Activation of Alkynols by [Cp*RuCl(PEt_3)$_2$]: New Intermediates and Alternative Dehydration Products. X-ray Crystal Structures of [Cp*Ru{=C=CHC(=CH_2)Ph}(PEt_3)$_2$][BPh_4], [Cp*Ru(=C=C=CPh_2)(PEt_3)$_2$][BPh_4], and [Cp*Ru{C≡CC(PEt_3)Me_2}(PEt_3)$_2$][BPh_4]

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The full sequence of species involved in the activation of alkynols by the fragment [Cp*Ru(PEt_3)$_2$]$^+$ was determined. The complex [Cp*RuCl(PEt_3)$_2$] (Cp* = C_5Me_5) reacts with 2-propyn-1-ol derivatives in the presence of $NaBPh_4$, yielding the metastable 3-hydroxyalkynyl hydrido complexes [Cp*Ru(H){C≡CC(OH)RR′}(PEt_3)$_2$][BPh_4], intermediates in the formation of the corresponding 3-hydroxyvinylidene complexes [Cp*Ru{=C=CHC(OH)RR′}(PEt_3)$_2$][BPh_4], to which these compounds rearrange both in solution and in the solid state. η^2-Alkynol derivatives have been detected by $^{31}P\{^1H\}$ NMR at −40 °C as the first species involved in the reaction of alkynols with [Cp*Ru(N_2)(PEt_3)$_2$][BPh_4]. Dehydration of 3-hydroxyalkynyl hydrido and 3-hydroxyvinylidene complexes may be spontaneous or forced, leading to vinylvinylidene, allenylidene, or the novel enynyl hydrido species. The unstable allenylidene led to the formation of an alkynylphosphonio compound without an external source of phosphine.

Introduction

It is reasonably well-established now that the reaction of propargyl alcohols HC≡CC(OH)R_2 with ruthenium complexes, which was reported for the first time by Selegue,[1] represents a simple and convenient route for the preparation of allenylidene complexes. These species, due to the unsaturated character of the carbon chain, exhibit unusual behavior, giving rise to a variety of C−C coupling reactions and yielding in many cases unexpected products.[2] So far, allenylidenes have been obtained and studied with several substrate complexes, and their synthesis has been extended to metals such as the Cr triad, Mn, Fe, Os, Ir, and Rh,[3] in addition to ruthenium allenylidenes, which constitute the largest group. At the moment, the reactivity and catalytic activity are centers of current scientific interest.[4]

Since the beginning, the dehydration of a hydroxyvinylidene intermediate has been proposed as the reasonable previous step to allenylidene.[1,5] These species have been isolated, both as complexes that cannot be dehydrated into allenylidene derivatives,[6] or as intermediates sufficiently stable toward dehydration.[7] The fact that the dehydration may take two different reaction pathways when deprotonatable groups are adjacent to the carbon bearing the hydroxy group has become in some cases a synthetic limitation in the preparation of allenylidenes, yielding mixtures with the alkenylvinylidene complex as side product.[6c,8] However, there has been increasing interest in a clean synthesis of alkenylvinylidene derivatives; these have not been frequently isolated and characterized[8,9] and have a less

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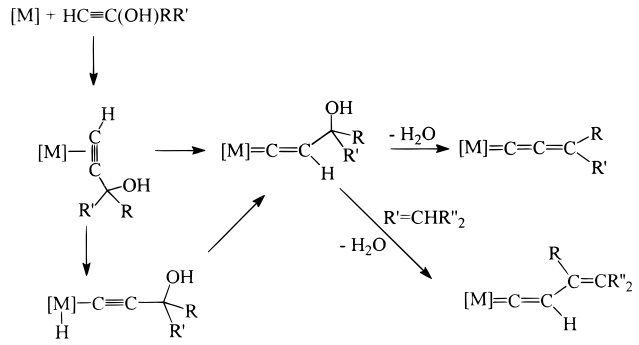
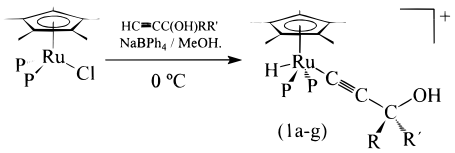
developed chemistry, despite the fact that they seem to be active species involved in some C−C coupling processes.[7b,10]



The way to hydroxyvinylidene species implicates C≡C bond coordination as the initial step in the activation of propargyl alcohols, followed by a subsequent tautomerization.[7a] Although an isomerization via a 1,2-H shift from η^2-alkyne into vinylidene seems to be the most feasible explanation for the tautomerization process,[11] there is another way that has been proven to be accessible by the $[Cp^*Ru(dippe)]^+$ system. On the basis of the ability of Cp* to stabilize Ru(IV) complexes,[12] it goes via oxidative addition of the alkyne, yielding metastable alkynyl hydrido compounds, the tautomerization process of which to vinylidene was studied in depth.[13] In the case of alkynols, the interaction with $[OsCl(NO)(P^iPr_2R)_2]$ (R = Ph, ^{i}Pr) afforded stable (3-hydroxyalkynyl)hydridoosmium(II) complexes.[14] Likewise, the reactions of $[RhCl(P^iPr_3)_2]$ and $[IrH_2Cl(P^iPr_3)_2]$ with alkynols led to the formation of either (η^2-alkynol)- or (3-hydroxyalkynyl)hydridorhodium and (3-hydroxyalkynyl)hydridoiridium complexes, respectively, as the first isolable products,[15] but until now, there has not been evidence for analogous ruthenium species.

η^2 coordination of alkynols has been observed in some osmium complexes such as $[CpOsCl\{\eta^2\text{-}HC{\equiv}CC(OH)RR'\}(P^iPr_3)]$ (R, R′= Me, C_5H_{10}, Ph) previous to the formation of the alkenylvinylidene or allenylidene derivative,[16] as well as in the complex $[CpOs\{\kappa^1\text{-}OC(O)CH_3\}\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(P^iPr_3)]$.[17] In the $[CpRu(dippe)]^+$ and $[CpRu(PMe_3)_2]^+$ systems the η^2 coordination of monosubstituted alkynes[13b,18] is well-known, but such is not the case for $[Cp^*Ru(dippe)]^+$: although the use of a Cp*Ru system containing this large, strong electron-releasing phosphine seems to be the key for the isolation of these Ru(IV) species, due to its electronic and steric properties, it is also true that steric hindrance should make more difficult the detection of the η^2-alkynol precursor which would be the first step in the overall activation of alkynols. Despite this, we now show the results of the activation of alkynols by the fragment $[Cp^*Ru(PEt_3)_2]^+$, which has allowed us to complete the full sequence of the aforementioned intermediates: η^2-alkynol, 3-hydroxyalkynyl hydrido, and 3-hydroxyvinylidene.[19] Alkenylvinylidene and allenylidene have been obtained separately as dehydration products, but this system makes also possible the novel synthesis of hydrido enynyl complexes by carrying out the dehydration before isomerization of the 3-hydroxyalkynyl hydrido derivative. An unexpected nucleophilic phosphine addition on an allenylidene moiety without an external source of phosphine is reported as well.

Scheme 1. Synthesis of 3-Hydroxyalkynyl Hydride Complexes



Results and Discussion

As we reported in a recent communication,[19] when $[Cp^*RuCl(PEt_3)_2]$[12b] is added to a MeOH solution containing $NaBPh_4$ and an alkynol HC≡CC(OH)RR′ at 0 °C, the 3-hydroxyalkynyl hydrido complexes $[Cp^*RuH\{C{\equiv}CC(OH)RR'\}(PEt_3)_2][BPh_4]$ (R,R′ = H, H (**1a**); H, Me (**1b**); H, Ph (**1c**); Me, Ph (**1d**); Ph, Ph (**1e**); Me, Me (**1f**); C_5H_{10} (**1g**)) precipitate immediately as white-yellow solids. (Scheme 1) If the order in which the reagents are mixed is reversed, the reaction is not so clean, and mixtures of products of different natures are obtained depending upon the alkynol used. Complexes **1a**−**g** are derived from the formal insertion of the metal atom into the C−H bond of the alkynol, and hence, they must be regarded as Ru^{IV} species. These compounds rearrange irreversibly both in solution and in the solid state to the corresponding 3-hydroxyvinylidene isomers; therefore, they must be handled and stored at temperatures close to 0 °C in order to prevent isomerization. This behavior is analogous to that previously observed in the course of the reaction of $[Cp^*RuCl(dippe)]$ with 1-alkynes,[13b] which also led to the isolation of metastable Ru^{IV} hydrido−alkynyl derivatives which rearrange to their vinylidene tautomers. In this case, so far, a similar behavior toward alkynols has not been observed.[7b] The

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Table 1. Selected IR and ^{1}H and ^{31}P{^{1}H} NMR Data for [Cp*RuH{C≡CC(OH)RR′}(PEt$_3$)$_2$][BPh$_4$]

		IR (Nujol, cm^{-1})[a]	^{31}P{^{1}H} NMR[b]		^{1}H NMR[c]					
	R, R′	OH, C≡C, Ru−H		$^2J_{PP'}$	Ru−H	$^2J_{HP}$	C_5Me_5	$^4J_{HP}$	R	R′
1a	H, H	n.o., 2117, 2024	36.8 s		−9.25 t	30.5	1.67 t	1.2	4.29 t	
1b	H, Me	3528, 2109, 2074	36.6 s		−9.37 t	29.8	1.67 t	1.1	4.53 sa	1.38 d (6.4 Hz)
1c	H, Ph	n.o., 2108, 2018	37.1, 37.2, d	20.1	−9.36 t	29.9	1.63 t	1.4	5.46 sa	7.30, 7.36, 7.37
1d	Me, Ph	3312, 2104, 2020	37.4, 37.2, d	21.3	−9.35 t	29.9	1.65 t	1.2	1.82 s	7.29, 7.37, 7.55
1e	Ph, Ph	3450, 2103, 2026	38.0 s		−9.39 t	29.8	1.67 t	1.0		7.29, 7.33, 7.50
1f	Me, Me	3353, 2120, 2028	36.8 s		−9.28 t	30.6	1.66 t	1.2	1.46 s	
1g	C_5H_{10}	3331, 2105, 2029	37.2 s		−9.31 t	30.2	1.67 t	1.1	1.45 m	1.58 m

[a] n.o. = not observed. [b] Conditions: 161.89 MHz, $CDCl_3$, 273 K. Resonances are given in ppm, and coupling constants are given in Hz. [c] Conditions: 400 MHz, $CDCl_3$, 273 K. Resonances are given in ppm, and coupling constants are given in Hz.

Table 2. Selected ^{13}C{^{1}H} NMR Data for [Cp*RuH{C≡CC(OH)RR′}(PEt$_3$)$_2$][BPh$_4$]

		^{13}C{^{1}H} NMR[a]							
	R, R′	C_5Me_5	C_5Me_5	C_α	$^2J_{CP}$	C_β	C_γ	R	R′
1a	H, H	10.11	101.4	91.4 t	30.1	112.9	53.1		
1b	H, Me	10.14	101.4	89.6 t	30.1	116.9	59.9		25.8
1c	H, Ph	10.04	101.4	94.6 t	31.2	114.7	66.1		127.7, 128.4, 128.7, 142.8
1d	Me, Ph	10.08	101.3	91.2 t	30.2	118.2	58.3	32.3	124.3, 127.1, 128.1, 146.4
1e	Ph, Ph	10.15	101.5	97.1 t	29.5	115.9	50.7		126.1, 127.4, 128.0, 145.9
1f	Me, Me	10.09	101.3	87.1 t	30.2	119.3	66.2	32.3	
1g	C_5H_{10}	10.15	101.3	88.0 t	31.0	119.0	68.9		22.3, 25.1, 40.4

[a] Conditions: 201.12 MHz, $CDCl_3$, 273 K. Resonances are given in ppm, and coupling constants are given in Hz.

Table 3. Selected IR and ^{1}H and ^{31}P{^{1}H} NMR Data for [Cp*Ru{=C=CH$_a$CH$_b$(OH$_c$)R}-(PEt$_3$)$_2$][BPh$_4$]

		IR[a]	^{31}P{^{1}H} NMR[b]		^{1}H NMR[c]						
	R, R′	OH, C=C		$^2J_{PP'}$	C_5Me_5	$^4J_{HP}$	H^a	$^4J_{HP}$	$^3J_{H^aH^b}$	R	R′
2a	H, H	3459, 1679	30.6 s		1.74 t	1.8	4.21 tt	1.6	8.4	4.05 dd, $^3J_{HbOH}$ = 5.4	
2b	H, Me	3444, 1643	30.6, 31.0, d	35.9	1.73 t	1.0	4.12 dt	1.6	8.4	4.56 dc, $^3J_{HbMe}$ = 6.2	1.27 d
2c	H, Ph	3592, 1631	30.5, 30.8, d	34.5	1.71 t	1.1	4.39 dt	1.4	8.4	5.45 dd, $^3J_{HbOH}$ = 3.6	7.29, 7.31, 7.34
2d	Me, Ph	3598, 1633	28.9, 29.1, d	35.5	1.71 t	1.1	4.38 sa			1.63 s	7.28, 7.34, 7.36
2e	Ph, Ph	3576, 1634	29.3 s		1.72 t	1.0	4.73 sa			7.30, 7.35, 7.62	
2f	Me, Me	3543, 1643	28.9 s		1.75 t	1.3	4.05 sa			1.37 s	
2g	C_5H_{10}	3573, 1651	29.1 s		1.76 t	1.1	4.08 sa			1.44−1.57 m	1.84−1.95 m

[a] As Nujol mulls, in cm^{-1}. [b] Conditions: 161.89 MHz, $CDCl_3$, 273 K. Resonances are given in ppm, and coupling constants are given in Hz. [c] Conditions: 400 MHz, $CDCl_3$, 273 K. Resonances are given in ppm, and coupling constants are given in Hz.

spectral properties of compounds **1a**−**g** resemble those of the [Cp*RuH(C≡CR)(dippe)][BPh$_4$] to a great extent. IR and NMR spectral data are displayed in Tables 1 and 2. Thus, they exhibit in their IR spectra one strong ν(C≡C) band at 2100−2120 cm^{-1} and a weak ν(RuH) absorption at 2020−2030 cm^{-1}, besides a ν(OH) band about 3350 cm^{-1}. The hydride resonance appears as one high-field triplet in all cases, whereas the ^{31}P{^{1}H} NMR spectra consist of one sharp singlet, except for the complexes **1b**−**d**, for which two partially overlapped doublet signals ($^2J_{PP'} \cong$ 20 Hz) corresponding to an AB spin system are observed. This is attributed to the presence of the chiral γ-carbon atom in the alkynyl group, which induces the magnetic nonequivalence of the phosphorus atoms, as has been previously noted.[2d] It was possible to register the ^{13}C{^{1}H} NMR spectra of compounds **1a**−**g** at 0 °C (Table 2). The most relevant feature of these spectra is the resonance of the metal-bound carbon atom, which is observed as a triplet ($^2J_{CP} \cong$ 30 Hz) in the range δ 85−100 ppm, while the β-carbon appears as a singlet at δ 110−120 ppm.[20] The spectral data are consistent with a transoid four-legged piano-stool structure for these compounds, similar to that found by X-ray crystallography for [Cp*RuH(C≡CC-OOMe)(dippe)][BPh$_4$].[21]

As has been already mentioned, the 3-hydroxyalkynyl hydrides **1a**−**g** rearrange spontaneously to their 3-hydroxyvinylidene isomers [Cp*Ru{=C=CHC(OH)RR′}-(PEt$_3$)$_2$][BPh$_4$] (R,R′ = H, H (**2a**); H, Me (**2b**); H, Ph (**2c**); Me, Ph (**2d**); Ph, Ph (**2e**); Me, Me (**2f**); C_5H_{10} (**2g**)). This process takes place both in solution and in the solid state. However, since the subsequent process of dehydration of the 3-hydroxyvinylidene ligand takes place in solution in most cases, the best synthetic procedure for the isolation of these derivatives in pure form has proven to be the solid-state isomerization at 30−35 °C.[22] This process can be monitored by IR spectroscopy following the decrease of the ν(C≡C) band and the increase in a new band in the range 1630−1680 cm^{-1} attributable to ν(C=C) of the orange complexes **2a**−**g**, besides the nearby ν(OH) band at 3500 cm^{-1}. IR and NMR data for them are listed in Tables 3 and 4. The vinylidene proton appears either as one multiplet due to coupling to phosphorus nuclei and to protons present at the γ-carbon (**2a**−**c**) or just as a broad resonance (**2d**−**g**). The ^{13}C{^{1}H} NMR spectra (Table 4) show the typical low-field resonance for the α-carbon as a triplet at δ 345 ppm ($^2J_{CP} \cong$ 15 Hz) and the β-carbon at δ 110−120 ppm.

(20) It is not unusual that the signal of the α-carbon appears at higher field than the signal of the β-carbon. Although there are not analogous Ru(II) compounds to compare, this sequence agrees with the data for neutral 3-methoxy or 3-hydroxyalkynyl compounds of Ru(II),[6] Os(II),[14] Rh(III),[15] and Ir(I): Esteruelas, M. A.; Oro, L. A.; Schrickel, J. *Organometallics* **1997**, *16*, 796.

(21) In this case, inhibition of isomerization by acid made recrystallization possible, but with the [Cp*Ru(PEt$_3$)$_2$]$^+$ system this method does not work, leading to extensive decomposition products. For the structure, see ref 13b.

(22) Except complex **2e**, in which dehydration also occurs in the solid state.

Table 4. Selected $^{13}C\{^1H\}$ NMR Data for [Cp*Ru{=C=CHC(OH)RR′}(PEt$_3$)$_2$][BPh$_4$]

		$^{13}C\{^1H\}$ NMR[a]							
	R, R′	C_5Me_5	C_5Me_5	C_α	$^2J_{CP}$	C_β	C_γ	R	R′
2a	H, H	10.77	102.4	345.4 t	15.5	110.1	54.4		
2b	H, Me	10.79	102.7	344.5 t	15.0	115.5	62.1		26.5
2c	H, Ph	10.74	102.8	343.7 t	15.2	114.5	67.9		128.2, 128.8, 135.5, 143.8
2d	Me, Ph	10.93	102.6	344.8 t	14.3	120.3	106.3	34.4	123.8, 127.2, 128.4, 148.9
2f	Me, Me	10.88	102.3	345.9 t	15.6	120.0	68.6	33.0	
2g	Cy	10.92	102.2	345.5 t	17.0	118.9	70.1		22.3, 24.8, 41.0

[a] Conditions: 201.12 MHz, $CDCl_3$, 273 K. Resonances are given in ppm, and coupling constants are given in Hz. For **2e** see ref 22.

As was the case for their precursors, the $^{31}P\{^1H\}$ NMR consists of one singlet except for compounds **2b**−**d**, for which the presence of a chiral group makes the phosphorus nuclei nonequivalent, and therefore two completely separated doublet signals ($^2J_{PP'} \cong 35$ Hz) are observed. This has been also reported for the analogous chiral methoxyvinylidene complexes [Cp*Ru{=C=CHCH(OMe)Me}(PMe$_2$Ph)$_2$][PF$_6$][6b] and [(η^5-C$_9$H$_7$)Ru{=C=CHCH(OMe)Ph}(PPh$_3$)$_2$][PF$_6$].[6c] Formation of such methoxy compounds is avoided for **2a**−**g**, since the formation of those derivatives should implicate a nucleophilic addition of methanol to allenylidene.[6b] Instead of this, the 3-hydroxyvinylidene compounds are quite stable, as expected for a very electron-rich ruthenium moiety,[2f] but not as stable as [Cp*RuCl{=C=CHC(OH)Ph$_2$}{κ^2(P,O)-^{i}Pr$_2$PCH$_2$CO$_2$Me}],[7a] and they spontaneously dehydrate in solution just as [Cp*Ru{=C=CHC(OH)Me$_2$}(dippe)][BPh$_4$],[7b] except for those derived from primary or secondary alcohols (**2a**−**c**). These two aforementioned complexes are the only precedents of 3-hydroxyvinylidene isolation as intermediates prior to allenylidene formation. So far, attempts to carry out a kinetic study of the isomerization of 3-hydroxyalkynyl into 3-hydroxyvinylidene complexes in solution did not show a good fit with a first-order process. In contrast, although η^2 coordination of an alkynol seemed to be quite hindered due to the steric requirement of the Cp* ring along with the two phosphines, it was possible to detect the formation of [Cp*Ru{η^2-HC≡CCH(OH)R}(PEt$_3$)$_2$][BPh$_4$] (R = H (**3a**), Me (**3b**), Ph (**3c**)) complexes by addition of alkynol into a precooled (CD_3)$_2$CO solution of the complex [Cp*Ru(N$_2$)(PEt$_3$)$_2$][BPh$_4$][23] at −40 °C. When HC≡CCH$_2$OH is added, the resonance for the dinitrogen complex (a singlet at δ 21.7 ppm) is replaced by two doublets (at δ 22.1 and 22.5 ppm, $^2J_{PP'} = 44.5$ Hz) corresponding to an AB spin system. If temperature is raised, the two doublets coalesce and eventually become a singlet at −20 °C. Above −10 °C, this resonance dissappears, and signals corresponding to the 3-hydroxyalkynyl hydride **1a** and to the 3-hydroxyvinylidene **2a** arise. Since only above 0 °C does the 3-hydroxyalkynyl hydrido complex **1a** isomerize perceptibly[24] into the 3-hydroxyvinylidene complex **2a**, the simultaneous formation of **1a** and **2a** at −10 °C must occur by two independent reaction pathways, namely C−H oxidative addition and a 1,2-hydrogen shift from the η^2 derivative **3a**, as shown in Scheme 2. These processes have been the subject of theoretical studies,[25] and the detection of this η^2-alkyne as an intermediate may add an interesting supplementary experimental support.

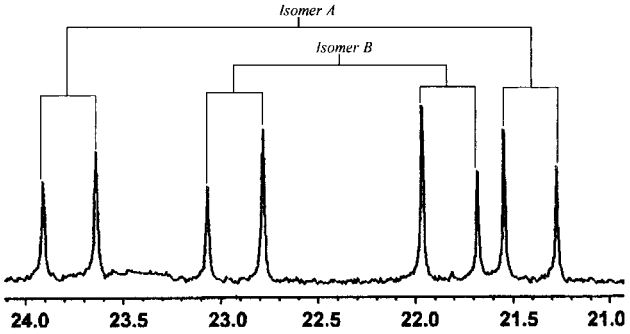
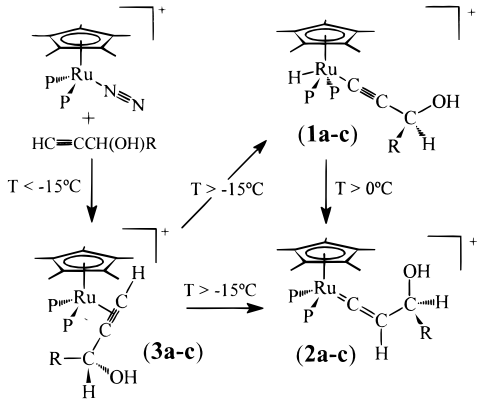


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of [Cp*Ru{η^2-HC≡CCH(OH)Me}(PEt$_3$)$_2$][BPh$_4$] (**3b**) in (CD_3)$_2$CO at −40 °C, showing the two sets of two doublets, corresponding each of the two possible stereoisomers for the cation complex.

Scheme 2. Species Involved in the Interaction of [Cp*Ru(N$_2$)(PEt$_3$)$_2$][BPh$_4$] with HC≡CCH(OH)R (R = H, Me, Ph) in (CD_3)$_2$CO



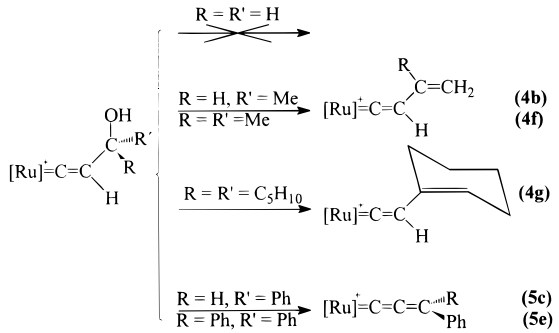
The dynamic process responsible for the observed fluxional behavior is possibly the spinning of the alkynol ligand around the π metal−carbon bond, as has been suggested elsewhere.[13b] The π-alkynol adducts **3b** and **3c** exhibit at −40 °C two sets of two doublets in their $^{31}P\{^1H\}$ NMR spectra (Figure 1). This has been attributed to the occurrence in solution of two possible isomers for both **3b** and **3c**, due to the chirality of the γ-carbon of the alkynol ligand. The doublet signals for both isomers dissappear before coalescence when the temperature is raised over −15 °C, yielding mixtures of 3-hydroxyalkynyl hydrides **1b**,**c** and 3-hydroxyvinylidenes **2b**,**c**. When tertiary propargyl alcohols are added under the same conditions, the resonance of the dinitrogen complex disappears, being directly replaced

(23) Jiménez-Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. Manuscript in preparation.

(24) Attempts to carry out a $^{31}P\{^1H\}$ NMR kinetic study were made in the range 25−50 °C.

(25) Pérez-Carreño, E.; Paoli, P.; Ienco, A.; Mealli, C. *Eur. J. Inorg. Chem.*, in press. Chen, W. C.; Yu, C. H. *Chem. Phys. Lett.* **1997**, *277*, 245 and references therein. Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360. Stegmann, R.; Frenking, G. *Organometallics* **1998**, *17*, 2089.

Scheme 3. Summary of Dehydration Products of 3-Hydroxyvinylidene Complexes



by the signals corresponding to 3-hydroxyalkynyl hydrido and 3-hydroxyvinylidene species, in a ratio similar to that observed after the **3a**−**c** signals decreased (about 3:1), but without η^2-alkynol detection. ^{1}H NMR spectra of the complexes **3a**−**c** were obscured by the excess of free alkynol added into the NMR tube, and the signals were not assigned. All attempts to isolate these π-alkyne complexes as solids were unsuccessful, due to that the fast isomerization operates even in the solid state. The fact that all of the **1a**−**g** complexes could be isolated as solids from [Cp*RuCl(PEt$_3$)$_2$] by precipitation in MeOH without contamination of the **2a**−**g** isomers can be attributed to their higher insolubility, along with the fact that in this system the C−H oxidative addition seems to occur faster than the 1,2-H shift.

The next step in the activation of alkynols, dehydration of the 3-hydroxyvinylidene moiety, although better established, is still an open question with regard to the control of the allenylidene vs alkenylvinylidene formation (Scheme 3). The nature and stability of the dehydration products mainly depend on the substituents of the alkynol, which is also manifested in the [Cp*Ru(PEt$_3$)$_2$]$^+$ system. We show the possibility of a selective synthetic route to give either alkenylvinylidene or allenylidene, by using the appropriate method: (A) spontaneous dehydration in solution,[26] by starting from [Cp*RuCl(PEt$_3$)$_2$] in MeOH and the alkynol and stirring for 6−8 h, leading to the most stable compound (thermodynamic control) and (B) forced dehydration by passing a CH_2Cl_2 solution of the 3-hydroxyvinylidene complex through acidic alumina,[27] yielding a rapid dehydration which sometimes leads to metastable products (kinetic control). The hydroxyvinylidene **2a**, as expected for a primary alcohol, does not undergo dehydration by any method. Likewise, neither **2b** nor **2c** dehydrates spontaneously, but they do dehydrate by method B and the complexes [Cp*Ru(=C=CHCH=CH$_2$)(PEt$_3$)$_2$][BPh$_4$] (**4b**) and [Cp*Ru(=C=C=CHPh)(PEt$_3$)$_2$][BPh$_4$] (**5c**) were obtained. The IR spectra of these dehydration products show one ν(C=C) band at 1620 cm^{-1} for **4b**, or one strong ν(C=C=C) absorption at 1907 cm^{-1} in the case of **5c**. The ^{31}P{^{1}H} NMR spectra of both compounds consist of one singlet at δ 30.9 and 32.1 ppm, respectively. The most relevant features in the ^{1}H NMR spectrum of the vinylvinylidene are the signal for the vinylidene proton and two resonances corresponding to each of the protons of the =CH$_2$ group. The ^{13}C{^{1}H} NMR spectra show the typical low-field resonances for the metal-bound carbon atoms at δ 351.4 ppm ($^2J_{CP}$ = 15.1 Hz) for **4b** and 301.6 ppm ($^2J_{CP}$ = 17.5 Hz) for **5c**, consistent with those expected for these sorts of species.[6c,8] There are no significant differences between these data for **4b** and **5c** with the rest of the alkenylvinylidene and allenylidene species obtained with different alkynols.

The formation of the allenylidene complex **5c** by activation of a secondary propargyl alcohol results particularly remarkable, since this sort of compound still remains very scarce and exhibits a higher reactivity than the disubstituted species. The proton attached at the γ-carbon appears as one broad resonance at δ 9.13 ppm in the ^{1}H NMR spectrum. Such resonances have been observed for the previously reported monosubstituted allenylidenes [(η^5-C$_9$H$_7$)Ru(=C=C=CHPh)(PPh$_3$)$_2$][PF$_6$][6c] and [RuCl(=C=C=CHR)(dppm)$_2$][PF$_6$] (R = Ph, *p*-PhCl, *p*-PhF, *p*-PhOMe)[8] at δ 9.09 and in the range δ 8.0−8.5 ppm, respectively.

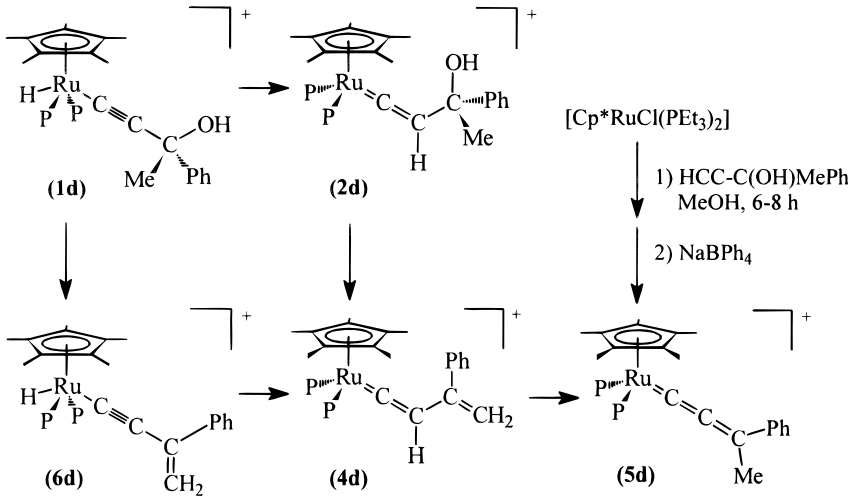
In contrast with **5c**, [Cp*Ru(=C=C=CPhR)(PEt$_3$)$_2$][BPh$_4$] (R = Me (**5d**), Ph (**5e**)) could be obtained easily by method A. The X-ray crystal structure of **5e** was determined. It seems that the presence and number of aromatic groups as substituents at the γ-carbon contribute to the stabilization of allenylidene complexes in an additive form, as can be inferred from the increasing stability of the allenylidenes (**5e** > **5d** > **5c**). In this connection, the complex **5d** exhibits behavior halfway between the quite reactive **5c** and the nearly inert **5e** allenylidene.

In the case of alkynols bearing deprotonatable alkyl groups at the γ-carbon, method B may be applied to 3-hydroxyvinylidene as well as to 3-hydroxyalkynyl hydrido species to force dehydration. Scheme 4 summarizes all observed intermediates and final products for the reaction of HC≡CC(OH)MePh with [Cp*RuCl(PEt$_3$)$_2$]. Whereas the activation of the alkynol HC≡CC(OH)MePh by method A yielded cleanly the allenylidene **5d**, the dehydration of the 3-hydroxyvinylidene **2d** by method B gave rise to a mixture of the allenylidene/vinylvinylidene isomers. Similar mixtures were obtained in the activation of the same alkynol by the fragment [(η^5-C$_9$H$_7$)RuL$_2$]$^+$ (L$_2$ = 2 PPh$_3$, dppe, dppm)[6c] and represent a synthetic limitation of this method, because these isomers can be hardly separated. However, if method B is applied to the 3-hydroxyalkynyl hydrido complex **1d**, the dehydration occurs prior to isomerization, leading to the Ru^{IV} hydrido η^1-enynyl derivative [Cp*RuH{C≡CC(Ph)=CH$_2$}(PEt$_3$)$_2$][BPh$_4$] (**6d**), a novel compound which is obtained for the first time. The spectral properties of **6d** resemble those of the 3-hydroxyalkynyl hydride **1d**. Both types of compounds exhibit one strong ν(C≡C) band in their IR spectra at 2090 and 2104 cm^{-1}, respectively. However, the former lack the ν(OH) band, as expected. One high-field triplet is observed for the hydride ligand at δ −9.23 ppm (δ −9.35 ppm for **1d**) and two resonances for the protons of the methylidene group at δ 5.27 and 5.61 ppm as

(26) This is the most useful way to allenylidene, employed for the first time by Selegue,[1] although it may lead to a mixture with alkenylvinylidene[6c,8] or even to a selective synthesis of alkenylvinylidenes.[9b]

(27) Werner et al. used this method to dehydrate some stable 3-hydroxyvinylidene compounds: Martin, M.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2275. See also ref 7a and 15. We had to avoid the use of catalytic amounts of a strong acid such as HBF$_4$ because it usually caused an extensive decomposition of the complexes.

Scheme 4. Reactions and Species Involved in the Activation of HC≡CC(OH)MePh by the Complex [Cp*RuCl(PEt$_3$)$_2$]



broad singlets. In contrast to **1d**, the phosphorus atoms are equivalent, as inferred from the presence of one singlet in the $^{31}P\{^1H\}$ NMR spectra, due to the disappearance of the chirality of the γ-carbon. These spectral data also suggest a transoid four-legged piano-stool structure for these species. Although it was possible to detect appreciable formation of hydrido enynyl complexes from those 3-hydroxyalkynyl hydrido compounds with deprotonatable groups at the δ-carbon, it was unable to obtain them with enough purity due to the intrinsic limitations of the method B, namely that the longer the acidic alumina column, the more the isomerization takes place, a mixture being obtained with at least four species.

The compound **6d** rearranges both in solution and in the solid state to the vinylvinylidene isomer [Cp*Ru{=C=CHC(=CH$_2$)Ph}(PEt$_3$)$_2$][BPh$_4$] (**4d**). This solid-state isomerization is the best synthetic method to obtain **4d** in pure form and allowed us to obtain not only the NMR spectral data but also single crystals suitable for X-ray diffraction analysis. As mentioned earlier, the allenylidene **5d** is the most stable product; therefore, it is not surprising that in solution the vinylvinylidene **4d** spontaneously isomerizes into **5d**. This observation makes clear that the formation of 3-hydroxyvinylidene intermediates is not always necessary for the formation of alkenylvinylidene or allenylidene derivatives, which explains the possibility of synthesizing allenylidene complexes by activation of HC≡CC(=CH$_2$)CH$_3$ with [(η^6-arene)Ru(L)Cl$_2$] (L = PR$_3$, CNR)[28] as well as with *cis*-[RuCl$_2$(dppm)$_2$],[8,29] through an overall reaction of 1,4-migration of the alkyne proton likely via a vinylvinylidene intermediate.

The X-ray crystal structures of [Cp*Ru{=C=CHC(=CH$_2$)Ph}(PEt$_3$)$_2$][BPh$_4$] (**4d**) and of [Cp*Ru(=C=C=CPh$_2$)(PEt$_3$)$_2$][BPh$_4$] (**5e**) were determined. General crystallographic data for these compounds are shown in Table 5. Selected bond lengths and angles for **4d** and **5e** are listed in Tables 6 and 7, respectively. ORTEP views of the cationic complexes are shown in Figures 2 and 3. Both complexes adopt three-legged piano-stool geometries. The vinylvinylidene ligand in **4d** is characterized by a Ru(1)−C(11) distance of 1.81(2) Å, a C(11)−C(12) separation of 1.37(2) Å, and a Ru(1)−C(11)−C(12) angle of 172(1)°. The angle C(11)−C(12)−C(13) of 129(1)° indicates sp^2 hybridization for C(12), as expected for the β-carbon of a vinylidene ligand. The separations C(12)−C(13) = 1.44(2) Å and C(13)−C(14) = 1.27(3) Å correspond respectively to a single and to a double bond. These dimensions compare well in general with those reported for the few other ruthenium vinylvinylidene complexes structurally characterized, i.e., [CpRu{=C=CHC=CH(CH$_2$)$_4$}(PMe$_3$)$_2$][PF$_6$],[9a] [(η^5-C$_9$H$_7$)-Ru{=C=C(Me)C=CH(CH$_2$)$_4$}(PPh$_3$)$_2$][CF$_3$SO$_3$],[9b] and [TpRu{=C=C(COOMe)CH=CHCOOMe}(dippe)]-[BPh$_4$].[9d] In the case of **5e**, the diphenylallenylidene ligand appears almost linearly assembled to ruthenium. The observed sequence of C−C bond distances across the carbon chain is quite representative of what is expected for an allenylidene ligand having substantial contribution of two different mesomeric forms. Thus, the bond distances Ru(1)−C(11) = 1.876(5) Å, C(11)−(12) = 1.245(7) Å, and C(12)−C(13) = 1.352(8) Å compare well with the values found in other allenylidene complexes such as [Cp*Ru(=C=C=CMePh)(dippe)][BPh$_4$] (1.884(5), 1.257(6), and 1.338(7) Å),[7b] [(η^5-C$_9$H$_7$)Ru{=C=C=C(C$_{13}$H$_{20}$)}(PPh$_3$)$_2$][PF$_6$] (1.889(5), 1.256(7), and 1.339(7) Å),[10b] or [CpRu(=C=C=CPh$_2$)(PMe$_3$)$_2$][PF$_6$] (1.884(5), 1.255(8), and 1.329(9) Å).[1] The atoms C(12), C(13), C(14), and C(20) define a plane which forms a dihedral angle of 8.59° with the plane defined by C(11), Ru(1), and the centroid of the Cp* ring. This disposition has been commonly observed in other half-sandwich Ru allenylidene derivatives, since it appears to maximize the effectiveness of the metal−ligand π-overlap.[30]

Finally, the activation of the dialkyl-substituted alkynols 2-methyl-3-butyn-2-ol and 1-ethynylcyclohexanol by method A led as final products to the zwitterionic compounds [Cp*Ru{C≡CC(PEt$_3$)Me$_2$}(PEt$_3$)$_2$][BPh$_4$]

(28) Devanne, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 641. Dussel, R.; Pilette, D.; Dixneuf, P. H.; Fehlhammer, W. P. *Organometallics* **1991**, *16*, 3287.

(29) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980.

(30) Schelling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1977**, *101*, 585.

Table 5. Summary of Data for the Crystal Structure Analysis of 4d, 5e, and 7f

	4d	5e	7f
formula	$C_{56}H_{73}BP_2Ru$	$C_{61}H_{75}BP_2Ru$	$C_{57}H_{86}BP_3Ru$
fw	920.02	982.09	976.11
cryst size (mm)	0.30 × 0.15 × 0.12	0.27 × 0.25 × 0.08	0.32 × 0.25 × 0.15
cryst syst	orthorhombic	triclinic	triclinic
space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cell params			
a, Å	16.160(6)	13.573(5)	14.538(7)
b, Å	19.838(5)	18.174(5)	18.503(9)
c, Å	15.309(4)	11.020(4)	10.755(4)
α, deg		91.47(3)	92.04(3)
β, deg		101.53(3)	99.95(3)
γ, deg		84.80(3)	107.40(4)
V (Å^3)	4907(4)	2652(1)	2707(2)
Z	4	2	2
ρ_{calcd} (g cm^{-3})	1.245	1.230	1.197
λ(Mo Kα) (Å)	0.710 69	0.710 69	0.710 69
μ(Mo Kα) (cm^{-1})	4.11	3.84	4.03
F(000)	1952.00	1040.00	1044.00
decay (%)	−0.80	−3.60	−0.65
transmissn factors	0.802−1.000	0.887−1.000	0.751−1.000
scan speed (ω) (deg min^{-1})	4	4	4
no.of measd rflns	4177	8576	8672
no. of obsd rflns ($I > 3\sigma_I$)	2351	5377	5000
no.of params	306	586	461
rfln/param ratio	7.68	9.18	10.85
R^a	0.0697	0.0491	0.0717
R_w ($w = \sigma_F^{-2}$)^b	0.0812	0.0565	0.0871
max Δ/σ in final cycle	0.9823	0.2314	8.953
GOF	2.113	1.625	2.545

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 6. Selected Bond Distances (Å) for 4d, 5e, and 7f

4d		5e		7f	
Ru(1)−P(1)	2.351(4)	Ru(1)−P(1)	2.336(2)	Ru(1)−P(1)	2.293(3)
Ru(1)−P(2)	2.321(5)	Ru(1)−P(2)	2.344(2)	Ru(1)−P(2)	2.283(3)
Ru(1)−C(1)	2.25(2)	Ru(1)−C(1)	2.246(6)	Ru(1)−C(1)	2.22(1)
Ru(1)−C(2)	2.27(2)	Ru(1)−C(2)	2.276(6)	Ru(1)−C(2)	2.234(10)
Ru(1)−C(3)	2.27(2)	Ru(1)−C(3)	2.311(6)	Ru(1)−C(3)	2.23(1)
Ru(1)−C(4)	2.35(2)	Ru(1)−C(4)	2.315(6)	Ru(1)−C(4)	2.28(1)
Ru(1)−C(5)	2.30(2)	Ru(1)−C(5)	2.282(6)	Ru(1)−C(5)	2.29(1)
Ru(1)−C(11)	1.81(2)	Ru(1)−C(11)	1.876(5)	Ru(1)−C(11)	1.984(9)
C(11)−C(12)	1.37(2)	C(11)−C(12)	1.245(7)	C(11)−C(12)	1.22(1)
C(12)−C(13)	1.44(3)	C(12)−C(13)	1.352(8)	C(12)−C(13)	1.45(1)
C(13)−C(14)	1.27(3)	C(13)−C(14)	1.463(7)	C(13)−C(14)	1.54(1)
C(13)−C(15)	1.45(3)	C(13)−(20)	1.493(8)	C(13)−(15)	1.49(2)
				P(3)−C(13)	1.83(1)

Table 7. Selected Angles (deg) for 4d, 5e and 7f

4d		5e		7f	
P(1)−Ru(1)−P(2)	93.3(2)	P(1)−Ru(1)−P(2)	96.67(7)	P(1)−Ru(1)−P(2)	97.8(1)
P(1)−Ru(1)−C(11)	90.5(6)	P(1)−Ru(1)−C(11)	89.5(2)	P(1)−Ru(1)−C(11)	88.5(3)
P(2)−Ru(1)−C(11)	90.3(5)	P(2)−Ru(1)−C(11)	91.0(2)	P(2)−Ru(1)−C(11)	87.7(3)
Ru(1)−C(11)−C(12)	172(1)	Ru(1)−C(11)−C(12)	172.1(5)	Ru(1)−C(11)−C(12)	169.7(8)
C(11)−C(12)−C(13)	129(1)	C(11)−C(12)−C(13)	170.8(6)	C(11)−C(12)−C(13)	173(1)
C(12)−C(13)−C(14)	123(2)	C(12)−C(13)−C(14)	122.3(6)	C(12)−C(13)−C(14)	110.9(9)
C(12)C(13)−C(15)	116(1)	C(12)−C(13)−C(20)	118.4(5)	C(12)−C(13)−C(15)	113(1)
C(14)−C(13)−C(15)	120(2)	C(14)−C(13)−C(20)	119.2(5)	C(14)−C(13)−C(15)	106(1)
				P(3)−C(13)−C(12)	108.8(8)
				P(3)−C(13)−C(14)	105.9(8)
				P(3)−C(13)−C(15)	111.2(8)

(**7f**) and [Cp*Ru{C≡CC(PEt$_3$)(CH$_2$)$_5$}(PEt$_3$)$_2$][BPh$_4$] (**7g**), which result from the nucleophilic attack of PEt$_3$ at the *γ*-carbon of intermediate allenylidene complexes, [Cp*Ru(=C=C=CR$_2$)(PEt$_3$)$_2$][BPh$_4$] (Scheme 5). Compounds **7f**,**g** exhibit one strong *ν*(C≡C) band in their IR spectra at significantly higher wavenumber than the observed *ν*(C=C=C) band in allenylidene complexes. The ^{31}P{^{1}H} NMR spectra display a pattern corresponding to a A_2M spin system, with $^5J_{PP}$ coupling constants of 3.5 and 4.7 Hz, respectively. These spectral data, along with the ^{13}C{^{1}H} shifts and coupling constant values, are in accord with those previously reported for alkynylphosphonio derivatives, generated by external addition of free phosphine and regioselective attack at the *γ*-carbon of allenylidene complexes.[2d,9b] The X-ray crystal structure of **7f** was determined. Selected bond lengths and angles are listed in Tables 6 and 7. An ORTEP view of the complex cation is shown in Figure 4. This compound

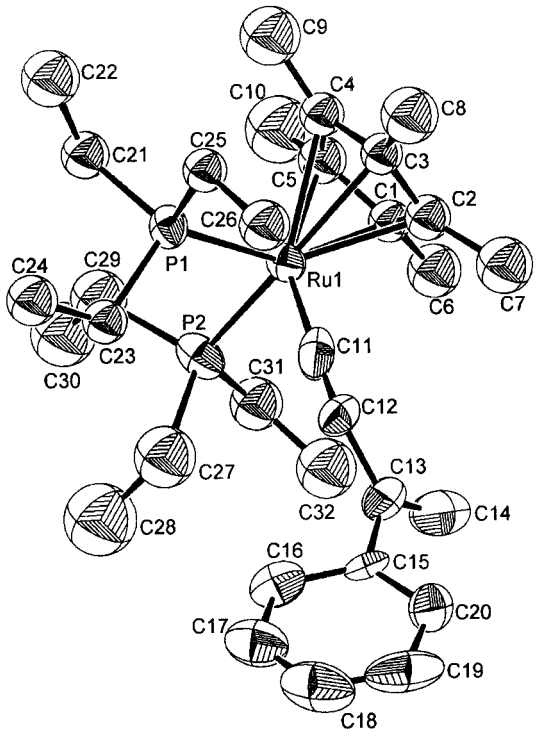


Figure 2. ORTEP view (50% probability) of the cation $[Cp^*Ru\{=C=CHC(Ph)=CH_2\}(PEt_3)_2]^+$ in complex **4d**, showing the atom-labeling scheme. Hydrogen atoms have been omitted.

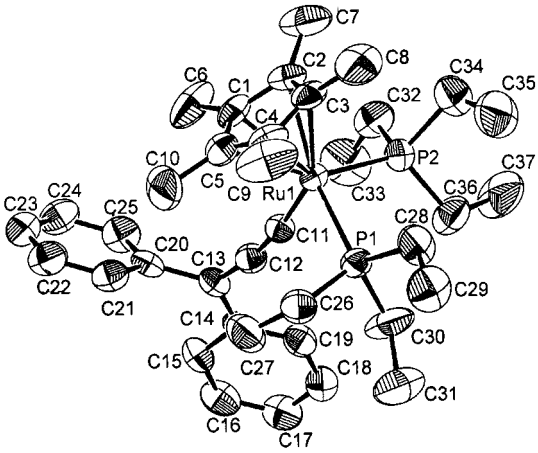
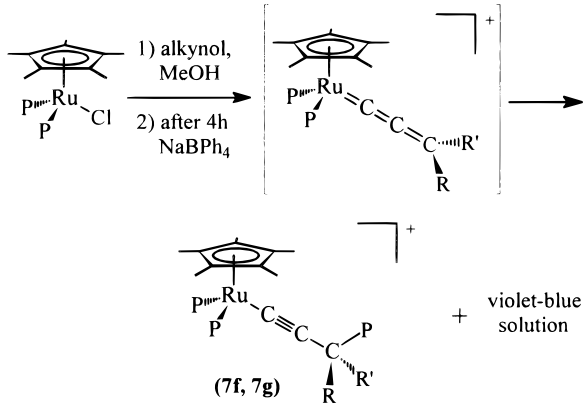


Figure 3. ORTEP view (50% probability) of the cation $[Cp^*Ru(=C=C=CPh_2)(PEt_3)_2]^+$ in complex **5e**, showing the atom-labeling scheme. Hydrogen atoms have been omitted.

also displays a three legged piano-stool structure. The C(11)−C(12)−C(13) chain shows only slight deviation from linearity, as inferred from the angles Ru(1)−C(11)−C(12) = 169.7(8)°, and C(11)−C(12)−C(13) = 173(1)°. The Ru−C(11) separation of 1.984(9) Å is longer than in the vinylvinylidene **4d** or in the allenylidene derivative **5e** but is similar to Ru−C distances observed in σ-alkynyl complexes of ruthenium such as $[Cp^*Ru\{C{\equiv}CC(=CH_2)Ph\}(dippe)]$ (1.994(7) Å)[7b] and $[(\eta^5\text{-}C_9H_7)Ru\{C{\equiv}CC(C{\equiv}CH)Ph_2\}(PPh_3)_2]$ (1.993(2) Å),[2d] corresponding to a single Ru−C bond. The C(11)−C(12) bond distance of 1.22(1) Å is short and characteristic of a carbon−carbon triple bond, whereas the C(12)−C(15) separation of 1.45(1) Å suggests a single bond. All angles around C(13) are consistent with a tetrahedral sp^3 hybridization for this carbon atom. The C(13)−P(3) distance of 1.83(1) Å is on the same order of all the other P−C separations observed within this complex cation, being in the expected range. We have found no other structural report for alkynylphosphonio complexes resulting from the attack of the phosphine at the γ-carbon of an allenylidene moiety, although the crystal structure of the alkenylphosphonio species $[(\eta^7\text{-}C_9H_7)Ru\{CH{=}C(PPh_3)\overline{C{=}CH(CH_2)_4}\}(PPh_3)_2][PF_6]$ has been recently described,[9b] which results from the attack of PPh_3 at the β-carbon of a vinylvinylidene complex. Despite this, the arrangement observed for the complex cation in **7f** has also been found in related half-sandwich derivatives resulting from the regioselective addition of other kinds of nucleophiles to the γ-carbon of an allenylidene ligand, e.g. in $[(\eta^7\text{-}C_9H_7)Ru\{C{\equiv}C{-}C(C{\equiv}CH)Ph_2\}(PPh_3)_2]$.[2d]

The products resulting from the phosphine loss remain uncharacterized. Apparently, phosphine dissocia-

Scheme 5. Formation of Alkynylphosphonio Complexes $[Cp^*Ru\{C{\equiv}CC(PEt_3)RR'\}(PEt_3)][BPh_4]$ (R = R′ = Me (7f); R = R′ = C_5H_{10} (7g))



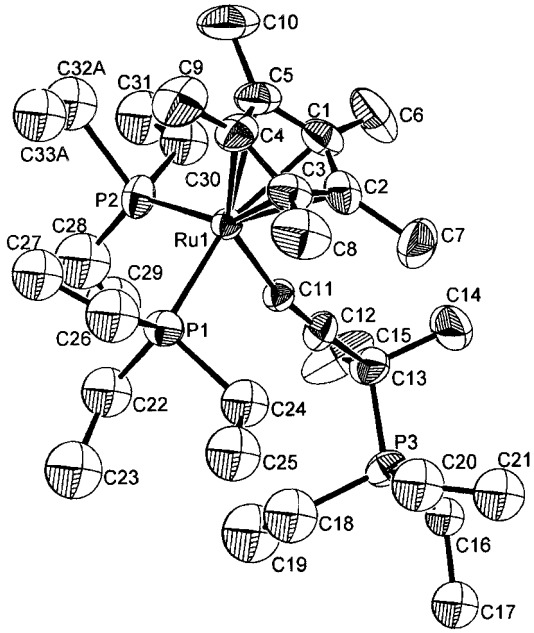


Figure 4. ORTEP view (50% probability) of the cation $[Cp^*Ru\{C{\equiv}CC(PEt_3)Me_2\}(PEt_3)_2]^+$ in complex **7f**, showing the atom-labeling scheme. Hydrogen atoms have been omitted.

tion occurs to some extent in solution, reacting with allenylidene complexes. However, it is also possible that the high electrophilicity of the γ-carbon, in the absence of aromatic substituents, is responsible for the abstraction of PEt_3 from other species present in solution.

When a solution of the 3-hydroxyvinylidene compounds **2f**,**g** was passed through an acidic alumina column (method B), a brown band was first collected, corresponding to the alkenylvinylidenes [Cp*Ru{=C=CHC(=CH$_2$)CH$_3$}(PEt$_3$)$_2$][BPh$_4$] (**4f**) and [Cp*Ru{=C=CHC=CH(CH$_2$)$_4$}(PEt$_3$)$_2$][BPh$_4$] (**4g**) (Scheme 3). Minimal amounts of allenylidene were detected both by IR and $^{31}P\{^1H\}$ NMR, but they could not be isolated. After this, a second blue-violet band appeared, but attempts at characterization were unsuccessful. This band, which exhibits a continuous color change from blue to violet and vice versa, seems to be related to the processes leading to the formation of the mentioned alkynylphosphonio compounds and resembles the case reported by Dixneuf et al. for the reaction of [Cp*RuCl(PMe$_2$Ph)$_2$] with HC≡CCMe$_2$OH,[6b] where the presence of a bimetallic structure is suggested on the basis of the characterized product obtained by Selegue et al.[10a] Our detection in solution of both allenylidene and alkenylvinylidene species supports this idea, and the in situ phosphine release represents a new insight into this hypothetical C−C coupling reaction involving a Cp* system.

Conclusions

The isolation of (3-hydroxyalkynyl)hydridoruthenium (IV) compounds (**1**) contributes to expand the number and nature of ruthenium complexes known to be able to follow this pathway in the alkynyl to vinylidene isomerization.[13b] In this case we have shown a system containing monodentate phosphines, which is used in the activation of alkynols, connecting with the increasing field of allenylidene chemistry. Methodologically, these species are also the key for a clean synthesis and characterization of 3-hydroxyvinylidene complexes (**2**), making possible in some cases the control of the direction of the dehydration into alkenylvinylidene (**4**) or allenylidene (**5**) and a change in the order of the isomerization/dehydration processes, yielding a novel hydrido enynyl species (**6**). We have detected the existence of η^2-alkynol species (**3**) as the step after which 1,2-H shift and C−H oxidative addition take place competitively. New attempts to acquire kinetic data from which we can extract any mechanistic conclusions about these isomerization processes are in progress with related Cp* systems.

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. [Cp*RuCl(PEt$_3$)$_2$][12b] and [Cp*Ru(N$_2$)(PEt$_3$)$_2$][BPh$_4$][23] were prepared according to reported procedures. IR spectra were recorded in Nujol mulls on Perkin-Elmer FTIR Spectrum 1000 spectrophotometers. NMR spectra were taken on a Varian Unity 400 MHz or Varian Gemini 200 MHz spectrometer. Chemical shifts are given in parts per million from SiMe$_4$ (^1H and $^{13}C\{^1H\}$) or 85% H$_3$PO$_4$ ($^{31}P\{^1H\}$). Triethylphosphine and tetraphenylborate protons and carbons appeared for all the compounds in the appropriate shift ranges and are not listed. The ^1H NMR resonance for the OH proton, when observed, appeared most times overlapping with the phosphine signals and it was not possible to assign them accurately. Microanalysis was performed by the Serveis Científico-Tècnics, Universitat of Barcelona.

Preparation of 3-Hydroxyalkynyl Hydrido Complexes [Cp*RuH{C≡CC(OH)RR′}(PEt$_3$)$_2$][BPh$_4$] (R, R′ = H, H (1a), H, Me (1b), H, Ph (1c), Me, Ph (1d), Ph, Ph (1e), Me, Me (1f), C$_5$H$_{10}$ (1g)). [Cp*RuCl(PEt$_3$)$_2$] (127 mg, 0.25 mmol) was added to a solution of the corresponding alkynol (0.30 mmol) and NaBPh$_4$ (81 mg, 0.50 mmol) in 10 mL of MeOH at 0 °C (ice bath). The mixture was warmed until a white/yellow microcrystalline solid precipitated, which was filtered, washed with cold EtOH and petroleum ether, and stored at −20 °C. Yield: 80−90% in all cases. Microanalysis was not carried out because these compounds rearrange to their vinylidene isomers in the solid state. Selected IR and NMR spectral data for these compounds are given in Tables 1 and 2.

Preparation of 3-Hydroxyvinylidene Complexes [Cp*Ru{=C=CHC(OH)RR′}(PEt$_3$)$_2$][BPh$_4$] (R, R′ = H, H (2a), H, Me (2b), H, Ph (2c), Me, Ph (2d), Ph, Ph (2e), Me, Me (2f), C$_5$H$_{10}$ (2g)). Complexes **1a**−**g** were heated as solids at 35 °C for 3 h under an inert atmosphere, resulting in a gradual color change from white-yellow to orange. A quantitative and clean isomerization process into **2a**−**g** takes place, except for complex **2e**, whose dehydration also occurs in the solid state. Complexes **2a**,**b** can also be obtained cleanly by starting from a solution of [Cp*RuCl(PEt$_3$)$_2$] (127 mg, 0.25 mmol) in 15 mL of MeOH to which the alkynol (0.30 mmol) was added. After this mixture was stirred for 4 h at room temperature, addition of NaBPh$_4$ (81 mg, 0.50 mmol) produced an orange solid precipitate, which was filtered, washed with EtOH and petroleum ether, and dried in vacuo. Selected IR and NMR data for these compounds are given in Tables 3 and 4.

2a: Anal. Calcd for C$_{49}$H$_{69}$BP$_2$RuO: C, 69.4; H, 8.20. Found: C, 69.5; H, 8.16. **2b**: Anal. Calcd for C$_{50}$H$_{71}$BP$_2$RuO: C, 69.7; H, 8.30. Found: C, 69.7; H, 8.30. **2c**: Anal. Calcd for C$_{55}$H$_{73}$BP$_2$RuO: C, 71.5; H, 7.96. Found: C, 71.5; H, 7.90. **2d**: Anal. Calcd for C$_{56}$H$_{75}$BP$_2$RuO: C, 71.7; H, 8.06. Found: C, 71.7; H, 8.07. **2e**: unstable toward dehydration even in the solid state. **2f**: Anal. Calcd for C$_{51}$H$_{73}$BP$_2$RuO: C, 69.9; H, 8.40. Found: C, 69.9; H, 8.47. **2g**: Anal. Calcd for C$_{54}$H$_{77}$BP$_2$RuO: C, 70.8; H, 8.47. Found: C, 70.9; H, 8.51.

Detection of [Cp*Ru{η^2-HC≡CCH(OH)R}(PEt$_3$)$_2$][BPh$_4$] (R = H (3a), Me (3b), Ph (3c)) by NMR Spectroscopy. [Cp*Ru(N$_2$)(PEt$_3$)$_2$][BPh$_4$] was dissolved in (CD$_3$)$_2$CO in a NMR tube. The solution was cooled at −40 °C with a liquid N$_2$−ethanol bath, and then an excess of alkynol was added. The samples were inserted into the precooled NMR probe, and $^{31}P\{^1H\}$ NMR spectra were recorded. ^1H NMR data are not available due to the overlapping with the free alkynol signals. Attempts to isolate any of these species as solids failed because of the fast isomerization into **1a**−**c** even in the solid state.

3a: $^{31}P\{^1H\}$ NMR (161.89 MHz, (CD$_3$)$_2$CO, 233 K): δ 22.11 and 22.53 (d, $^2J_{PP'}$ = 44.5 Hz). **3b**: $^{31}P\{^1H\}$ NMR (161.89 MHz, (CD$_3$)$_2$CO, 233 K): δ 21.43 and 23.72 (d, $^2J_{PP'}$ = 44.0 Hz, isomer *a*), 21.84 and 22.88 (d, $^2J_{PP'}$ = 46.4 Hz, isomer *b*). **3c**: $^{31}P\{^1H\}$ NMR (161.89 MHz, (CD$_3$)$_2$CO, 233 K): δ 21.30 and 23.44 (d, $^2J_{PP'}$ = 44.0 Hz, isomer *a*), 21.76 and 22.60 (d, $^2J_{PP'}$ = 45.2 Hz, isomer *b*).

Preparation of Alkenylvinylidene Complexes [Cp*Ru{=C=CHC(=CH$_2$)R}(PEt$_3$)$_2$][BPh$_4$] (R = H (4b), Ph (4d), Me (4f)) and [Cp*Ru{=C=CHC=CH(CH$_2$)$_4$}(PEt$_3$)$_2$][BPh$_4$] (4g). A solution of the corresponding hydroxyvinylidene complex (0.25 mmol) in 1 mL of CH$_2$Cl$_2$ was passed through a column with Al$_2$O$_3$ (acidic, activity grade I, height of column 5 cm). During the elution with CH$_2$Cl$_2$ and acetone (5:1) a color

change was observed from orange to orange-brown. This fraction was collected and taken to dryness in vacuo, and the residue was suspended in Et_2O and the suspension treated for 5 min in a ultrasonic bath. The solvent was removed and the solid dried in vacuo and recrystallized in a acetone/ethanol (1:2) mixture. Yield: 70−80%. The complex **4d** could not be cleanly obtained in this way but was obtained quantitatively by solid-state isomerization at 35 °C of the hydrido enynyl complex **6d**, and its recrystallization had to be accomplished at −20 °C, preventing the isomerization into the allenylidene **5d**, yielding brown crystals. Selected spectral data are as follows.

4b: Anal. Calcd for $C_{50}H_{69}BP_2Ru$: C, 71.2; H, 8.24. Found: C, 71.1; H, 8.22. IR (Nujol): ν(C═C) 1620 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.73 (t, $^4J_{HP}$ = 1.0 Hz, $C_5(CH_3)_5$), 4.86 (dt, $^4J_{H^aP}$ = 1.5 Hz, $^3J_{H^aH^b}$ = 16.9 Hz, Ru═C═CH^aCH^b(═CH_2)), 4.43 and 5.01 (d, 1H each, $^3J_{H^cH^b}$ = 10.1 Hz, Ru═C═CHCH^b(═C$H^c{}_2$)), 6.15 (dt, $^3J_{H^aH^b}$ = 16.9 Hz, $^3J_{H^bH^c}$ = 10.1 Hz, Ru═C═CH^aCH^b(═C$H^c{}_2$)). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 30.9 (s). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 10.71 (s, $C_5(CH_3)_5$), 103.0 (s, $C_5(CH_3)_5$), 351.4 (t, $^2J_{CP}$ = 15.1 Hz, C_α), 110.6 (s, C_β), 121.9 (s, C_γ), 114.5 (s, ═CH_2).

4d: Anal. Calcd for $C_{56}H_{73}BP_2Ru$: C, 73.1; H, 8.00. Found: C, 73.2; H, 8.02. IR (Nujol): ν(C═C) 1622 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.78 (t, $^4J_{HP}$ = 1.0 Hz, $C_5(CH_3)_5$), 4.90 (t, $^4J_{HP}$ = 1.9 Hz, Ru═C═CHC(═CH_2)Ph), 5.02 and 5.29 (br s, 1H each, Ru═C═CHC(═CH_2)Ph), 7.34, 7.35, and 7.36 (m, C_6H_5). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 28.9 (s). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 10.97 (s, $C_5(CH_3)_5$), 103.7 (s, $C_5(CH_3)_5$), 350.5 (t, $^4J_{CP}$ = 14.8 Hz, C_α), 112.0 (s, C_β), 126.2 (s, C_γ), 113.6 (s, ═CH_2), 128.2, 128.5, 138.1 and 140.5 (s, C_6H_5).

4f: Anal. Calcd for $C_{51}H_{71}BP_2Ru$: C, 71.4; H, 8.34. Found: C, 71.4; H, 8.32. IR (Nujol): ν(C═C) 1607 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.74 (t, $^4J_{HP}$ = 1.1 Hz, $C_5(CH_3)_5$), 4.74 (br s, Ru═C═CHC(═CH_2)CH_3), 4.42 (dc, $^2J_{H^aH^b}$ = 2.0 Hz, $^4J_{H^aH^c}$ = 1.5 Hz, Ru═C═CHC(═CH^aH^b)C$H^c{}_3$), 4.58 (br s, Ru═C═CHC(═CH^aH^b)CH_3), 1.70 (br s, Ru═C═CHC(═CH_2)CH_3). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 27.8 (s). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 10.82 (s, $C_5(CH_3)_5$), 103.0 (s, $C_5(CH_3)_5$), 352.9 (t, $^2J_{CP}$ = 15.3 Hz, C_α), 109.8 (s, C_β), 132.2 (s, C_γ), 116.3 (s, ═CH_2), overlapping with phosphine methyl groups (s, CH_3).

4g: Anal. Calcd for $C_{54}H_{75}BP_2Ru$: C, 72.2; H, 8.42. Found: C, 72.3; H, 8.50. IR (Nujol): ν(C═C) 1633 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.75 (t, $^4J_{HP}$ = 1.0 Hz, $C_5(CH_3)_5$), 4.60 (br s, Ru═C═CH(C_6H_9)), 5.33 (t, $^3J_{H^aH^b}$ = 3.9 Hz, Ru═C═CHC(═CH^aC$H^b{}_2$CH_2CH_2CH_2)), 1.60, 1.85 and 2.18 (m, Ru═C═CHC(═CH(CH_2)$_4$). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 28.3 (s). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 10.82 (s, $C_5(CH_3)_5$), 102.7 (s, $C_5(CH_3)_5$), 354.5 (t, $^2J_{CP}$ = 15.5 Hz, C_α), 116.6 (s, C_β), 125.0 (s, C_γ), 121.7 (s, ═CH_2), 21.9, 22.7, 25.4, and 29.7 (s, Ru═C═CHC(═CH(CH_2)$_4$)).

Preparation of Allenylidene Complexes [Cp*Ru(═C═C═CRR′)(PEt$_3$)$_2$][BPh$_4$] (R, R′ = H, Ph (5c), Me, Ph (5d), Ph, Ph (5e)). Complex **5c** was obtained from the hydroxyvinylidene **3c** by passing through a Al_2O_3 column (acidic, activity grade I, height of column 10 cm) as previously described, collecting a dark brown band. Yield: 70−80%. Complexes **5d**,**e** were obtained starting from a solution of [Cp*RuCl(PEt$_3$)$_2$] (127 mg, 0.25 mmol) in 15 mL of MeOH to which the alkynol (0.30 mmol) was added. After the mixture was stirred for 8 h at room temperature, addition of $NaBPh_4$ (81 mg, 0.50 mmol) caused the precipitation of a dark brown solid, which was filtered, washed with EtOH and petroleum ether, and dried in vacuo. The solids were recrystallized in a acetone/ethanol (1:2) mixture, yielding dark brown crystals. Yield: 85−90%. Selected spectral data are as follows.

5c: Anal. Calcd for $C_{55}H_{71}BP_2Ru$: C, 72.9; H, 7.90. Found: C, 72.9; H, 7.93. IR (Nujol): ν(C═C═C) 1907 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.92 (t, $^4J_{HP}$ = 1.0 Hz, $C_5(CH_3)_5$), 7.47, 7.74 and 7.86 (m, Ru═C═C═CH(C_6H_5)), 9.13 (s, Ru═C═C═CHPh). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 32.1 (s). ^{13}C{^{1}H} NMR (50.28 MHz, CD_2Cl_2, 298 K): 11.17 (s, $C_5(CH_3)_5$), 103.3 (s, $C_5(CH_3)_5$), 301.6 (t, $^2J_{CP}$ = 17.5 Hz, C_α), 222.2 (s, C_β), 143.2 (s, C_γ), 129.8, 130.4, 131.6, and 140.3 (s, C_6H_5).

5d: Anal. Calcd for $C_{56}H_{73}BP_2Ru$: C, 73.1; H, 8.00 Found: C, 73.2; H, 7.97. IR (Nujol): ν(C═C═C) 1908 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.82 (t, $^4J_{HP}$ = 1.2 Hz, $C_5(CH_3)_5$), 7.38, 7.67, and 7.96 (m, Ru═C═C═CMe(C_6H_5)), 1.94 (s, Ru═C═C═CMePh). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 32.8 (s). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 10.95 (s, $C_5(CH_3)_5$), 102.1 (s, $C_5(CH_3)_5$), 293.9 (t, $^2J_{CP}$ = 18.2 Hz, C_α), 210.3 (s, C_β), 149.8 (s, C_γ), 127.0, 129.3, 131.5, and 142.3 (s, C_6H_5), 30.77 (s, CH_3).

5e: Anal. Calcd for $C_{61}H_{75}BP_2Ru$: C, 74.6; H, 7.70. Found: C, 74.6; H, 7.76. IR (Nujol): ν(C═C═C) 1907 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.86 (t, $^4J_{HP}$ = 1.1 Hz, $C_5(CH_3)_5$), 7.45, 7.67 and 7.72 (m, Ru═C═C═C(C_6H_5)$_2$). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 33.1 (s). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 10.89 (s, $C_5(CH_3)_5$), 102.4 (s, $C_5(CH_3)_5$), 293.1 (t, $^2J_{CP}$ = 18.3 Hz, C_α), 217.0 (t, $^3J_{CP}$ = 2.2 Hz, C_β), 150.8 (s, C_γ), 128.6, 128.8, 130.4, and 144.2 (s, C_6H_5).

Preparation of Hydrido Enynyl Complexes [Cp*RuH{C≡CC(═CH$_2$)Ph}(PEt$_3$)$_2$][BPh$_4$] (6d). A solution of the hydroxyalkynyl hydride **1d** was passed through a column with Al_2O_3 (acidic, activity grade I, height of column 5 cm) as previously described, but with cold solvents (0 °C) as eluents being used as a precaution. A yellow band was obtained, giving rise to a pale yellow solid after the solvent was removed. Yield: 70−80%. Microanalysis was not carried out because this compound rearranges to the vinylvinylidene isomer **4d** in the solid state. Selected spectral data for **6d** are as follows. IR (Nujol): ν(C≡C) 2090, ν(Ru−H) 2020, ν(C═C) 1560 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 273 K): δ −9.23 (t, $^2J_{HP}$ = 29.7 Hz, Ru−H), 1.71 (t, $^4J_{HP}$ = 1.1 Hz, $C_5(CH_3)_5$), 5.27 and 5.61 (br s, 1H each, RuC≡CC(═CH_2)Ph)), 7.32, 7.34, and 7.55 (m, RuC≡CC(═CH_2)(C_6H_5)). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 37.6 (s). ^{13}C{^{1}H} NMR (201.12 MHz, $CDCl_3$, 273 K): 10.21 (s, $C_5(CH_3)_5$), 101.7 (s, $C_5(CH_3)_5$), 100.0 (t, $^2J_{CP}$ = 30.9 Hz, C_α), 115.0 (s, C_β), 133.2 (s, C_γ), 116.9 (s, RuC≡CC(═CH_2)Ph)), 125.9, 127.9, 128.1, and 139.0 (s, C_6H_5).

Preparation of Alkynylphosphonio Complexes [Cp*Ru{C≡CC(PEt$_3$)RR′}(PEt$_3$)$_2$][BPh$_4$] (R, R′ = Me, Me (7f), C$_5$H$_{10}$ (7g)). Complexes **7f**,**g** were obtained by starting from a solution of [Cp*RuCl(PEt$_3$)$_2$] (127 mg, 0.25 mmol) in 15 mL of MeOH to which the alkynol (0.30 mmol) was added. After the mixture was stirred for 8 h at room temperature, addition of $NaBPh_4$ (81 mg, 0.50 mmol) caused the precipitation of a brown solid, which was filtered, washed with EtOH and petroleum ether, and dried in vacuo. Slow crystallization from a acetone/ethanol (1:2) mixture gave dark red crystals. Yield: 40−45%. Selected spectral data are as follows.

7f: Anal. Calcd for $C_{57}H_{86}BP_3Ru$: C, 70.1; H, 8.88. Found: C, 70.1; H, 8.86. IR (Nujol): ν(C≡C) 2050 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.68 (t, $^4J_{HP}$ = 1.2 Hz, $C_5(CH_3)_5$), 1.27 (d, $^3J_{HP'}$ = 15.5 Hz, RuC≡CC(PEt$_3$)(CH_3)$_2$). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 31.9 (d, $^5J_{PP'}$ = 3.6 Hz, Cp*Ru(PEt_3)$_2$), 40.3 (t, $^5J_{PP'}$ = 3.6 Hz, RuC≡CC(PEt_3)Me_2). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 11.03 (s, $C_5(CH_3)_5$), 91.43 (t, $^2J_{CP}$ = 1.8 Hz, $C_5(CH_3)_5$), 103.4 (t, $^2J_{CP}$ = 2.9 Hz, C_α), 99.03 (d, $^2J_{CP'}$ = 5.2 Hz, C_β), 33.55 (d, $^1J_{CP'}$ = 47.2 Hz, C_γ), 6.88 (d, $^2J_{CP'}$ = 5.7 Hz, Ru−C≡CC(PEt$_3$)(CH_3)$_2$).

7g: Anal. Calcd for $C_{60}H_{90}BP_3Ru$: C, 70.8; H, 8.92. Found: C, 70.7; H, 8.88. IR (Nujol): ν(C≡C) 2037 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.69 (t, $^4J_{HP}$ = 1.6 Hz, $C_5(CH_3)_5$), 1.16, 1.27, and 1.58 (m, RuC≡CC(PEt$_3$)(CH_2)$_5$). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 32.8 (d, $^5J_{PP'}$ = 4.7 Hz, Cp*Ru(PEt_3)$_2$),

38.8 (t, $^5J_{PP'}$ = 4.7 Hz, RuC≡CC(*P*Et$_3$)Me$_2$). ^{13}C{^{1}H} NMR (50.28 MHz, $CDCl_3$, 298 K): 11.20 (s, $C_5(CH_3)_5$), 91.52 (t, $^2J_{CP}$ = 2.1 Hz, $C_5(CH_3)_5$), 116.7 (t, $^2J_{CP}$ = 1.8 Hz, C_α), 96.12 (d, $^2J_{CP'}$ = 7.3 Hz, C_β), 40.47 (d, $^1J_{CP'}$ = 47.0 Hz, C_γ), 10.42 (d, $^2J_{CP'}$ = 10.4 Hz, RuC≡C$\overline{C(PEt_3)(CH_2(CH_2)_3CH_2)}$), 24.93 and 33.26 (s, RuC≡C$\overline{C(PEt_3)(CH_2(CH_2)_3CH_2)}$).

X-ray Structure Determination of the Compounds 4d, 5e, and 7f. X-ray diffraction measurements were made on crystals of the appropriate size, which were mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer (T = 290 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). Accurate unit cell parameters and an orientation matrix were determined in each case by least-squares fitting from the settings of 25 high-angle reflections. Crystal data and details of the data collection and refinement are given in Table 5. Data were collected by the $\omega/2\theta$ scan method. Lorentz and polarization corrections were applied. Decay was monitored by measuring 3 standard reflections every 100 measurements. Decay and semiempirical absorption corrections (ψ method) were also applied.

The structure was solved in each case by Patterson methods and subsequent expansion of the model using DIRDIF.[31] Reflections having $I > 3\sigma(I)$ were used for structure refinement. For compound **4d** Ru, P, and the C atoms in the vinylvinylidene ligand were anisotropically refined; the remaining non-hydrogen atoms were isotropically refined. For compound **5e** all non-hydrogen atoms were anisotropically refined. Disorder was found for an ethyl group in compound **7f**, and it was modeled using two positions for C(32) and C(33) with aproximately two-thirds and one-third occupation. All non-hydrogen atoms for **7f** except C atoms in ethyl groups were anisotropically refined. In every case the hydrogen atoms were included at idealized positions and not refined. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[32] software system and ORTEP[33] for plotting.

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Supporting Information Available: Tables giving crystallographic data for **4d**, **5e**, and **7f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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