of obsd reflns ($I > 2\sigma_I$)	19 065	9604	10 484
no. of params	1476	416	425
final R1,[a] wR2[b] values ($I > 2\sigma_I$)	0.053, 0.132	0.036, 0.089	0.047, 0.096
Final R1,[a] wR2[b] values (all data)	0.063, 0.140	0.044, 0.098	0.049, 0.097
residual electron density peaks (e Å^{-3})	+1.10/−1.10	+1.21/−1.01	+0.68/−1.63

[a] $R1 = \sum\{[F_o] - [F_c]\}/\sum[F_o]$. [b] $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$.

Scheme 5



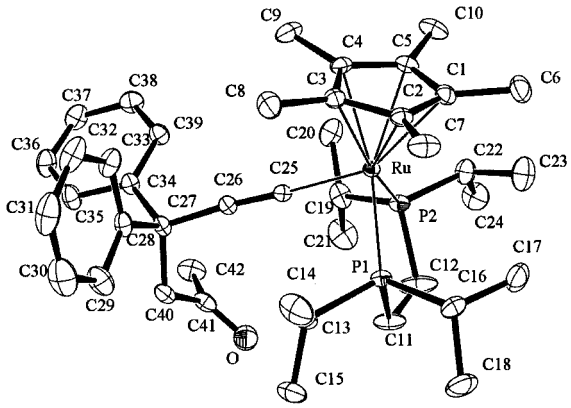


Figure 2. ORTEP drawing (20% thermal ellipsoids) of [Cp*Ru(dippe)(C≡CC(CH$_2$COCH$_3$)Ph$_2$)] (**11**). Hydrogen atoms have been omitted.

neutral functionalized alkynyl compounds have also been obtained. Although complexes **1** and **2** are stable in acetone solution, addition of strong bases (KOH or ^{t}BuOK) yields keto-functionalized alkynyl complexes [Cp*Ru{C≡CCR(CH$_2$COCH$_3$)Ph}(dippe)] (R = H (**10**), Ph (**11**)), which are isolated as yellow solids in good yield. The IR spectra show ν(C≡C) and ν(CO) bands at 2076 and 1714 cm^{-1} for **10** and at 2054 and 1693 cm^{-1} for **11**, respectively. The ^{13}C{^{1}H} NMR spectra show the C=O carbon nucleus at δ 205.1 ppm in both cases and the alkynyl α- and β-carbons in the range δ 114−121 ppm for Cα and δ 105−107 ppm for Cβ. The relation δ(Cα) > δ(Cβ) is opposite of that observed for [CpRu{C≡CC(CH$_2$COCH$_3$)Ph$_2$}(CO)(P^{i}Pr$_3$)][17a] or [Ru(η^5-C$_9$H$_7$){C≡CCH(CH$_2$COR)Ph}(PPh$_3$)$_2$] (R = Ph, ^{i}Pr).[30]

Slow evaporation of the solvent in a Et$_2$O solution of **11** afforded suitable crystals for X-ray diffraction analysis, and its X-ray crystal structure was determined. Selected bond lengths and angles are listed in Tables 2 and 3. An ORTEP[27] view of the complex cation is shown in Figure 2. This compound displays a three-legged piano stool structure. The C(25)−C(26)−C(27) chain shows only a slight deviation from linearity, as inferred from the angles Ru(1)−C(25)−C(26), 173.9(2)°, and C(25)−C(26)−C(27), 173.1(2)°. The Ru−C(25) separation of 2.006(2) Å is similar to Ru−C distances observed in σ-alkynyl complexes of ruthenium such as [Cp*Ru{C≡CC(=CH$_2$)Ph}(dippe)] (1.994(7) Å)[15] or [(η^5-C$_9$H$_7$)Ru{C≡CC(C≡CH)Ph$_2$}(PPh$_3$)$_2$] (1.993(2) Å),[31] corresponding to a single Ru−C bond. The C(25)−C(26) bond distance of 1.215(3) Å is short and characteristic of a carbon−carbon triple bond, whereas the C(26)−C(27) separation of 1.485(3) Å suggests a single bond. All angles around C(27) are consistent with a tetrahedral sp^3 hybridization for this carbon atom.

(30) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; Ienco, A. *Organometallics* **1998**, *17*, 5216.

(31) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López Gonzalez, M. C.; Borge, J.; García Granda, S. *Organometallics* **1997**, *16*, 4453.

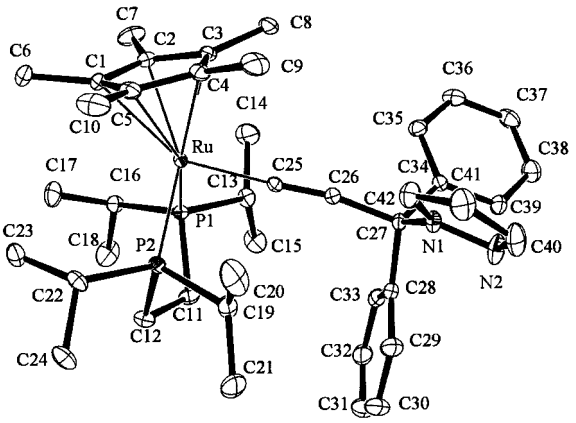


Figure 3. ORTEP drawing (20% thermal ellipsoids) of [Cp*Ru(dippe)(C≡CC($C_3N_2H_3$)Ph_2)] (**13**). Hydrogen atoms have been omitted.

In analogous fashion, complexes [Cp*Ru{C≡CCR-($C_3N_2H_3$)Ph}(dippe)] (R = H (**12**), Ph (**13**)) are readily obtained in good yields by reaction with potassium pyrazolate. Furthermore, complex **12** has also been synthesized by deprotonation of the vinylidene **3**. The most relevant spectroscopic feature is their respective IR ν(C≡C) band at 2072 and 2051 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum, the alkynyl α- and β-carbons appear around δ 127 and 103 ppm, respectively. Again, the relation $\delta(C_\alpha) > \delta(C_\beta)$ for the alkynyl ligand is opposite of what is found for the analogous complex [CpRu{C≡CC($C_3N_2H_3$)Ph_2}(CO)(P^iPr_3)][21] (at δ 100.2 and 107.1 ppm, respectively). Phosphorus nuclei appear in the range δ 87.9−89.5 ppm for all alkynyl complexes.

The X-ray crystal structure of compound **13** was also determined. The molecular structure (Figure 3) shows the typical pseudo-octahedral three-legged piano stool geometry around the ruthenium atom, which is linked to the two phosphorus atoms of the diphosphine ligand in addition to an almost linear alkynyl fragment (Ru(1)−C(25)−C(26) 176.8(2)° and C(25)−C(26)−C(27) 169.9(3)°). The alkynyl chain shows typical Ru(1)−C(25) and C(25)−C(26) bond lengths of 2.004(2) and 1.214(3) Å, comparing well with those observed for complex **11**, although with a distinctly different orientation of the −C(R)Ph_2 moiety. Selected bond lengths and angles are listed in Tables 2 and 3.

Addition of electrophiles to the β-carbon of alkynyl complexes is one versatile entry into vinylidene derivatives.[1] Protonation of **10** and **11** by HBF_4 affords keto-functionalized vinylidene complexes [Cp*Ru{=C=CHCR-(CH_2COCH_3)Ph}][BPh_4] (R = H (**14**), Ph (**15**)). The ^1H NMR spectrum of **14** and **15** shows the vinylidene proton at δ 4.50 and 4.38 ppm, respectively. The vinylidene α-carbon appears at δ 339.2 and 334.7 ppm, and the C=O carbon atom around δ 207 ppm in their respective $^{13}C\{^1H\}$ NMR spectra. Complexes **14** and **15** can be regarded as the result of a formal addition of acetone on the $C_\beta-C_\gamma$ double bond of the former allenylidene. In contrast, protonation of [CpRu{C≡CC(CH_2-$COCH_3$)Ph_2}(CO)(P^iPr_3)] leads to an unsaturated cyclic carbene complex.[17a] As in the case of analogous complexes containing the fragment [Ru(η^5-C_9H_7)(PPh_3)$_2$],[30] an efficient steric protection and the lower electrophilic character of the α-carbon atom may explain the different behavior.

Attempts to obtain the 3-pyrazolylvinylidene derivative by protonation of **13** with HBF_4·Et_2O failed, recovering the initial allenylidene complex and the released pyrazole. It is possible to conclude that the diphenylallenylidene complex **2** is thermodynamically more stable than the functionalized vinylidene, which reverts to allenylidene whenever possible, in this case due to the lability of the C−N bond.

Conclusions

In the present paper we have reported a synthetic strategy for the direct preparation of substituted vinylidene complexes based on the nucleophilic character of the β-carbon in electron-rich allenylidenes such as **1**. This kind of product has already been prepared by a two-step synthesis (nucleophilic addition to γ-carbon plus protonation) when more electrophilic complexes have been used.[17a,30] The proposed mechanism via ruthenium−carbyne intermediates is reasonably consistent with the observed chemical behavior and is strongly supported by the isolation and characterization of such unusual species. Complex **2** does not react with weak nucleophiles, likely because of the low electrophilic character of the γ-carbon. However, it reacts with anionic species, yielding neutral alkynyl complexes, which can be subsequently protonated. In view of these results, it is worth highlighting the potential utility of such electron-rich allenylidene complexes to promote C−C couplings in mildly acid or basic conditions. Furthermore, secondary alcohols can been used to create stereocenters, as described elsewhere.[32]

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere by following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40−60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. Na[$B(Ar_F)_4$] and [$H(Et_2O)_2$][$B(Ar_F)_4$] (Ar_F = 3,5-$(CF_3)_2C_6H_3$) were prepared according to reported procedures.[33] IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were taken on a Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in parts per million from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). NMR data of the [BPh_4]$^-$ or [$B(Ar_F)_4$]$^-$ ions appeared in the appropriate shift and frequency ranges for cationic compounds isolated as their salts and are omitted for clarity. Microanalysis was performed by the Serveis Científico-Tècnics, Universitat of Barcelona.

Preparation of Substituted Vinylidene Complexes [Cp*Ru{=C=CHCH(L)Ph}(dippe)][BPh_4] (L = pyrazolyl (3), 3,5-dimethylpyrazolyl (4), phenylsulfanyl (5)). The allenylidene complex **1** (300 mg, 0.32 mmol) was dissolved in 5 mL of CH_2Cl_2, and then 0.8 mmol of the corresponding reagent was added (54 mg of pyrazole, 77 mg of 3,5-dimethylpyrazole, or 82.1 μL of thiophenol). A slow color change was observed from dark green to orange-brown. The mixture was stirred for 2 h. The solid formed by elimination of the solvent under vacuum was washed with Et_2O and dried. Yield: 310 mg (96%) for **3**, 320 mg (97%) for **4**, and 302 mg (91%) for **5**. Microanalysis and selected spectral data are as follows.

(32) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **2001**, *20*, 3175.
(33) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

3. Anal. Calcd for $C_{60}H_{77}BN_2P_2Ru$: C, 72.1; H, 7.76. Found: C, 72.1; H, 7.75. IR (Nujol): ν(C=C) 1650, ν(BPh_4) 1580 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.87−1.21 (m, 24 H, PCH(CH_3)$_2$), 1.78 (s, 15 H, $C_5(CH_3)_5$), 1.99 and 2.07 (m, 8 H, PC*H* and PCH_2), 4.64 (d, 1 H, $^3J_{HaHb}$ = 10.8 Hz, =C=CH_a−CH_b), 6.08 (d, 1 H, $^3J_{HaHb}$ = 10.8 Hz, =C=CH_a−CH_b), 6.26 (t, 1 H, $^3J_{HH}$ = 2.1 Hz, $C_3H_3N_2$), 7.23 (d, 1 H, $^3J_{HH}$ = 2.1 Hz, $C_3H_3N_2$), 7.16, 7.34 and 7.36 (m, 5 H, C_6H_5), 7.51 (d, 1 H, $^3J_{HH}$ = 2.1 Hz, $C_3H_3N_2$). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 87.5 and 87.3 (d, $^2J_{PP'}$ = 17.0 Hz). $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ 10.99 (s, $C_5(CH_3)_5$), 18.46, 19.40, and 19.95 (m, PCH(CH_3)$_3$), 21.52 (m, PCH_2), 25.34 and 32.49 (m, P*C*H), 58.09 (s, *C*γ), 103.3 (s, $C_5(CH_3)_5$), 106.4, 128.7, and 139.4 (s, $C_3H_3N_2$), 113.2 (s, *C*β), 126.2, 127.1, 129.1, and 139.7 (s, C_6H_5), 335.4 (t, $^2J_{CP}$ = 16.0 Hz, *C*α).

4. Anal. Calcd for $C_{62}H_{81}BN_2P_2Ru$: C, 72.4; H, 7.94. Found: C, 72.4; H, 7.94. IR (Nujol): ν(C=C) 1633, ν(BPh_4) 1580 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.93−1.18 (m, 24 H, PCH(CH_3)$_2$), 1.78 (s, 15 H, $C_5(CH_3)_5$), 1.80−2.19 (m, 8 H, PC*H* and PCH_2), 2.04 and 2.26 (s, 3 H each, $(CH_3)_2$−C_3HN_2), 4.70 (d, 1 H, $^3J_{HaHb}$ = 10.3 Hz, =C=CH_a−CH_b), 5.86 (s, 1 H, $(CH_3)_2$−C_3HN_2), 6.00 (d, 1 H, $^3J_{HaHb}$ = 10.3 Hz, =C=CH_a−CH_b), 7.28−7.36 (m, 5 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 86.9 and 86.5 (d, $^2J_{PP'}$ = 17.0 Hz). $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ 10.75 (s, $C_5(CH_3)_5$), 11.08 and 13.47 (s, $(CH_3)_2$−C_3HN_2), 18.41, 19.34 and 19.87 (m, PCH(CH_3)$_3$), 21.36 (m, PCH_2), 25.42 and 32.22 (m, P*C*H), 55.22 (s, *C*γ), 103.1 (s, $C_5(CH_3)_5$), 106.2, 137.8, and 147.2 (s, $(CH_3)_2$−C_3HN_2), 113.2 (s, *C*β), 125.5, 127.9, 128.9, and 140.7 (s, C_6H_5), 335.8 (t, $^2J_{CP}$ = 15.0 Hz, *C*α).

5. Anal. Calcd for $C_{63}H_{79}BP_2RuS$: C, 72.6; H, 7.64. Found: C, 72.6; H, 7.64. IR (Nujol): ν(C=C) 1632, ν(BPh_4) 1580 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.93−1.03 and 1.08−1.2 (m, 24 H, PCH(CH_3)$_2$), 1.78 (s, 15 H, $C_5(CH_3)_5$), 1.58, 2.03 and 2.17 (m, 8 H, PC*H* and PCH_2), 4.37 (d, 1 H, $^3J_{HaHb}$ = 11.4 Hz, =C=CH_a−CH_b), 4.89 (d, 1 H, $^3J_{HaHb}$ = 11.4 Hz, =C=CH_a−CH_b), 7.18−7.33 (m, 10 H, C_6H_5 and SC_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 87.2 and 87.5 (d, $^2J_{PP'}$ = 17.1 Hz). $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ 10.89 (s, $C_5(CH_3)_5$), 18.31, 18.47, 18.79, 19.21, 19.61, and 19.86 (s, PCH(CH_3)$_3$), 21.30 (m, PCH_2), 25.43 and 32.63 (m, P*C*H), 45.94 (s, *C*γ), 103.0 (s, $C_5(CH_3)_5$), 113.5 (s, *C*β), 126.7, 127.8, 128.5, 128.7, 128.8, 132.6, 134.7, and 141.2 (s, C_6H_5 and SC_6H_5), 335.9 (t, $^2J_{CP}$ = 14.8 Hz, *C*α).

Preparation of Substituted Vinylidene Complexes [Cp*Ru{=C=CHCH(L)Ph}(dippe)][BF_4] (L = 2-pyrrolyl (6), 5-methyl-2-furanyl (7)). The allenylidene complex **1** (300 mg, 0.32 mmol) was dissolved in 5 mL of CH_2Cl_2, and then 0.6 mmol of the corresponding reagent was added (41.6 μL of pyrrole or 54.1 μL of 2-methylfuran). Since no reaction was observed, HBF_4 (ca. 50 μL of a 85% solution of HBF_4·Et_2O) was added. After stirring for 2 h, a gradual color change was observed from dark green to orange-brown. The orange solid formed by elimination of the solvent under vacuum was washed with Et_2O and dried under vacuum. Yield: 223 mg (91%) for **6**, 225 mg (90%) for **7**. Microanalysis and selected spectral data are as follows.

6. Anal. Calcd for $C_{37}H_{58}BF_4NP_2Ru$: C, 58.0; H, 7.63. Found: C, 58.1; H, 7.65. IR (Nujol): ν(NH) 3374, ν(C=C) 1644, ν(BF_4) 1051 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.01−1.11 and 1.16−1.27 (m, 24 H, PCH(CH_3)$_2$), 1.83 (s, 15 H, $C_5(CH_3)_5$), 1.67 (m, 4 H, PC*H*), 2.09 (m, 4 H, PCH_2), 4.72 (d, 1 H, $^3J_{HaHb}$ = 10.8 Hz, =C=CH_a−CH_b), 4.87 (d, 1 H, $^3J_{HaHb}$ = 10.8 Hz, =C=CH_a−CH_b), 5.85 (bs, 1 H, C_4H_3NH), 6.00 (dd, 1 H, $^3J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 5.5 Hz, C_4H_3NH), 6.69 (dd, 1 H, $^3J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 4.2 Hz, C_4H_3NH), 7.16−7.31 (m, 5 H, C_6H_5), 8.77 (bs, 1 H, N*H*). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 87.9 and 86.9 (d, $^2J_{PP'}$ = 19.5 Hz). $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ 10.99 (s, $C_5(CH_3)_5$), 18.46, 19.31, and 20.17 (m, PCH(CH_3)$_3$), 21.23 (m, PCH_2), 25.53 and 32.86 (m, P*C*H), 36.97 (s, *C*γ), 102.6 (s, $C_5(CH_3)_5$), 114.2 (s, *C*β), 104.8, 107.4, 118.3, and 134.6 (s, C_4H_3NH), 126.8, 127.8, 128.6, and 143.7 (s, C_6H_5), 338.8 (t, $^2J_{CP}$ = 16.1 Hz, *C*α).

7. Anal. Calcd for $C_{38}H_{59}BF_4OP_2Ru$: C, 58.4; H, 7.61. Found: C, 58.6; H, 7.63. IR (Nujol): ν(C=C) 1648, ν(BF_4) 1055 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.95, 1.09, 1.15, and 1.26 (m, 24 H, PCH(CH_3)$_2$), 1.88 (s, 15 H, $C_5(CH_3)_5$), 1.92 and 2.04 (m, 4 H, PC*H*), 2.13 and 2.28 (m, 4 H, PCH_2), 2.23 (s, 3 H, CH_3−C_4H_2O), 4.45 (d, 1 H, $^3J_{HaHb}$ = 10.9 Hz, =C=CH_a−CH_b), 4.76 (d, 1 H, $^3J_{HaHb}$ = 10.9 Hz, =C=CH_a−CH_b), 5.67 (d, 1 H, $^3J_{HH}$ = 3.2 Hz, CH_3−C_4H_2O), 5.83 (d, 1 H, $^3J_{HH}$ = 3.2 Hz, CH_3−C_4H_2O), 7.16−7.35 (m, 5 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 87.7 and 88.0 (d, $^2J_{PP'}$ = 18.7 Hz). $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ 10.99 (s, $C_5(CH_3)_5$), 13.57 (s, *C*H_3−C_4H_2O), 18.26, 18.55, 19.16, 19.58, and 19.99 (m, PCH(CH_3)$_3$), 21.41 (m, PCH_2), 25.64 and 32.66 (m, P*C*H), 37.39 (s, *C*γ), 103.0 (t, $^2J_{CP}$ = 1.6 Hz, $C_5(CH_3)_5$), 106.2, 106.9, 151.5, and 155.1 (s, CH_3-C_4H_2O), 113.6 (s, *C*β), 127.1, 127.4, 128.8, and 141.4 (s, C_6H_5), 337.3 (t, $^2J_{CP}$ = 14.7 Hz, *C*α).

Preparation of Dicationic Carbyne Complexes [Cp*Ru(≡C−CH=CRPh)(dippe)][$B(Ar_F)_4$]$_2$ (R = H (8), Ph (9)). A 0.25 g (0.47 mmol) sample of [Cp*RuCl(dippe)][34] and 0.50 g (0.57 mmol) of Na[$B(Ar_F)_4$] were dissolved in 10 mL of fluorobenzene. A slight excess of the corresponding alkynol (0.70 mmol) was added, and the mixture was allowed to stir for 3 h. The solution was filtered through Celite to eliminate the suspension of NaCl and passed through a Al_2O_3 column (acidic, activity grade I, height of column 10 cm) to achieve a complete dehydration. Elimination of the solvent under vacuum yielded the corresponding allenylidene complex as a $[B(Ar_F)_4]^-$ salt. Protonation was carried out in an ethanol/liquid N_2 bath, by adding an excess of freshly prepared $[H(OEt_2)_2][B(Ar_F)_4]$ (0.51 mg, 0.50 mmol) to fluorobenzene solutions of the mentioned allenylidene complexes. The resulting solution was allowed to warm to room temperature. Afterward, the solvent was removed under vacuum and the residue washed with petroleum ether, yielding a dark red solid almost quantitatively. Recrystallization of **9** from Et_2O/petroleum ether yielded dark red crystals suitable for X-ray structural analysis. Yield (related to [Cp*RuCl(dippe)]): 869 mg (79%) for **8**, 977 mg (86%) for **9**. Microanalysis and selected spectral data are as follows.

8. Anal. Calcd for $C_{97}H_{78}B_2F_{48}P_2Ru$ C, 49.8; H, 3.36. Found: C, 49.9; H, 3.36. IR (Nujol): ν(Ar_F) 1789, 1610, and 1115, ν(Ph) 1576 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.07 and 1.36 (m, 24 H, PCH(CH_3)$_2$), 2.01 (t, 15 H, $^3J_{HH}$ = 1.3 Hz, $C_5(CH_3)_5$), 2.27 (m, 4 H, PCH_2), 2.37 and 2.56 (m, 4 H, PC*H*), 6.53 (d, 1 H, $^3J_{HH}$ = 16.0 Hz, C*H*=CHPh), 7.53 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_5), 7.69 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, *o*-C_6H_5), 7.86 (t, 1 H, $^3J_{HH}$ = 7.5 Hz, *p*-C_6H_5), 8.11 (d, 1 H, $^3J_{HH}$ = 16.0 Hz, CH=C*H*Ph). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 298 K): δ 88.8 (s). $^{13}C\{^1H\}$ NMR (50.29 MHz, CD_2Cl_2, 298 K): δ 11.60 (s, $C_5(CH_3)_5$), 18.34, 19.07, 19.76 and 20.23 (s, PCH(*C*H_3)$_3$), 23.31 (m, PCH_2), 25.76 and 33.17 (m, P*C*H), 110.1 (s, $C_5(CH_3)_5$), 129.5, 131.2, 132.5, and 133.3 (s, C_6H_5), 141.0 (s, *C*β) 167.9 (s, *C*γ), 332.4 (t, $^2J_{CP}$ = 13.1 Hz, *C*α).

9. Anal. Calcd for $C_{103}H_{82}B_2F_{48}P_2Ru$ C, 51.2; H, 3.42. Found: C, 51.2; H, 3.42. IR (Nujol): ν(Ar_F) 1789, 1608, and 1115, ν(Ph) 1591 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.07, 1.21, and 1.35 (m, 24 H, PCH(CH_3)$_2$), 1.84 and 2.04 (m, 4 H, PCH_2), 2.07 (s, 15 H, $C_5(CH_3)_5$), 2.18 and 2.37 (m, 4 H, PC*H*), 6.31 (s, 1 H, C*H*=CPh$_2$), 7.28 and 7.41 (both d, 1 H each, $^3J_{HH}$ = 7.5 Hz, *o*-C_6H_5), 7.53 and 7.67 (both t, 2 H each, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_5), 7.82 and 7.87 (both t, 1 H each, $^3J_{HH}$ = 7.5 Hz, *p*-C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 298 K): δ 83.1 (s). $^{13}C\{^1H\}$ NMR (50.29 MHz, CD_2Cl_2, 298 K): δ 11.59 (s, $C_5(CH_3)_5$), 18.36, 19.22, 19.86, and 20.18 (s, PCH(*C*H_3)$_3$), 24.39 (m, PCH_2), 25.72 and 35.43 (m, P*C*H), 109.8 (t, $^2J_{CP}$ = 2.0 Hz, $C_5(CH_3)_5$), 130.4, 130.6, 131.7, 132.5, 135.5, 136.7, and

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138.4 (s, C_6H_5), 138.3 (s, $C\beta$), 180.1 (s, $C\gamma$), 327.5 (t, $^2J_{CP}$ = 12.5 Hz, $C\alpha$).

Preparation of Substituted Alkynyl Complexes [Cp*Ru{C≡CCR(L)Ph}(dippe)] (L = CH_3COCH_2, R = H (10), R = Ph (11); L = pyrazolyl, R = H (12); R = Ph (13)). The allenylidene complex **1** (300 mg, 0.32 mmol) or **2** (302 mg, 0.30 mmol) was dissolved in 5 mL of THF, and then a suspension of KOH (50 mg, 85%, 0.76 mmol) in 2 mL of acetone was added. The mixture was stirred for 1 h, the solvent removed in vacuo, and the residue extracted with 2 × 5 mL of petroleum ether. The resulting yellow solution was filtered through Celite, and a yellow solid was obtained after removing the solvent under vacuum. Yield: 200 mg (93%) for **10**, 199 mg (89%) for **11**. Microanalysis and selected spectral data are as follows.

10. Anal. Calcd for $C_{36}H_{58}OP_2Ru$: C, 64.6; H, 8.73. Found: C, 64.6; H, 8.71. IR (Nujol): ν(C≡C) 2076, ν(CO) 1714, ν(Ph) 1598.4 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.87−1.24 (m, 27 H, PCH(CH_3)$_2$ and CH_2COCH_3), 1.42 (m, 4 H, PCH_2), 1.83 (s, 15 H, $C_5(CH_3)_5$), 2.57 (dd, 1 H, $^2J_{HbHc}$ = 15.3 Hz, $^3J_{HaHb}$ = 6.0 Hz, −C≡CCH$_a$(Ph)CH$_b$H$_c$−), 2.89 (dd, 1 H, $^2J_{HbHc}$ = 15.3 Hz, $^3J_{HaHc}$ = 9.4 Hz, −C≡CCH$_a$(Ph)CH$_b$H$_c$−), 2.93 (m, 4 H, PC*H*), 4.47 (t, 1 H, $^3J_{HaHb}$ = $^3J_{HaHc}$ = 7.7 Hz, −C≡CC*H*$_a$(Ph)-CH$_b$H$_c$−), 7.07 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, *p*-C_6H_5), 7.21 (t, 2 H, $^3J_{HH}$ = 7.7 Hz, *m*-C_6H_5), 7.45 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, *o*-C_6H_5). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 89.5 and 89.2 (d, $^2J_{PP'}$ = 24.4 Hz). ^{13}C{^{1}H} NMR (50.29 MHz, C_6D_6, 298 K): δ 11.56 (s, $C_5(CH_3)_5$), 19.00, 19.21, 19.62, and 21.42 (s, PCH-(CH_3)$_3$), 21.32 (m, PCH_2), 25.20 and 28.21 (m, PCH), 29.99 (s, CH_2COCH_3), 37.80 (s, $C\gamma$), 54.02 (s, CH_2COCH_3), 91.21 (t, $^2J_{CP}$ = 2.1 Hz, $C_5(CH_3)_5$), 105.4 (t, $^3J_{CP}$ = 1.1 Hz, $C\beta$), 113.9 (t, $^2J_{CP}$ = 23.0 Hz, $C\alpha$), 125.9, 127.9, 128.2, and 146.4 (s, C_6H_5), 205.1 (s, CH_2COCH_3).

11. Anal. Calcd for $C_{42}H_{62}OP_2Ru$: C, 67.6; H, 8.38. Found: C, 67.6; H, 8.35. IR (Nujol): ν(C≡C) 2054, ν(CO) 1693, ν(Ph) 1594 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.83, 0.99, 1.08 and 1.18 (m, 24 H, PCH(CH_3)$_2$), 1.54 (s, 3 H, CH_2COCH_3), 1.76 (s, 15 H, $C_5(CH_3)_5$), 1.86 (m, 4 H, PCH_2), 3.14 (m, 4 H, PC*H*), 3.32 (s, 2 H, CH_2COCH_3), 7.00 (t, 2 H, $^3J_{HH}$ = 7.2, *p*-C_6H_5), 7.12 (t, 4 H, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_5), 7.52 (m, 4 H, $^3J_{HH}$ = 7.2 Hz, *o*-C_6H_5). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 88.5 (s). ^{13}C{^{1}H} NMR (50.29 MHz, C_6D_6, 298 K): δ 11.64 (s, $C_5(CH_3)_5$), 18.75, 19.54, 19.65, and 21.60 (s, PCH(CH_3)$_3$), 20.77 (m, PCH_2), 24.99 and 27.98 (m, PCH), 31.00 (s, CH_2-$COCH_3$), 49.45 (s, $C\gamma$), 57.43 (s, CH_2COCH_3), 91.28 (t, $^2J_{CP}$ = 2.2 Hz, $C_5(CH_3)_5$), 107.0 (t, $^3J_{CP}$ = 1.0 Hz, $C\beta$), 121.0 (t, $^2J_{CP}$ = 21.8 Hz, $C\alpha$), 125.7, 127.7, 128.5, and 149.7 (s, C_6H_5), 205.1 (s, CH_2COCH_3).

12. The vinylidene complex **3** (300 mg, 0.30 mmol) was dissolved in 5 mL of THF, and then an excess of potassium *tert*-butoxide was added (172 mg, 95%, 1.5 mmol). A yellow precipitate was immediately formed. The solvent was removed under vacuum and the residue extracted with 2 × 5 mL of petroleum ether. The resulting yellow solution was filtered through Celite, and a yellow solid was obtained after removing the solvent under vacuum. Yield: 190 mg (93%). It should be noted that complex **12** can also be synthesized directly from the allenylidene **1** in a similar fashion, as will be described for **13**. Microanalysis and selected spectral data are as follows.

Anal. Calcd for $C_{36}H_{56}N_2P_2Ru$: C, 63.6; H, 8.30. Found: C, 63.7; H, 8.28. IR (Nujol): ν(C≡C) 2072, ν(C=C) 1599 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.82, 0.95, 1.06, and 1.19 (m, 24 H, PCH(CH_3)$_2$), 1.32 (m, 4 H, PCH_2), 1.77 (s, 15 H, C_5-(CH_3)$_5$), 2.83 (m, 4 H, PC*H*), 6.25 (t, 1 H, $^3J_{HH}$ = 2.1 Hz, $C_3H_3N_2$), 6.72 (s, 1 H, C≡C−C*H*−), 7.02 (t, 1 H, $^3J_{HH}$ = 7.2 Hz, *p*-C_6H_5), 7.14 (t, 2 H, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_5), 7.47 (d, 2 H, $^3J_{HH}$ = 7.2 Hz, *o*-C_6H_5), 7.62 (d, 1 H, $^3J_{HH}$ = 2.1 Hz, $C_3H_3N_2$), 8.17 (d, 1 H, $^3J_{HH}$ = 2.1 Hz, $C_3H_3N_2$). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 89.0 (s). ^{13}C{^{1}H} NMR (50.29 MHz, C_6D_6, 298 K): δ 11.63 (s, $C_5(CH_3)_5$), 19.07, 19.28, 19.65, and 21.84 (s, PCH(CH_3)$_3$), 21.94 (vt, $^{1,2}J_{CP}$ = 17.6 Hz, PCH_2), 25.40 and 28.41 (m, PCH), 61.74 (s, $C\gamma$), 91.72 (t, $^2J_{CP}$ = 2.3 Hz, $C_5(CH_3)_5$), 101.3 (t, $^3J_{CP}$ = 1.1 Hz, $C\beta$), 104.5, 127.2, and 138.9 (s, $C_3H_3N_2$), 126.8 (t, $^2J_{CP}$ = 21.9 Hz, $C\alpha$), 126.9, 127.2, 128.2, and 143.9 (s, C_6H_5).

13. The allenylidene complex **2** (302 mg, 0.30 mmol) was dissolved in 5 mL of THF together with an excess of pyrazole (54 mg, 0.80 mmol). After potassium *tert*-butoxide was added (168 mg, 95%, 1.5 mmol) a pale yellow precipitate was immediately formed. The solvent was removed under vacuum and the residue extracted with petroleum ether. The resulting yellow solution was filtered through Celite, and a yellow solid was obtained after removing the solvent under vacuum. Yield: 185 mg (82%). Microanalysis and selected spectral data are as follows.

Anal. Calcd for $C_{42}H_{60}N_2P_2Ru$: C, 66.7; H, 8.00. Found: C, 66.8; H, 7.99. IR (Nujol): ν(C≡C) 2051, ν(Ph) 1595. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.81, 0.93 and 1.14 (m, 24 H, PCH-(CH_3)$_2$), 1.82 (m, 4 H, PCH_2), 1.77 (s, 15 H, $C_5(CH_3)_5$), 3.05 (m, 4 H, PC*H*), 6.20 (t, 1 H, $^3J_{HH}$ = 2.3 Hz, $C_3H_3N_2$), 7.03 (t, 2 H, $^3J_{HH}$ = 7.2 Hz, *p*-C_6H_5), 7.12 (t, 4 H, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_5), 7.65 (m, 5 H, *o*-C_6H_5 and $C_3H_3N_2$), 8.55 (d, 1 H, $^3J_{HH}$ = 2.3 Hz, $C_3H_3N_2$). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 87.9 (s). ^{13}C{^{1}H} NMR (50.29 MHz, C_6D_6, 298 K): δ 11.66 (s, $C_5(CH_3)_5$), 18.67, 19.42 and 21.43 (s, PCH(CH_3)$_3$), 20.73 (m, PCH_2), 25.00 and 27.87 (m, PCH), 72.29 (s, $C\gamma$), 91.68 (t, $^2J_{CP}$ = 2.1 Hz, C_5-(CH_3)$_5$), 103.5, 130.5, and 139.4 (s, $C_3H_3N_2$), 105.5 (t, $^3J_{CP}$ = 1.0 Hz, $C\beta$), 128.4 (t, $^2J_{CP}$ = 21.8 Hz, $C\alpha$), 126.7, 127.4, 129.3, and 147.2 (s, C_6H_5).

Preparation of Keto-Functionalized Vinylidene Complexes [Cp*Ru{=C=CHCR(CH_2COCH_3)Ph}(dippe)][BF_4] (R = H (14), Ph (15)). A 0.24 mmol sample of the corresponding neutral alkynyl complex (160 mg of **10**, or 178 mg of **11**) were dissolved in 5 mL of Et_2O. The solution was cooled in an ethanol/liquid N_2 bath and treated with some drops of HBF_4 (85% solution of HBF_4·Et_2O). Once removed from the bath, the red suspension was allowed to warm to room temperature. The solvent was then removed under vacuum and the residue extracted with CH_2Cl_2. After filtration through Celite, a brown solid was obtained by elimination of the solvent under vacuum, which was washed with 2 × 5 mL of Et_2O and dried. Yield: 150 mg (83%) for **14**, 180 mg (90%) for **15**. Microanalysis and selected spectral data are as follows.

14. Anal. Calcd for $C_{36}H_{59}BF_4OP_2Ru$: C, 57.1; H, 7.85. Found: C, 57.0; H, 7.84. IR (Nujol): ν(CO) 1714, ν(C=C) 1644 cm^{-1}, ν(BF_4) 1051 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3, 298 K): δ 1.04−1.39 (m, 24 H, PCH(CH_3)$_2$), 1.83 (s, 15 H, $C_5(CH_3)_5$), 2.01 (s, 3 H, CH_2COCH_3), 2.21 and 2.42 (m, 8 H, PC*H* and PCH_2), 2.78 and 2.86 (both dd, 1 H each, $^2J_{HcHd}$ = 16.4 Hz, $^3J_{HbHc}$ = $^3J_{HbHd}$ = 7.0 Hz, =CH$_b$(Ph)C*H*$_c$*H*$_d$−), 4.18 (dt, 1 H, $^3J_{HaHb}$ = 10.9 Hz, $^3J_{HbHc}$ = $^3J_{HbHd}$ = 7.0 Hz, =CH$_a$C*H*$_b$(Ph)-CH$_c$H$_d$−), 4.50 (d, 1 H, $^3J_{HaHb}$ = 10.9 Hz, =C*H*$_a$CH$_b$−), 7.19 and 7.31 (m, 5 H, C_6H_5). ^{31}P{^{1}H} NMR (161.89 MHz, CD_3-$COCD_3$, 298 K): δ 87.1 and 88.6 (d, $^2J_{PP'}$ = 19.6 Hz). ^{13}C{^{1}H} NMR (50.29 MHz, CD_3COCD_3, 298 K): δ 11.04 (s, $C_5(CH_3)_5$), 18.87, 19.58, 19.89, and 20.53 (m, PCH(CH_3)$_3$), 21.95 (m, PCH_2), 26.25 and 33.73 (m, PCH), 30.83 (s, CH_2COCH_3), 34.73 (s, $C\gamma$), 52.76 (s, CH_2COCH_3), 103.3 (t, $^2J_{CP}$ = 1.6 Hz, $C_5(CH_3)_5$), 115.2 (t, $^3J_{CP}$ = 1.6 Hz, $C\beta$), 127.4, 127.8, 129.4, and 146.4 (s, C_6H_5), 206.7 (s, CH_2COCH_3), 339.2 (t, $^2J_{CP}$ = 15.1 Hz, $C\alpha$).

15. Anal. Calcd for $C_{42}H_{63}BF_4OP_2Ru$: C, 60.5; H, 7.62. Found: C, 60.5; H, 7.61. IR (Nujol): ν(CO) 1715, ν(C=C) 1633 cm^{-1}, ν(BF_4) 1051 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.95−1.00 and 1.12−1.20 (m, 24 H, PCH(CH_3)$_2$), 1.64 (s, 3 H, CH_2COCH_3), 1.78 (s, 15 H, $C_5(CH_3)_5$), 1.84 and 1.97 (m, 8 H, PC*H* and PCH_2), 3.24 (s, 2 H, CH_2COCH_3), 4.38 (s, 1 H, =C=C*H*−), 7.16 and 7.28 (m, 10 H, C_6H_5). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 83.1 (s). ^{13}C{^{1}H} NMR (50.29 MHz, $CDCl_3$, 298 K): δ 11.13 (s, $C_5(CH_3)_5$), 18.58, 19.66, and 20.36 (m, PCH(CH_3)$_3$), 21.81 (m, PCH_2), 25.50 and 33.66 (m, PCH), 32.24 (s, CH_2COCH_3), 48.57 (s, $C\gamma$), 55.00 (s, CH_2COCH_3),

102.4 (t, $^2J_{CP}$ = 1.5 Hz, $C_5(CH_3)_5$), 115.3 (s, *Cβ*), 127.0, 127.1, 128.5, and 138.6 (s, C_6H_5), 207.2 (s, CH_2COCH_3), 334.7 (t, $^2J_{CP}$ = 14.5 Hz, *C*α).

X-ray Structure Determinations. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, 0.3° *ω*-scan frames covering complete spheres of the reciprocal space). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. All structures were solved by direct methods using the program SHELXS97.[35] Structure refinement on F^2 was carried out with program SHELXL97.[36] All non-hydrogen atoms were anisotropically refined for compounds **11** and **13**. In the case of compound **9** most of non-hydrogen atoms were also anisotropically refined. But in both $B(Ar_F)_4$ anions some CF_3 groups showed the well-known orientation disorder (ca. 60° rotation about $C-CF_3$ bond axes, 7 out of 16 independent groups) and were refined with split F positions and anisotropic displacement parameters for predominately occupied F sites, whereas for subordinately occupied F sites a single isotropic displacement parameter was used. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Salient crystal and refinement data are summarized in Table 3; further details are given in the Supporting Information.

(35) Sheldrick, G. M. *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen, 1997.

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Supporting Information Available: Tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **9**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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