Hydrido(3-hydroxyalkynyl) Complexes as Intermediates in the Activation of Propargyl Alcohol Derivatives by [Cp*RuCl(dippe)] [Cp* = C_5Me_5, dippe = 1,2-bis(diisopropylphosphanyl)ethane]

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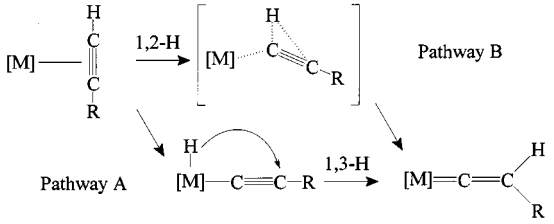
The reaction of propargyl alcohol derivatives with the complex [Cp*RuCl(dippe)] [dippe = 1,2-bis(diisopropylphosphane)ethane] and $NaBPh_4$ in MeOH yields hydrido(3-hydroxyalkynyl) compounds [Cp*Ru(H){C≡CC(OH)RR′}(dippe)][BPh_4] [R, R′ = Ph, Ph (**1a**); H, Ph (**1b**); H, Me (**1c**)]. These represent intermediates in the formation of 3-hydroxyvinylidene species [Cp*Ru{=C=CHC(OH)RR′}(dippe)][BPh_4] [R, R′ = Ph, Ph (**2a**); H, Ph (**2b**); H, Me (**2c**)], into which they irreversibly rearrange both in solution and in the solid state. Solution kinetic studies have been carried out on this isomerization process. Ulterior dehydration processes are feasible, resulting in the formation of allenylidene [Cp*Ru(=C=C=CRR′)(dippe)][BPh_4] [R, R′ = Ph, Ph (**3a**); H, Ph (**3b**)] or vinylvinylidene [Cp*Ru{=C=CHCH(=CH_2)}(dippe)][BPh_4] (**4**) species. The X-ray crystal structure of the novel secondary allenylidene complex [Cp*Ru(=C=C=CHPh)(dippe)][BPh_4] is presented.

Introduction

It is well known that coordination of terminal alkynes to metal complexes reverses the relative stabilities of acetylene and vinylidene, this being a general procedure used for the synthesis of a wide range of vinylidene complexes.[1] In the case of propargyl alcohols HC≡CC(OH)R_2, subsequent dehydration of the resulting 3-hydroxyvinylidene complex may eventually lead to allenylidene compounds.[2,3] By analogous methods, complexes containing even longer unsaturated carbon chains have been obtained.[2,4] Interest in vinylidene complexes has been partly focussed on their utility in stoichiometric or catalytic transformations of alkenes and alkynes.[5] On the other hand, how the alkyne to vinylidene tautomerization takes place is still subject of research.

As a first reasonable approach to the isomerization mechanism, one may envisage oxidative addition of the alkyne to the metal centre thereby furnishing an alkynyl(hydrido)-metal complex.[6] (Scheme 1, Pathway A). Several cases of this are known in the chemistry of Co, Rh, and Ir,[7] and it is supported by ab initio MO calculations.[8] In the case of d^6 systems (Ru^{II}, Os^{II}, Mn^{I}), however, a pathway involving oxidative addition would seem to be a thermodynamically unfavourable process,[9] and a direct 1,2-hydrogen shift in the initially formed alkyne complex would be the most plausible pathway to a vinylidene[10] (Scheme 1, Pathway B). Actually, reactions of $[CpM(PR_3)_2]^+$ (M = Fe, Ru, Os) fragments with 1-alkynes normally lead directly to vinylidene complexes $[CpM(=C=CHR)(PR_3)_2]^+$ without any observable intermediates.[1,11] In the case of the complex [CpOsCl(P*i*Pr_3)$_2$], the isomerization of the π-alkyne complex [CpOsCl(P*i*Pr_3)(η^2-HC≡CPh)] into the vinylidene derivative takes place without any evidence of the intermediacy of alkynyl(hydrido) species.[12] Its reaction with alkynes and alkynols to afford the first examples of alkynyl(hydrido)osmium(IV) complexes that do not rearrange to their vinylidene isomers has only recently been reported.[13] In the case of ruthenium, there are several examples of direct isomerization to vinylidene,[14] vinylidene/π-alkyne equilibria,[15] and vinylidene to π-alkyne isomerization,[16] for which alkynyl(hydrido) species have never been detected. The relatively recent use of basic ruthenium fragments containing η^5-C_5Me_5 and their application in the activation of terminal alkynes[17] has allowed new insights into this matter.



Scheme 1

Thus, study of the interaction of [Cp*RuCl(dippe)] with 1-alkynes allowed for the first time the isolation and characterization of metastable alkynyl(hydrido)ruthenium(IV) species as intermediates in the formation of the more stable vinylidene isomers.[18] These studies showed that the mechanism of this isomerization involves hydrido ligand dissociation as a proton and subsequent protonation on the β-carbon atom of the alkynyl ligand (Scheme 2).[19] It was also found that the isolation of these metastable intermediates is strongly dependent on the preparative method

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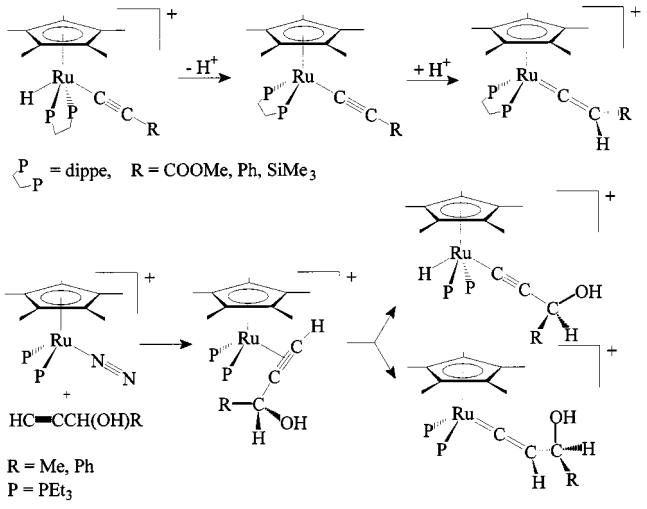
used. In the case of propargyl alcohols, which form complexes that are more soluble in the methanol used as solvent, this dependence proved to be crucial in that only 3-hydroxyvinylidene or dehydration products were isolated in the course of our earlier studies on [Cp*RuCl(dippe)].[20] A similar study has recently been carried out on the system [Cp*RuCl(PEt_3)$_2$], which contains a monodentate and sterically less demanding phosphane as a co-ligand. In this case, it was possible to detect η^2-alkynol derivatives and to monitor by $^{31}P\{^1H\}$ NMR their isomerization by two alternative pathways that are simultaneously operative at low temperature, namely direct 1,2-H shift and oxidative addition.[21] Furthermore, following an appropriate strategy, hydrido(3-hydroxyalkynyl) derivatives of the type [Cp*Ru(H){C≡CC(OH)R_2}(PEt_3)$_2$][BPh_4] were isolated and fully characterized. In view of these results, we have now re-examined the reactivity of [Cp*RuCl(dippe)] towards alkynols. As a result, we have been able to isolate new hydrido(3-hydroxyalkynyl) complexes, which have allowed us to perform further kinetic studies of the isomerization process into 3-hydroxyvinylidene species. Dehydration reactions of these compounds have led to new allenylidene and vinylvinylidene complexes, which have been fully characterized.



Scheme 2

Results and Discussion

The metastable complexes [Cp*Ru(H){C≡CC(OH)RR′}(dippe)][BPh_4] [R, R′ = Ph, Ph (**1a**); H, Ph (**1b**); H, Me (**1c**)] were isolated by precipitation following addition of the solid chloro complex [Cp*RuCl(dippe)] to a solution of $NaBPh_4$ and the alkyne in the minimum volume of MeOH at 0 °C. With an alkyne such as HC≡CCOOEt, the complex [Cp*Ru(H)(C≡CCOOEt)(dippe)][BPh_4] (**1d**) is easily obtained by adding $NaBPh_4$ prior to the alkyne. However, alkynols form more alcohol-soluble complexes owing to the presence of the hydroxy group. As a consequence, hydrido(3-hydroxyalkynyl) compounds can remain unnoticed due to the fact that isomerization to the vinylidene may occur to a greater or lesser extent prior to precipitation. This could only be avoided by adhering strictly to the aforementioned procedure and accounts for the fact that species analogous to compounds **1a**−**1c** were not detected in our previous work on this system. Furthermore, the reaction with HC≡C−CH_2OH yields the alkynyl(hydrido) complex only as a minor product even under these experimental conditions. Only in the case of HC≡CC(OH)Ph_2 was it possible to isolate the complex [Cp*Ru(H){C≡CC(OH)Ph_2}(dippe)][BPh_4] as a solid in pure form, uncontaminated by any of the 3-hydroxyvinylidene isomer. In the IR spectrum of compound **1a**, the ν(OH), ν(C≡C), and ν(Ru−H) bands are seen at 3578, 2100, and 2045 cm^{-1}, respectively. The $^{31}P\{^1H\}$ NMR spectrum recorded in $CDCl_3$ at 0 °C consists of a singlet at δ = 73.1, whereas in the ^1H NMR spectrum the terminal hydride ligand appears as a triplet at δ = −9.17 with a coupling constant of 30.5 Hz. Since this compound does not isomerize at 0 °C, it was possible to record the $^{13}C\{^1H\}$ NMR spectrum, which features a triplet at δ = 103.7 and a singlet at δ = 116.4, in good accord with the expected resonances for the α- and β-carbon atoms of the alkynyl ligand. In the case of the alkynols HC≡CCH(OH)R (R = Me, Ph), the corresponding hydrido(3-hydroxyalkynyl) complexes **1b** and **1c** could also be obtained in good yields, but were invariably accompanied by minor amounts of their 3-hydroxyvinylidene isomers.

The spectral properties of these complexes closely resemble those of complex **1a**. The main difference is observed in the $^{31}P\{^1H\}$ NMR spectrum of **1b** (Figure 1), where the presence of a chiral centre at the γ-carbon atom induces a magnetic nonequivalence of the phosphorus atoms, giving rise to an AB spin system at low temperatures ($^3J_{PP'}$ = 18 Hz). This pattern has also been observed in some analogous complexes such as [Cp*Ru(H){C≡CC(OH)RR′}(PEt_3)$_2$][BPh_4] (R, R′ = H, Ph; Me, Ph) ($^3J_{PP'}$ = 20−21 Hz)[21] and [CpOs(H){C≡CC(OH)MePh}(P*i*Pr_3)$_2$][PF_6] ($^3J_{PP'}$ = 23.5 Hz).[13] The pattern is

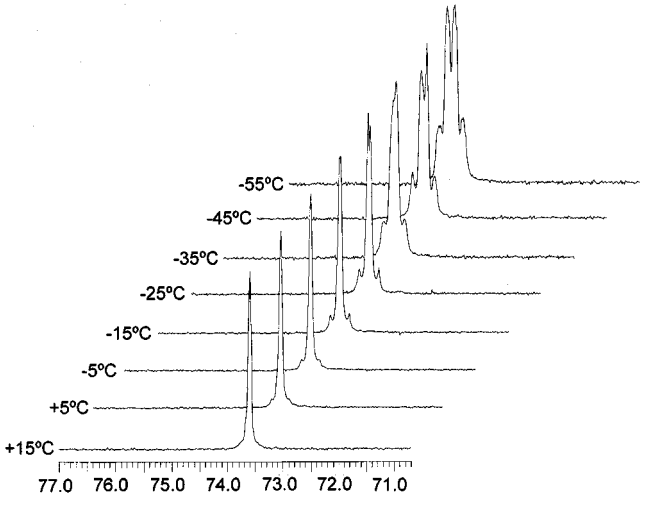


Figure 1. Stacked $^{31}P\{^1H\}$ NMR spectra illustrating the evolution of the [Cp*Ru(H){C≡CCH(OH)Ph}(dippe)][BPh_4] (**1b**) signal with temperature

temperature-dependent and the doublets coalesce to a singlet above +15 °C, most likely due to an averaging of the anisotropy of the phosphorus atom environments through rotation of the CH(OH)Ph group about the C−C bond.

Compounds **1a−1c** isomerize into the vinylidene species [Cp*Ru{=C=CHC(OH)RR′}(dippe)][BPh_4] [R, R′ = Ph, Ph (**2a**); H, Ph (**2b**); H, Me (**2c**)] both in solution and in the solid state at room temperature (see Scheme 3), as has also been reported elsewhere.[6,18,21] However, as for [Cp*RuH(C≡CCOOMe)(dippe)][BPh_4],[19] the tautomerization of **1d** into the vinylidene complex [Cp*Ru(=C=CHCOOEt)(dippe)][BPh_4] (**2d**) only occurs in solution, and not in the solid state. Orange crystalline products, identified as vinylidene complexes by IR and NMR spectroscopy, were obtained when samples of **2a−2c** were heated in the solid state for several hours at 40 °C. In contrast to the other complexes, a clean preparation of [Cp*Ru{=C=CHC(OH)Ph_2}(dippe)][BPh_4] (**2a**) by isomerization of **1a** in solution is not possible due to the fact that spontaneous dehydration ensues. The vinylidene protons of **2a** and **2d** appear as broad singlets at δ = 4.37 and 4.52 in the respective ^{1}H NMR spectra, while in the ^{13}C{^{1}H} NMR spectra, the vinylidene α-carbon atoms give triplets at δ = 338.8 and 338.7 with coupling constants of 16.1 and 14.3 Hz, respectively. In the ^{1}H NMR spectra of **2b** and **2c**, the vinylidene protons appear as doublets at δ = 4.33 and 3.98, while the protons on the γ-carbon atoms give signals at δ = 5.40 (doublet) and 4.51 (doublet of quadruplets), respectively. The ^{31}P{^{1}H} NMR spectra of **2b** (Figure 2) and **2c** at 25 °C each consist of an AB spin pattern with a coupling constant of 17.1 Hz. In these cases, the doublets are more clearly separated from each other. This suggests an increased anisotropy in the chemical environments of the phosphorus atoms of **2b** and **2c** as compared to **1b** and **1c** due to the effect of the chiral centre on the γ-carbon atom. This can be attributed to the change in hybridization from sp to sp^2 at the β-carbon atom. The doublets move closer to each other as the temperature is increased, indicating chemical shift averaging, but do not coalesce even at 45 °C. In fact, the phosphorus atoms are expected to remain magnetically nonequivalent even at the fast-exchange limit due to the presence of the chiral substituent. This is consistent with the observed pattern, which has also been reported for related compounds such as [Cp*Ru{=C=CHCH(OMe)-Me}(PMe_2Ph)$_2$][PF_6] [17a] and [(η^5-C_9H_7)Ru{=C=CHCH(OMe)Ph}(PPh_3)$_2$][PF_6].[22]

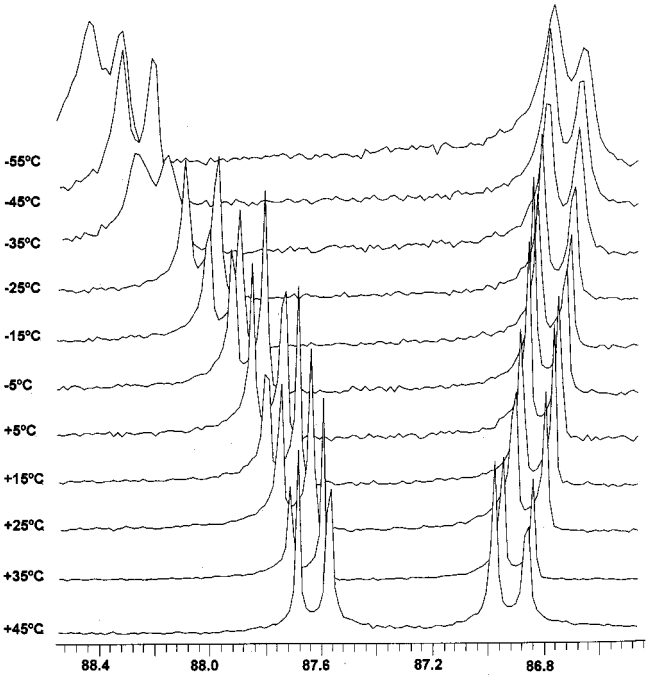
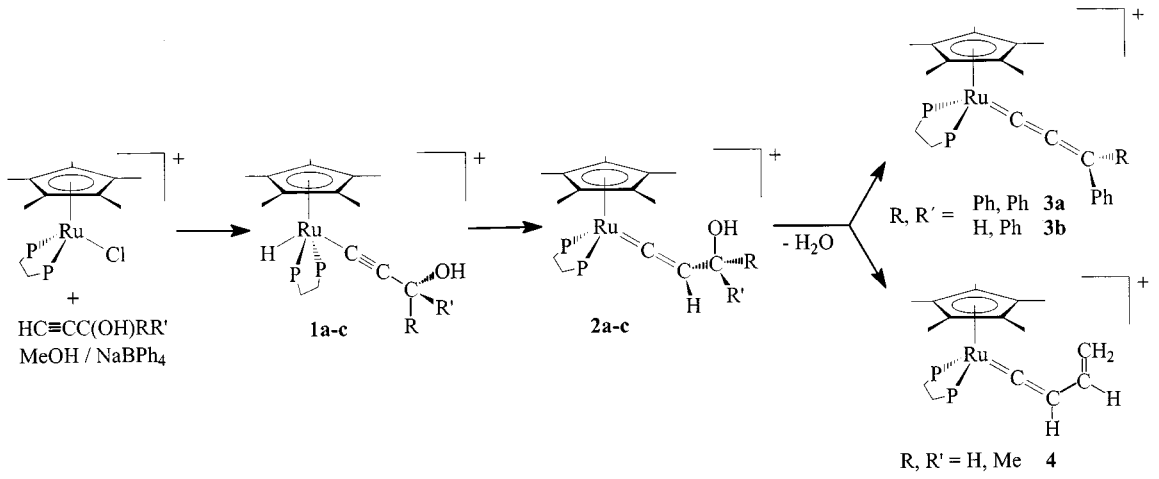


Figure 2. Stacked ^{31}P{^{1}H} NMR spectra illustrating the evolution of the [Cp*Ru{=C=CHCH(OH)Ph}(dippe)][BPh_4] (**2b**) signal with temperature

In order to establish the sequence of intermediates in the activation of alkynes and alkynols by the moiety {[Cp*Ru(dippe)]$^+$}, we first attempted to detect the intermediacy of π-alkyne complexes in the first step of the overall process. While an equilibrium between the π-alkyne and alkynyl(hydrido) species was found for the previously described [Cp*Ru(η^2-HC≡CH)(dippe)][BPh_4],[19] in the case of substituted alkynes these adducts are expected to be thermodyn-



Scheme 3

amically less favourable. The substituent on the alkyne makes steric interactions with the phosphane and Cp* methyl groups much stronger when this ligand is bound to the metal centre in an η^2-fashion as compared to those in an η^1-alkynyl or -vinylidene complex.

At variance with our latest results on the system containing the moiety $\{[Cp^*Ru(PEt_3)_2]^+\}$, the reaction of alkynes with labile cationic adducts of the type $[Cp^*Ru(L)(dippe)]^+$ (L = C_2H_4, N_2)[23] at low temperature did not provide any supporting evidence for the formation of π-alkyne intermediates. Upon addition of an excess of the appropriate alkynol (or HC≡CCOOEt) to a precooled $CDCl_3$ solution of the ethylene complex $[Cp^*Ru(C_2H_4)(dippe)][BPh_4]$[23] at −40 °C, the initial resonance in the $^{31}P\{^1H\}$ NMR spectrum (one singlet at δ = 77.9) remained unchanged below −20 °C. Above this temperature, this signal irreversibly disappeared, being replaced by a single resonance attributable to the corresponding alkynyl(hydrido) species **1a−1d**. The metallic fragments $\{[Cp^*Ru(PEt_3)_2]^+\}$ and $\{[Cp^*Ru(dippe)]^+\}$ are able to activate C−H bonds in alkynes by virtue of their high basicities. This ability is enhanced for the $\{[Cp^*Ru(dippe)]^+\}$ moiety: While complexes containing PEt_3 give mixtures of alkynyl(hydrido) and vinylidene species, formed through the intermediacy of π-alkyne adducts, the analogous compounds containing dippe only form vinylidene species, according to a pathway involving the intermediacy of the alkynyl(hydrido) species. Prior coordination of the alkyne seems to favour the formation of the vinylidene isomer by a direct pathway involving a 1,2-hydrogen shift, as has been observed for $[Cp^*Ru(\eta^2\text{-}HC{\equiv}CH)(dippe)]^+$,[19] $[Cp^*Ru\{\eta^2\text{-}HC{\equiv}CCH(OH)R\}(PEt_3)_2]^+$,[21] and $[CpOsCl(\eta^2\text{-}HC{\equiv}CPh)(P\mathit{i}Pr_3)]$.[13]

The kinetics of the isomerization of complexes **1a−1d** into **2a−2d** has been studied. The temperature range in which the process takes place at measurable rates is clearly determined by the substituent on the γ-carbon atom (see Table 1). Thus, the isomerization of **1a** proceeds at measurable rates in the range 25−45 °C, whereas for **1d** it can only be observed at 10−30 °C. The stepwise substitution of the phenyl groups on the γ-carbon atom decreases the temperature range by ca. 10 °C. In all cases, the rate is first order with respect to the alkynyl(hydrido) complex. From Eyring plots, the activation parameter was determined (Table 1) to be $\Delta G^{\ddagger}_{298} \approx 21$ kcal mol^{-1} in each case. These results can be compared with those reported for cobalt complexes, i.e. $\Delta G^{\ddagger}_{298} \approx 31$ kcal mol^{-1} for $[Co(H)(C{\equiv}CPh)PP_3]^+$ [PP_3 = $P(CH_2CH_2PPh_2)_3$],[7a] and with our earlier kinetic studies on the isomerization of $[Cp^*Ru(H)(C{\equiv}CR)(dippe)]^+$ [19] (R = COOMe, Ph, $SiMe_3$), in which $\Delta G^{\ddagger}_{298}$ was estimated to be ca. 20 kcal mol^{-1}. Migration of the hydrido ligand as a proton following dissociation and subsequent protonation of the β-carbon atom has previously been proposed as the mechanism for this transformation in solution, and it is supported by sound experimental evidence.[7a,19] It is further supported in the present case by the observed solvent effect on the isomerization rate. The formation of the vinylidene complex **2d** from **1d** is subject to a strong solvent dependence: the process takes place more rapidly in acetone, in which the constant at 5 °C is $(3.16 \pm 0.16) \times 10^{-3}$ s^{-1}, whereas a comparable constant of $(3.74 \pm 0.21) \times 10^{-3}$ s^{-1} is only found at 25 °C in $CDCl_3$. The slower rate in $CDCl_3$ made this the solvent of choice for our kinetic NMR studies. In acetone, the time scale of the faster isomerization overlaps with that of the process of ethylene substitution used to obtain the alkynyl(hydrido) species in situ. Chloroform invariably contains trace amounts of HCl (DCl), which may hamper the dissociation of the hydride as a proton during the course of isomerization. Given the small quantities of acid present, it merely slows down the process, but it is known that strong acids such as HBF_4 can completely inhibit the isomerization. On the other hand, the Lewis base character of acetone possibly has the reverse effect (i.e. base catalysis), accelerating the proton transfer from the metal centre to the β-carbon atom.

As a consequence of the steric hindrance and electron-releasing ability of the $\{[Cp^*Ru(dippe)]^+\}$ moiety, its vinylidene complexes are less electrophilic and more stable towards the addition of an alcohol to the α-carbon atom, but dehydration should also be disfavoured in electron-rich complexes.[4] However, complex **2a** undergoes spontaneous

Table 1. Pseudo first order rate constants and activation parameters for alkynyl(hydrido) to vinylidene isomerization

R =	**1a → 2a** C(OH)Ph_2	**1b → 2b** CH(OH)Ph	**1c → 2c** CH(OH)Me	**1d → 2d** COOEt
T [K]	$k \times 10^{-3}$ s^{-1}	$k \times 10^{-3}$ s^{-1}	$k \times 10^{-3}$ s^{-1}	$k \times 10^{-3}$ s^{-1}
283	−	−	1.22 ± 0.03	0.6 ± 0.1
288	−	0.93 ± 0.03	2.20 ± 0.03	1.04 ± 0.08
293	−	1.91 ± 0.03	5.5 ± 0.4	1.9 ± 0.2
298	0.42 ± 0.02	3.2 ± 0.1	8.3 ± 0.4	3.7 ± 0.2
303	1.11 ± 0.03	7.4 ± 0.5	14.3 ± 0.6	6.4 ± 0.1
308	2.17 ± 0.07	10.0 ± 0.6	−	−
313	3.8 ± 0.1	−	−	−
318	5.9 ± 0.6	−	−	−
$\Delta H^{\ddagger}$ [kcal/mol]	24 ± 2	21.0 ± 1.5	21 ± 1	20 ± 1
$\Delta S^{\ddagger}$ [cal/mol K]	7 ± 6	1 ± 5	1 ± 5	−4 ± 4
$\Delta G^{\ddagger}_{298}$ [kcal/mol]	22 ± 2	21 ± 2	21 ± 2	21 ± 2

dehydration in solution, yielding the allenylidene complex [Cp*Ru(=C=C=CPh_2)(dippe)][BPh_4] (**3a**) as a dark-red solid after workup. In the case of 3-hydroxyvinylidene complexes bearing one H on the γ-carbon atom (**2b** and **2c**), complete dehydration can only be achieved by passing a solution in CH_2Cl_2 through an acidic alumina column. In the first case, the *secondary* allenylidene [Cp*Ru(=C=C=CHPh)(dippe)][BPh_4] (**3b**) is obtained as a dark-green solid (see Scheme 3). The IR absorption due to the cumulated C=C=C in **3a** and **3b** appears at 1890 and 1915 cm^{-1}, respectively, i.e. at the lower end of the usual range (1800−2100 cm^{-1}).[2] Other monosubstituted allenylidenes have been obtained by activation of secondary propargyl alcohols with the fragments $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2]^+$ [22] and $[Ru(Ph_2PCH_2PPh_2)_2Cl]^+$.[25] In both cases, the infrared absorption is seen at higher $\tilde{\nu}$ [cm^{-1}] for monosubstituted than for disubstituted systems. Monosubstituted allenylidenes are very scarce due to their higher reactivity, and are only known in electron-rich complexes. Ongoing studies on allenylidene reactivity have confirmed that **3b** is indeed more reactive than **3a**.

In the $^{13}C\{^1H\}$ NMR spectra of compounds **3a** and **3b**, the metal-bound carbon atoms show characteristic low-field resonances (δ = 287.2 and 294.3), and the order $\delta(C^\alpha) > \delta(C^\beta) > \delta(C^\gamma)$ is found in both cases. The ^1H NMR spectrum of the allenylidene compound **3b** shows a broad singlet at δ = 9.20 due to the proton on the γ-carbon atom as the only notable feature. Slow recrystallization of **3b** from acetone/ethanol (1:2) afforded green crystals suitable for X-ray diffraction analysis, and its X-ray crystal structure was determined. An ORTEP[24] view of the cationic complex is shown in Figure 3.

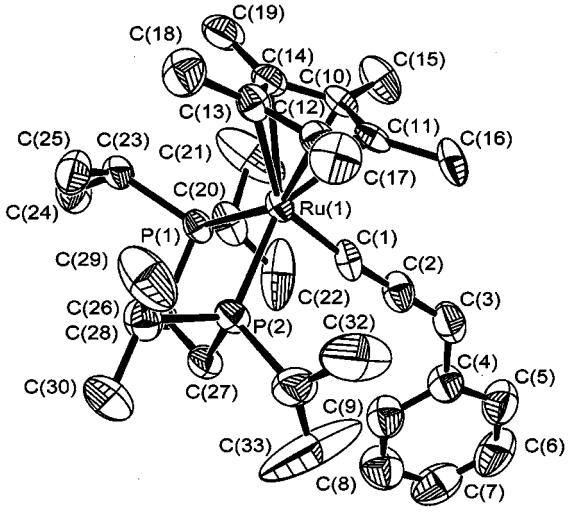


Figure 3. ORTEP view of the cation [Cp*Ru(=C=C=CHPh)(dippe)]$^+$ in compound **3b** showing the atom labelling scheme; hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ru1−C10 2.266(7), Ru1−C11 2.258(6), Ru1−C12 2.294(7), Ru1−C13 2.337(7), Ru1−C14 2.329(7), Ru1−C1 1.865(8), Ru1−P1 2.3479(19), Ru1−P2 2.336(2), C1−C2 1.249(10), C2−C3 1.320(12); P1−Ru1−P2 81.99(7), Ru1−C1−C2 172.8(7), C1−C2−C3 177.5(9), C2−C3−C4 128.1(8)

The allenylidene ligand appears to be almost linearly assembled on the ruthenium centre. The bond lengths Ru(1)−C(1) = 1.865(8) Å, C(1)−C(2) = 1.249(10) Å, and C(2)−C(3) = 1.320(12) Å are consistent with a substantial contribution from the alkynyl mesomer, as is usually the case for compounds of this type. In a recent review, the normal ranges of such distances for a variety of allenylidene complexes were quoted as $Ru-C^\alpha$ = 1.84−2.00 Å, $C^\alpha-C^\beta$ = 1.18−1.27 Å, and $C^\beta-C_\gamma$ = 1.35−1.41 Å, respectively.[2] From a rapid overview, it can be concluded that electron-rich allenylidenes of this type more closely resemble the mesomeric form A, which is the usual way of representing them.

The atoms of the allenylidene ligand define a least-squares plane that forms a dihedral angle of 3.51° with the plane defined by C(1), Ru(1), and the centroid of the Cp*. This disposition has been commonly observed in other half-sandwich (allenylidene)Ru derivatives, since it appears to maximize the effectiveness of the metal−ligand π-overlap.[26] It is interesting to note that in this structure the phenyl substituent of the allenylidene ligand is oriented in an *endo* fashion, being directed away from the methyl substituents of the Cp* ring in order to minimize steric interactions. This is in contrast to the structure of the closely related derivative [CpRu(=C=C=CMePh)(dippe)][BPh_4],[20] in which the phenyl group is *exo*-oriented with respect to the Cp ligand and points away from the phosphane isopropyl groups. This example once again illustrates the effect of the differences in the steric properties of the Cp and Cp* ligands on the stereochemistry of their complexes.

Finally, dehydration of compound **2c** leads to the vinylvinylidene complex [Cp*Ru(=C=CH−CH=CH_2)(dippe)][BPh_4] (**4**) rather than to the corresponding allenylidene derivative (see Scheme 3). This is expected for 3-hydroxyvinylidene compounds bearing labile protons on their δ-carbon atoms, as a consequence of the reduced stabilization of the partial positive charge generated on the γ-carbon atom in allenylidene ligands (Scheme 4, canonical form B). The ^1H NMR spectrum of **4** exhibits four signals in the range δ = 4.4−6.2, which were assigned by two-dimensional correlation (COSY) and show an appropriate coupling pattern. The vinylidene carbon atom gives rise to a low-field triplet at δ = 347.7 in the $^{13}C\{^1H\}$ NMR spectrum.

$$[Ru]^+{=}C{=}C{=}CRR' \longleftrightarrow [Ru]{-}C{\equiv}C{-}\overset{+}{C}RR'$$

A B

Scheme 4

Our current interest is centred on the reactivity of the allenylidene complexes described in this work. Despite their electron-rich character, they are able to undergo nucleophilic attack by a series of donor molecules. The resulting species will be described in detail in a forthcoming paper.

Conclusion

It has been demonstrated that previously overlooked hydrido(3-hydroxyalkynyl)Ru^{IV} complexes of the type [Cp*

Ru(H){C≡CC(OH)RR′}(dippe)][BPh_4] are the only observable intermediates in the activation of propargyl alcohols by [Cp*RuCl(dippe)], and that they can be isolated in high yields by careful control of the reaction conditions. These species rearrange into their vinylidene tautomers according to a dissociative mechanism. The thus generated 3-hydroxyvinylidene complexes undergo dehydration yielding either allenylidene or vinylvinylidene species depending upon the substituents present at the γ-carbon atom.

Experimental Section

General Remarks: All synthetic operations were performed under dry dinitrogen or argon using 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 prior to use. [Cp*RuCl(dippe)][27] and [Cp*Ru(η²-CH_2=CH_2)(dippe)][BPh_4][23] were prepared according to reported procedures. − IR spectra were recorded from Nujol mulls of the samples with a Perkin−Elmer FT-IR Spectrum 1000 spectrophotometer. − NMR spectra were recorded with a Varian Unity 400 MHz or a Varian Gemini 200 MHz instrument. Chemical shifts are given in parts per million relative to $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). In the NMR spectra, the tetraphenylborate protons and carbon atoms of all cationic compounds showed signals in the appropriate shift ranges, while in the IR spectra a band was seen at 1580 cm^{-1}. − Microanalyses were performed by the Serveis Científico-Tècnics, Universitat of Barcelona.

Preparation of Alkynyl(hydrido) Derivatives [Cp*RuH(C≡CR)(dippe)][BPh_4] [R = C(OH)Ph_2 (1a), CH(OH)Ph (1b), CH(OH)Me (1c), COOEt (1d)]: [Cp*RuCl(dippe)] (133 mg, 0.25 mmol) was added to a solution of the appropriate alkyne or alkynol (0.30 mmol) and $NaBPh_4$ (81 mg, 0.50 mmol) in MeOH (5 mL) at 0 °C (ice bath). The mixture was allowed to warm until a white microcrystalline solid precipitated, which was collected by filtration, washed with cold EtOH and petroleum ether, and stored at −20 °C. As expected for isomeric compounds, microanalytical data were identical to those for 3-hydroxyvinylidenes **2a**−**2d**. Selected spectroscopic data are as follows.

1a: Yield 226 mg (88%). − $C_{63}H_{79}BOP_2Ru$ (1026.1): calcd. C 73.7, H 7.76; found C 73.8, H 7.74. − IR (Nujol): $\tilde{\nu}$ = 3578 ν(OH), 2100 ν(C≡C), 2045 cm^{-1} ν(RuH). − ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ = −9.17 (t, $^2J_{HP}$ = 30.5 Hz, 1 H, Ru−H), 1.84 [s, 15 H, $C_5(CH_3)_5$], 2.52 (br. s, 1 H, OH), 0.99−1.14 [m, 24 H, PCH(CH_3)$_2$], 1.37 and 1.63 (m, 2 H each, PCH_2), 2.12 and 3.12 (m, 2 H each, PCH), 7.30−7.36 (m, 6 H, C_6H_5), 7.47 (m, 4 H, C_6H_5). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 273 K): δ = 73.1 (s). − $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$, 273 K): δ = 10.97 [s, $C_5(CH_3)_5$], 18.17, 18.77, 19.11, and 20.69 [s, PCH(CH_3)$_2$], 21.43 (m, PCH_2), 24.89 and 27.93 (m, PCH), 75.34 (s, C^γ), 101.3 [s, $C_5(CH_3)_5$], 103.7 (t, $^2J_{CP}$ = 25.2 Hz, C^α), 116.4 (s, C^β), 126.0, 127.6, 128.2, and 145.7 (s, C_6H_5).

1b: Yield 195 mg (82%). − $C_{57}H_{75}BOP_2Ru$ (950.0): calcd. C 72.1, H 7.96; found C 72.1, H 7.90. − IR (Nujol): $\tilde{\nu}$ = 3563 ν(OH), 2106 ν(C≡C), 2062 cm^{-1} ν(RuH). − ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ = −9.11 (t, $^2J_{HP}$ = 30.5 Hz, 1 H, Ru−H), 1.04−1.17 and 1.26−1.36 [m, 24 H, PCH(CH_3)$_2$], 1.82 [s, 15 H, $C_5(CH_3)_5$], 2.08 (m, 4 H, PCH_2), 2.88 and 3.01 (m, 2 H each, PCH), 3.10 (br. s, 1 H, OH), 5.45 [s, 1 H, Ru−C≡CC*H*(OH)Ph], 7.40 and 7.56 (m, 5 H, C_6H_5). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 273 K): δ = 73.7 (s).

1c: Yield 189 mg (85%). − $C_{52}H_{73}BOP_2Ru$ (888.0): calcd. C 70.3, H 8.29; found C 70.1, H 8.29. − IR (Nujol): $\tilde{\nu}$ = 3532 ν(OH), 2115 ν(C≡C), 2050 cm^{-1} ν(RuH). − ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ = −9.10 (t, $^2J_{HP}$ = 31.0 Hz, 1 H, Ru−H), 0.96−1.11 and 1.16−1.21 [m, 24 H, PCH(CH_3)$_2$], 1.35 [d, $^3J_{HH}$ = 6.0 Hz, 3 H, Ru−C≡C−CH(OH)CH_3], 1.84 [s, 15 H, $C_5(CH_3)_5$], 2.08 (m, 4 H, PCH_2), 3.09 (m, 4 H, PCH), 3.43 (br. s, 1 H, OH), 4.50 [q, $^3J_{HH}$ = 6.0 Hz, 1 H, Ru−C≡C−C*H*(OH)CH_3]. − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 233 K): δ = 73.20 (s).

1d: Yield 211 mg (92%). − $C_{53}H_{73}BO_2P_2Ru$ (916.0): calcd. C 69.5, H 8.03; found C 69.4, H 7.89. − IR (Nujol): $\tilde{\nu}$ = 2099 ν(C≡C), 2062 ν(RuH), 1681 cm^{-1} ν(C=O). − ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ = −8.78 (t, $^2J_{HP}$ = 28.2 Hz, 1 H, Ru−H), 0.98−1.27 [m, 24 H, PCH(CH_3)$_2$], 1.19 (t, $^3J_{HH}$ = 6.8 Hz, 3 H, $COOCH_2CH_3$), 1.84 [s, 15 H, $C_5(CH_3)_5$], 1.98 and 2.07 (m, 2 H each, PCH_2), 2.90 (m, 4 H, PCH), 4.12 (q, $^3J_{HH}$ = 6.8 Hz, 2 H, $COOCH_2CH_3$). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 273 K): δ = 72.3 (s). − $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$, 273 K): δ = 10.89 [s, $C_5(CH_3)_5$], 14.37 (s, $COOCH_2CH_3$), 18.24, 18.30, 19.45, and 19.88 [s, PCH(CH_3)$_2$], 21.74 (m, PCH_2), 25.94 and 25.60 (m, PCH), 60.52 (s, $COOCH_2CH_3$), 102.0 (t, $^2J_{CP}$ = 23.0 Hz, C^α), 104.2 [s, $C_5(CH_3)_5$], 109.4 (s, C^β), 164.1 (s, *C*OOEt).

Preparation of Vinylidene Derivatives [Cp*Ru(=C=CHR)(dippe)][BPh_4] [R = C(OH)Ph_2 (2a), CH(OH)Ph (2b), CH(OH)Me (2c), COOEt (2d)]: The solid complexes **1a**−**1c** (1 mmol) were heated at 35 °C for 3 h under an inert gas, in the course of which they gradually underwent a colour change from white/yellow to orange. This corresponded to a quantitative and clean isomerization process to give the respective vinylidene isomers. Complex **2d** was obtained after stirring a solution of **1d** (916 mg, 1 mmol) in acetone for 2 h at room temperature, followed by removal of the solvent. Selected IR and NMR spectroscopic data are as follows.

2a: Yield 1026 mg (100%). − $C_{63}H_{79}BOP_2Ru$ (1026.1): calcd. C 73.7, H 7.76; found C 73.8, H 7.72. − IR (Nujol): $\tilde{\nu}$ = 3558 ν(OH), 1633 cm^{-1} ν(C=C). − ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.94−1.18 [m, 24 H, PCH(CH_3)$_2$], 1.81 [s, 15 H, $C_5(CH_3)_5$], 1.73 and 1.86 (m, 2 H each, PCH_2), 2.02 and 2.23 (m, 2 H each, PCH), 2.32 (br. s, 1 H, OH), 4.37 (br. s, 1 H, Ru=C=CHR), 7.27−7.34 (m, 10 H, C_6H_5). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ = 83.7 (s). − $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ = 11.04 [s, $C_5(CH_3)_5$], 18.46, 18.67, 19.58, and 20.27 [s, PCH(CH_3)$_2$], 21.44 (vt, $^{1,3}J_{CP}$ = 21.5 Hz, PCH_2), 25.50 and 33.39 (m, PCH), 102.8 [s, $C_5(CH_3)_5$], 121.3 (s, C^β), 95.63 (s, C^γ), 125.4, 127.9, 128.6, and 145.5 (s, C_6H_5), 338.7 (t, $^2J_{CP}$ = 16.1 Hz, C^α).

2b: Yield 950 mg (100%). − $C_{57}H_{75}BOP_2Ru$ (950.0): calcd. C 72.1, H 7.96; found C 72.1, H 7.90. − IR (Nujol): $\tilde{\nu}$ = ν(OH) not obsd., 1643 cm^{-1} ν(C=C). − ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.94−1.20 [m, 24 H, PCH(CH_3)$_2$], 1.83 [s, 15 H, $C_5(CH_3)_5$], 2.00 (m, 4 H, PCH_2), 2.11 and 2.30 (m, 2 H each, PCH), 2.57 (br. s, 1 H, OH), 4.33 [d, $^3J_{H^aH^b}$ = 9.0 Hz, 1 H, Ru=C=C*H*^{a}CH^b(OH)Ph], 5.40 [d, $^3J_{H^aH^b}$ = 9.0 Hz, 1 H, Ru=C=CH^{a}C*H*^{b}(OH)Ph], 7.28, 7.36, and 7.39 (m, 5 H, C_6H_5). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ = 87.7 and 86.9 (d, $^2J_{PP'}$ = 17.1 Hz). − $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ = 10.88 [s, $C_5(CH_3)_5$], 18.14, 19.18, 19.42, and 19.69 [m, PCH(CH_3)$_2$], 21.13, 25.23, and 31.74 (m, PCH and PCH_2), 66.97 (s, C^γ), 102.6 [s, $C_5(CH_3)_5$], 116.0 (s, C^β), 128.3, 128.5, 128.8, and 143.1 (s, C_6H_5), 337.4 (t, $^2J_{CP}$ = 14.3 Hz, C^α).

2c: Yield 888 mg (100%). − $C_{52}H_{73}BOP_2Ru$ (888.0): calcd. C 70.3, H 8.29; found C 70.1, H 8.28. − IR (Nujol): $\tilde{\nu}$ = ν(OH) not obsd., 1643 cm^{-1} ν(C=C). − ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.94−1.99 and 1.05−1.21 [m, 24 H, PCH(CH_3)$_2$], 1.28 [d, $^3J_{H^bH^c}$ = 6.0 Hz, 3 H, Ru=C=CH^{a}CH^b(OH)CH^c_3], 1.83 [s, 15 H, $C_5(CH_3)_5$], 2.01 (m, 4 H, PCH_2), 2.14 and 2.23 (m, 2 H each, PCH), 3.23 (br. s, 1 H, OH), 3.98 (d, $^3J_{H^aH^b}$ = 9.0 Hz, 1 H, Ru=C=CH^aCH^b), 4.51 [dq, $^3J_{H^aH^b}$ = 9.0 Hz, $^3J_{H^bH^c}$ = 6.0 Hz, 1 H, Ru=C=CH^a−CH^b(OH)CH$^c_3$]. − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ = 87.1 and 87.5 (d, $^2J_{PP'}$ = 17.1 Hz). − $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ = 10.88 [s, $C_5(CH_3)_5$], 18.22, 19.80, and 19.36 [d, PCH(CH_3)$_2$], 21.98 [s, Ru=C=CH−CH(OH)CH_3], 21.39 and 25.39 (m, PCH_2), 31.22 and 32.64 (m, PCH), 69.03 (s, C^γ), 102.7 [s, $C_5(CH_3)_5$], 115.4 (s, C^β), 337.2 (t, $^2J_{CP}$ = 14.7 Hz, C^α).

2d: Yield 916 mg (100%). − $C_{53}H_{73}BO_2P_2Ru$ (916.0): calcd. C 69.5, H 8.03; found C 69.2, H 8.00. − IR (Nujol): $\tilde{\nu}$ = 1693 ν(C=C), 1680 cm^{-1} ν(C=O). − ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88−1.00 and 1.08−1.30 [m, 24 H, PCH(CH_3)$_2$], 1.18 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, $COOCH_2CH_3$), 1.84 [s, 15 H, $C_5(CH_3)_5$], 1.96 (m, 4 H, PCH_2), 2.28 and 2.85 (m, 2 H each, PCH), 4.13 (q, $^3J_{HH}$ = 7.0 Hz, 2 H, $COOCH_2CH_3$), 4.52 (br. s, 1 H, Ru=C=CH−). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ = 84.6 (s). − $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ = 10.85 [s, $C_5(CH_3)_5$], 14.37 (s, $COOCH_2CH_3$), 18.32, 19.50, and 19.90 [s, PCH(CH_3)$_2$], 21.89 (vt, $^{1,3}J_{CP}$ = 20.2 Hz, PCH_2), 25.20 and 32.25 (m, PCH), 60.46 (s, $COOCH_2CH_3$), 104.3 [s, $C_5(CH_3)_5$], 109.5 (s, C^β), 164.0 (s, *C*OOEt), 338.8 (t, $^2J_{CP}$ = 14.3 Hz, C^α).

Preparation of Allenylidene Complexes [Cp*Ru(=C=C=CRPh)(dippe)][BPh$_4$] [R = Ph (3a), H (3b)] and Vinylvinylidene Complex [Cp*Ru(=C=CHCH=CH$_2$)(dippe)][BPh$_4$] (4): Complex **3a** was obtained by adding the alkynol (0.30 mmol) to a solution of [Cp*RuCl(dippe)] (133 mg, 0.25 mmol) in MeOH (15 mL). After stirring the mixture for 6 h under reflux, the addition of $NaBPh_4$ (81 mg, 0.50 mmol) caused the precipitation of a dark-red solid, which was collected by filtration, washed with EtOH and petroleum ether, and dried in vacuo. The solid was recrystallized from acetone/ethanol (1:2) to give dark-red needles. Complexes **3b** and **4** were obtained by passing a solution of the corresponding 3-hydroxyvinylidene complex (0.25 mmol) in CH_2Cl_2 (1 mL) through a column of Al_2O_3 (acidic, activity grade I, height of column 10 cm) and collecting a dark-green band of **3b** and a brown band of **4**. Removal of the solvent from these fractions left solids, which were dried in vacuo and recrystallized from acetone/ethanol (1:2). Slow crystallization gave dark-green crystals of **3b**. Selected spectroscopic data are as follows:

3a: Yield 238 mg (94%). − $C_{63}H_{77}BP_2Ru$ (1008.1): calcd. C 75.1, H 7.70; found C 75.0, H 7.67. − IR (Nujol): $\tilde{\nu}$ = 1890 cm^{-1} ν(C=C=C). − ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88−0.96, 1.00−1.06, and 1.13−1.18 [m, 24 H, PCH(CH_3)$_2$], 1.84 [s, 15 H, $C_5(CH_3)_5$], 1.89 (m, 4 H, PCH_2), 1.99 and 2.17 (m, 2 H each, PCH), 7.36 (t, $^3J_{HH}$ = 8.3 Hz, 2 H, *p*-C_6H_5), 7.57 (d, $^3J_{HH}$ = 8.3 Hz, 4 H, *o*-C_6H_5), 7.59 (t, $^3J_{HH}$ = 8.3 Hz, 4 H, *m*-C_6H_5). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ = 87.9 (s). − $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ = 11.27 [s, $C_5(CH_3)_5$], 18.15, 19.80, and 19.43 [s, PCH(CH_3)$_3$], 21.29 (vt, $^{1,3}J_{CP}$ = 18.8 Hz, PCH_2), 25.83 and 30.79 (m, PCH), 102.7 [s, $C_5(CH_3)_5$], 128.5, 129.0, 130.5, and 144.2 (s, C_6H_5), 150.1 (s, C^γ), 214.7 (s, C^β), 287.2 (t, $^2J_{CP}$ = 17.2 Hz, C^α).

3b: Yield 170 mg (73%). − $C_{57}H_{73}BP_2Ru$ (932.0): calcd. C 73.5, H 7.89; found C 73.6, H 7.85. − IR (Nujol): $\tilde{\nu}$ = 1915 cm^{-1} ν(C=C=C). − ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 0.84−0.95, 1.01−1.09, and 1.13−1.18 [m, 24 H, PCH(CH_3)$_2$], 1.89 [s, 15 H, $C_5(CH_3)_5$], 1.97 (m, 4 H, PCH_2), 2.21 (m, 4 H, PCH), 7.36 (t, $^3J_{HH}$ = 8.3 Hz, 1 H, *p*-C_6H_5), 7.66 and 7.69 (m, 4 H, C_6H_5), 9.20 (br. s, 1 H, Ru=C=C=C*H*Ph). − $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 298 K): δ = 88.3 (s). − $^{13}C\{^1H\}$ NMR (50.29 MHz, CD_2Cl_2, 298 K): δ = 11.36 [s, $C_5(CH_3)_5$], 18.41, 19.47, and 19.90 [s, PCH(CH_3)$_3$], 21.87 (vt, $^{1,3}J_{CP}$ = 20.1 Hz, PCH_2), 26.14 and 30.57 (m, PCH), 103.5 [s, $C_5(CH_3)_5$], 129.9, 130.4, 131.6, and 142.8 (s, C_6H_5), 139.3 (s, C^γ), 219.8 (s, C^β), 294.3 (t, $^2J_{CP}$ = 17.6 Hz, C^α).

4: Yield 163 mg (75%). − $C_{52}H_{71}BP_2Ru$ (870.0): calcd. C 71.8, H 8.23; found C 71.6, H 8.21. − IR (Nujol): $\tilde{\nu}$ = 1633 cm^{-1} ν(C=C). − ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.93−1.19 [m, 24 H, PCH(CH_3)$_2$], 1.62 and 1.79 (m, 2 H each, PCH_2), 1.81 [s, 15 H, $C_5(CH_3)_5$], 1.99 and 2.16 (m, 2 H each, PCH), 4.88 (d, $^3J_{H^aH^b}$ = 17.0 Hz, 1 H, Ru=C=CH^a−CH^b = CH$^c_2$), 4.46 and 4.91 (d, $^3J_{H^bH^c}$ = 10.0 Hz, 1 H each, Ru=C=CH^a−CH^b = CH^c_2), 6.19 (dt, $^3J_{H^aH^b}$ = 17.0 Hz, $^3J_{HbHc}$ = 10.0 Hz, 1 H, Ru=C=CH^a−CH^b = CH$^c_2$). − $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ = 87.3 (s). − $^{13}C\{^1H\}$ NMR (50.29 MHz, $CDCl_3$, 298 K): δ = 11.00 [s, $C_5(CH_3)_5$], 18.35, 19.31, and 19.79 [s, PCH(CH_3)$_3$], 21.61 (vt, $^{1,3}J_{CP}$ = 18.8 Hz, PCH_2), 25.45 and 31.42 (m, PCH), 111.1 (s, C^β), 103.3 [s, $C_5(CH_3)_5$], 117.2 (s, Cδ), 121.4 (s, C^γ), 347.7 (t, $^2J_{CP}$ = 14.8 Hz, C^α).

Kinetics Studies of Alkynyl−Hydride to Vinylidene Isomerization: Solutions of the complex [Cp*Ru(η^2-H_2C=CH_2)(dippe)][BPh_4] were prepared in $CDCl_3$ under an inert gas in NMR tubes and were cooled to −80 °C in a liquid N_2/ethanol bath. An excess of the appropriate alkyne or alkynol was added and the tubes were kept at this temperature to arrest the isomerization process during transport and handling. A tube was then removed from the cooling bath and inserted into the precooled probe head of a Varian UNITY 400 spectrometer at 243 K. Once shims had been adjusted, the probe was warmed to 263 K to allow the in situ formation of the corresponding alkynyl(hydrido) complexes. After completion of this reaction, the temperature was raised to the desired level for study. The NMR temperature controller was previously calibrated against a methanol sample, the reproducibility being ± 0.5 °C. $^{31}P\{^1H\}$ NMR spectra were recorded at regular intervals for at least three half-lives using the spectrometer software for accurate time control. Peak intensities were analysed from stacked plots of the $^{31}P\{^1H\}$ NMR spectra. First-order rate constants were derived from the least-squares best-fit lines of the ln(intensity) versus time plots. The uncertainty in the isomerization rate constants represents one standard deviation (± σ) derived from the slope of the best-fit line. Uncertainties in the activation enthalpies and entropies were calculated from the uncertainties in the slope and intercept of the best-fit lines of the Eyring plots.

X-ray Structure Determination of [Cp*Ru(=C=C=CHPh)(dippe)][BPh$_4$] (3b): Empirical formula $C_{57}H_{73}BP_2Ru$, molecular mass 931.97, crystal size 0.30 × 0.30 × 0.14 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 14.763(3) Å, b = 18.320(3) Å, c = 18.433(3) Å, β = 92.44(2) °, V = 4980(15) Å^3, Z = 4, $\rho_{calcd.}$ = 1.243 g cm^{-3}, T = 290(2) K, λ(Mo-$K_α$) = 0.71069 Å, graphite monochromator, μ(Mo-$K_α$) = 4.15 cm^{-1}, F(000) = 1976, transmission factor interval 0.76−1.00, scan speed (ω) 4° min^{-1}, 5.64° < 2θ < 50.12°, 7720 measured reflections, 7305 unique reflections, 4693 observed reflections [$I > 2\sigma(I)$], 550 parameters, reflection/parameter ratio 13.3. X-ray diffraction measurements were made on crystals of the appropriate size, which were mounted on a glass fibre and transferred to a Rigaku AFC6S automatic diffractometer. In each case, accurate unit cell parameters and an orientation matrix were determined by least-squares fitting from the settings of 25

high-angle reflections. Data were collected by the ω/2θ scan method. Decay was monitored by measuring three standard reflections every 100 measurements. Lorentz and polarization corrections were applied. Decay and semiempirical absorption corrections (ψ method) were also applied. The structure was solved by the Patterson method and subsequent expansion of the model using DIRDIF.[28] All calculations for data reduction and structure solution were carried out with a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[29] software system. All hydrogen atoms were included at idealized positions and were allowed to ride on the parent carbon atoms. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97,[30] concluding with the values $R1 = 0.0678$ and $wR2 = 0.1810$ for data having $I > 2\sigma(I)$. ORTEP[24] was used for plotting. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157842. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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