Activation of Propargylic Alcohols Derived from Hormonal Steroids by the Indenyl−Ruthenium(II) Complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$]: Experimental and Theoretical Evidence of an Allenylidene−Vinylvinylidene Equilibrium

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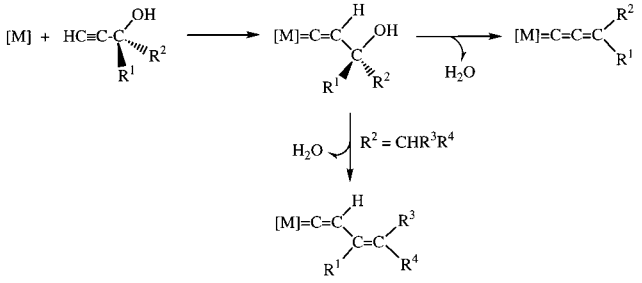
The indenyl−ruthenium(II) complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**1**) reacts with ethisterone (**2a**), 17α-ethynylestradiol (**2b**), and mestranol (**2c**), in methanol and in the presence of $NaPF_6$, to afford equilibrium mixtures containing the corresponding allenylidene **3a**−**c** and vinylvinylidene **4a**−**c** tautomers. Deprotonation of these mixtures with K_2CO_3 allows the preparation of σ-enynyl derivatives **5a**−**c**, which can be selectively alkylated with $MeOSO_2CF_3$ to yield disubstituted vinylvinylidene complexes **6a**−**c**. Displacement of these equilibriums can also be accomplished by treatment of the reaction mixtures with acetonitrile or PMe_2Ph. Thus, while in the first case terminal 1,3-enynes **7a**−**c** are selectively obtained by demetalation of vinylvinylidenes **4a**−**c**, phosphonio-alkynyl complexes **9a**−**c** are exclusively formed in the second case as the result of the nucleophilic addition of PMe_2Ph on the electrophilic C_γ atom of allenylidenes **3a**−**c**. Ab initio molecular orbital calculations on the models [Ru{=C=C=C(H)CH_3}(η^5-C_5H_5)(PH_3)$_2$]$^+$ and [Ru{=C=C(H)CH=CH_2}(η^5-C_5H_5)(PH_3)$_2$]$^+$ show that the vinylvinylidene tautomer is only 2.1 kcal/mol more stable than the allenylidene. The spontaneous tautomerization process between both complexes, which involves a [1,3]-hydrogen sigmatropic rearrangement, requires an activation energy of 66.5 kcal/mol.

Introduction

Within the context of organometallic complexes containing unsaturated carbene ligands, the chemistry of allenylidene derivatives [M]=C=C=CR_2 has emerged as a fascinating research field in its own right due probably to their potential applications in organic synthesis.[1] Remarkable developments in the catalytic activity of ruthenium(II) allenylidenes in ring-closing metathesis of olefins,[2] in the dehydrogenative dimerization of tin hydrides,[3] and in some propargylic substitution reactions[4] have been recently reported.[5]

Chart 1



The most general synthetic approach to mononuclear complexes with an allenylidene ligand, originally introduced by Selegue,[6] consists of the formal dehydration of propargylic alcohols by treatment with an unsaturated metallic fragment (see Chart 1). Unfortunately, the presence of hydrogen atoms in β position with respect

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(1) For comprehensive reviews on the synthesis and reactivity of allenylidene complexes see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Werner, H. *Chem. Commun.* **1997**, 903. (c) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (d) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178*−*180*, 409. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571.

(2) See for example: Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012, and references therein.

(3) Maddock, S. M.; Finn, M. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2138.

(4) (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (b) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393.

(5) It has been suggested that allenylidene−ruthenium(II) intermediates are also responsible for the catalytic coupling of 2-propyn-1-ols with allylic alcohols: (a) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476. (b) Trost, B. M.; Flygare, J. A. *Tetrahedron Lett.* **1994**, *35*, 4059.

(6) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

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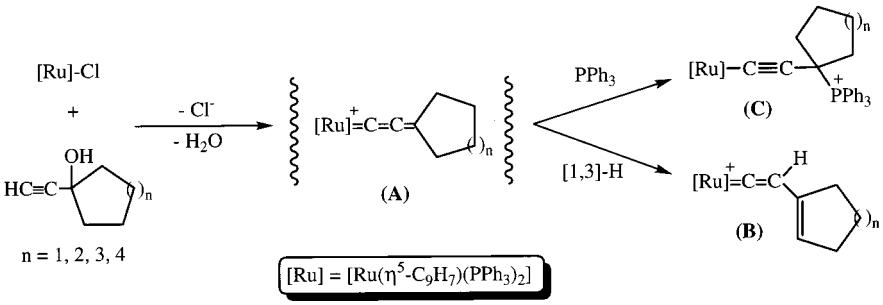
Chart 2

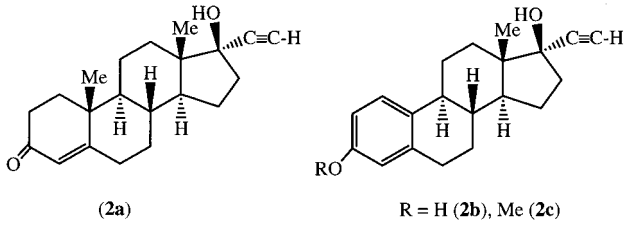


to the hydroxy group seems to be a synthetic drawback since tautomeric vinylvinylidene species can be formed.[7]

As a matter of fact, we have found that the activation of 1-ethynyl-1-cycloalkanols by $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ does not afford the desired allenylidene derivatives **A**, obtaining instead vinylvinylidene complexes **B** in a selective manner (see Chart 2).[7g] Nevertheless, the initial formation of transient allenylidene intermediates **A** was clearly evidenced since by performing these reactions in the presence of triphenylphosphine phosphonioalkynyl derivatives **C** are readily formed. These complexes result from the regioselective nucleophilic addition of the phosphine at the electrophilic C_γ atom of the cumulenic chain in **A**. This seems to suggest that allenylidenes **A** are the kinetic control products in the dehydration of 1-ethynyl-1-cycloalkanols, which undergo a spontaneous tautomerization process into the thermodynamically more stable vinylvinylidene tautomers **B**.

While conducting our research on the activation of terminal alkynes by indenyl−ruthenium(II) complexes,[1e,8] we became interested in investigating the chemical behavior of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**1**) toward biologically active propargylic alcohols. Thus, in this paper we report on the reactivity of **1** with the hormonal steroids ethisterone (**2a**), 17α-ethynylestradiol (**2b**), and mestranol (**2c**) (Chart 3).[9] In contrast to the expected formation of vinylidene species of type **B** (Chart 2) equilibrium mixtures of both tautomers (**A** and **B**) are in all cases observed. The occurrence of this equilibrium was, moreover, confirmed on the basis of reactivity studies and by ab initio molecular orbital calculations on the models $[Ru\{=C=C(H)CH=CH_2\}(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$ and $[Ru\{=C=C=C(H)CH_3\}(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$.

Chart 3



Results and Discussion

Synthetic Studies. Complex $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**1**) reacts with propargylic alcohols **2a**−**c**, in methanol at room temperature and in the presence of $NaPF_6$, to give a nonseparable mixture containing the allenylidene derivatives **3a**−**c** and the vinylvinylidene complexes **4a**−**c** (Scheme 1).[11a] The proposed structure for these species was confirmed by elemental analysis and IR and NMR ($^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$) spectroscopy (selected data are shown in the Experimental Section). In particular, $^{13}C\{^1H\}$ NMR spectra are very informative since they show the presence of two low-field virtual triplets at ca. 307 ($^2J_{CP}$ = 18.9−24.2) and 354 (ca. $^2J_{CP}$ = 16.4) ppm, assigned to the carbenic C_α atom of **3a**−**c** and **4a**−**c**, respectively. These chemical shifts and coupling constants are in accord with those previously reported by us for related indenyl−ruthenium(II) vinylidene $[Ru\{=C=C(H)R\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ and allenylidene $[Ru(=C=C=CRR')(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ derivatives.[7g,10]

(7) See for example: (a) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972. (b) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. (c) Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1996**, 2547. (d) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (e) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R. J.; López-Ortiz, F.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1996**, *15*, 4274. (f) Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636. (g) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (h) Bustelo, E.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. (i) Bianchini, C.; Peruzzini, M.; Zanobini, F.; de los Rios, I.; Lopez, C.; Romerosa, A. *Chem. Commun.* **1999**, 443. (j) Bianchini, C.; de los Rios, I.; Lopez, C.; Peruzzini, M.; Romerosa, A. *J. Organomet. Chem.* **2000**, *593*−*594*, 485. (k) Bianchini, C.; Mantovani, N.; Marvelli, L.; Peruzzini, M.; Rossi, R.; Romerosa, A. *J. Organomet. Chem.* **2001**, *617*−*618*, 233.

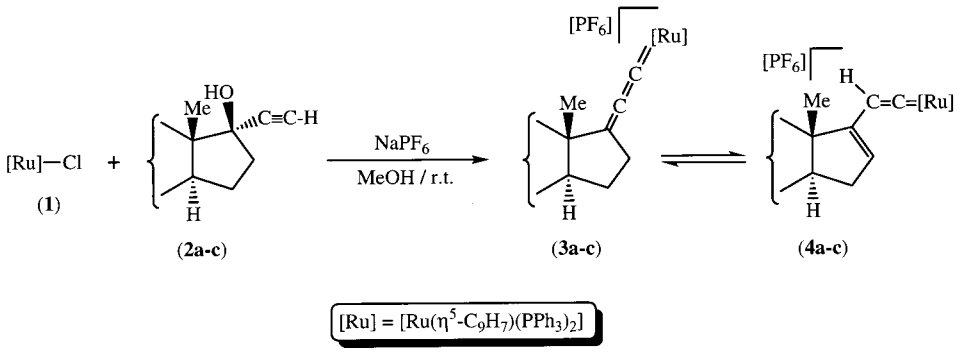
(8) Cadierno, V.; Díez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *Coord. Chem. Rev.* **1999**, *193*−*195*, 147.

(9) Coordination of these compounds to organometallic fragments is a research field of burgeoning interest with potential applications in molecular recognition. For recent reviews see: (a) Jaouen, G.; Vessières, A.; Butler, I. S. *Acc. Chem. Res.* **1993**, *26*, 361, and references therein. (b) Jaouen, G.; Top, S.; Vessières, A.; Alberto, R. *J. Organomet. Chem.* **2000**, *600*, 23, and references therein.

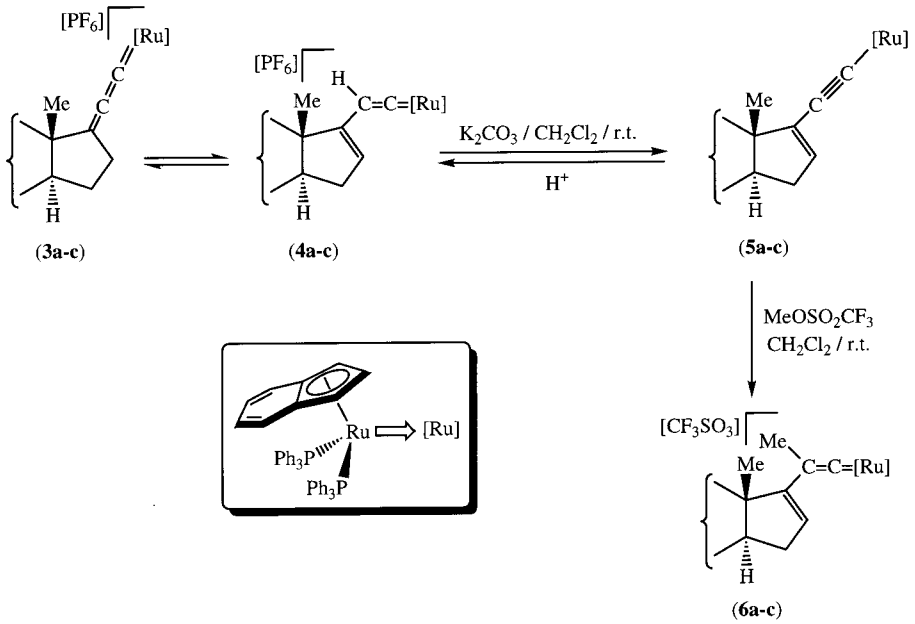
(10) (a) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M.; Borge, J.; García-Granda, S.; Pérez-Carreño. E. *Organometallics* **1994**, *13*, 4045. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; Ienco, A. *Organometallics* **1998**, *17*, 5216. (e) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Asselberghs, I.; Houbrechts, S.; Clays, K.; Persoons, A.; Borge, J.; García-Granda, S. *Organometallics* **1999**, *18*, 582. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño. E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821. (g) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1857. (h) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3235. (i) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **2000**, 451. (j) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *J. Organomet. Chem.* **2001**, *621*, 39. (k) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **2001**, *20*, 3175.

(11) (a) At room temperature the allenylidene/vinylvinylidene ratios observed are as follows: **3a/4a** = 1:1.7, **3b/4b** = 1:1, **3c/4c** = 1:1.2. (b) Variable-temperature $^{31}P\{^1H\}$ NMR experiments were also carried out with CD_2Cl_2 solutions containing complexes **3**−**4a**. No changes in the **3a**:**4a** ratio could be detected.

Scheme 1



Scheme 2



It is interesting to note that the same mixtures were also obtained when the reactions were performed in refluxing methanol.[11b] These observations contrast with our previous results using related 1-ethynyl-1-cycloalkanols, which led to the selective formation of vinylvinylidene derivatives.[7g]

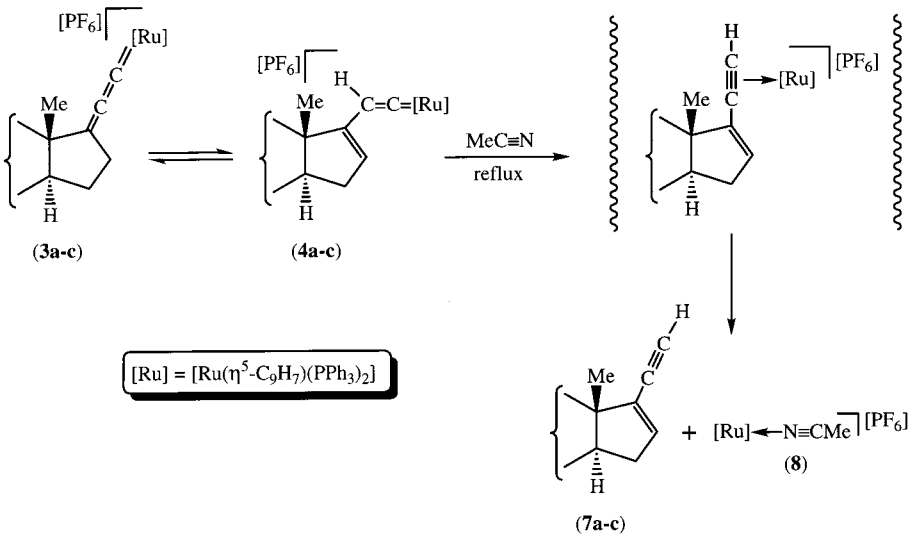
Taking into account the well-known acidity of the vinylidene protons,[12] the reactivity of these mixtures toward bases was explored. Thus, the treatment with an excess of K_2CO_3, in dichloromethane at room temperature, affords selectively *σ*-enynyl complexes **5a**−**c**, which are isolated as air-stable solids in 71−83% yield (Scheme 2). Analytical and spectroscopic data (IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR) for **5a**−**c** support the proposed formulations (see the Experimental Section and the Supporting Information). Remarkable features are (i) (IR) the presence of characteristic ν(C≡C) absorptions at ca. 2063 cm^{-1}, (ii) (^1H NMR) the appearance of virtual triplet signals (J_{HH} = 2.2−2.6 Hz) at δ 5.49−5.53 assigned to the olefinic =C*H*CH$_2$ protons, and (iii) ($^{13}C\{^1H\}$ NMR) typical Ru−C$_\alpha$ and C$_\beta$ resonances in the ranges 113.61−113.83 (vt, ca. $^2J_{CP}$ = 25 Hz) and 109.29−110.41 (s) ppm, respectively. The high-yield formation of complexes **5a**−**c** can be easily explained assuming the displacement of the tautomerization equilibrium toward the formation of **4a**−**c**, which undergo a deprotonation in the presence of the base.[13]

The selective synthesis of vinylvinylidene complexes has been achieved via methylation of **5a**−**c** with $MeOSO_2CF_3$, which affords **6a**−**c** (79−85% yield) (Scheme 2). These complexes have been isolated as the triflate salts and characterized by standard spectroscopic methods and elemental analyses (see the Experimental Section and the Supporting Information for details). The $^{13}C\{^1H\}$ NMR spectra of **6a**−**c** unambiguously indicate the presence of a vinylidene moiety disclosing resonances at ca. δ 352 (dd, $^2J_{CP}$ = 13.8−21.0 Hz) and 120 (s) ppm, attributable to the C$_\alpha$ and C$_\beta$ carbon nuclei, respectively. Surprisingly, treatment of **5a**−**c** with HBF_4 does not allow the isolation of pure vinylvinylidenes **4a**−**c**, obtaining instead reaction mixtures containing compounds **3a**−**c** and **4a**−**c**.[11a] Assuming that vinylvinylidenes **4a**−**c** are initially formed in these protonation processes, a partial tautomerization into allenylidenes **3a**−**c** to form equilibrium mixtures of both species could explain the experimental observations.

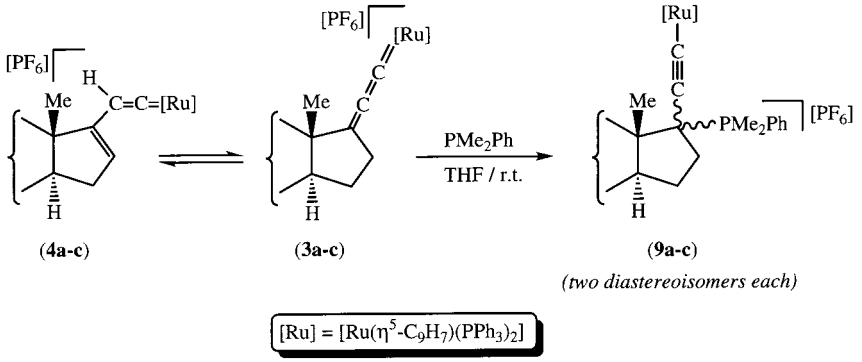
(12) For reviews on the chemistry of vinylidene complexes see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (c) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977.

(13) The direct deprotonation of one of the methylenic protons in δ position of **3a**−**c** cannot be totally discarded since it has been proposed that this type of proton is acidic (see ref 1).

Scheme 3



Scheme 4



We have recently reported a synthetic approach to functionalized terminal alkynes via removal of the metal fragment in the corresponding vinylidene complexes which is efficiently achieved by treatment with acetonitrile.[10f,i−k] In this regard, we have applied this synthetic protocol to the mixtures containing compounds **3a**−**c** and **4a**−**c**, which, after heating in acetonitrile under reflux, leads to the clean formation of the terminal 1,3-enynes **7a**−**c**[14] and the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**8**)[10f] (Scheme 3). Since allenylidene derivatives [Ru(=C=C=CRR′)(η^5-C_9H_7)(PPh_3)$_2$]$^+$ are inert toward acetonitrile, the selective formation of enynes **7a**−**c** involves again the conversion of the allenylidenes **3a**−**c** into vinylvinylidenes **4a**−**c** during the course of these reactions.

Enynes **7a**−**c** can be easily purified from the reaction mixture by column chromatography on silica gel (74−83% yield) after filtering off the unsoluble complex **8**. Elemental analyses and spectroscopic data are in accordance with the proposed formulations (see the Experimental Section and the Supporting Information for details). The most relevant spectroscopic features of **7a**−**c** are (i) (IR) the expected ν(C≡C) and ν(≡C−H) absorptions in the ranges 2082−2090 and 3254−3293 cm^{-1}, respectively, (ii) (^{1}H NMR) the singlet resonance for the acetylenic proton (δ 2.84−2.90), and (iii) (^{13}C{^{1}H} NMR) typical signals for the HC≡C carbons, which appear at ca. 81 and 79 ppm, respectively.

A different displacement of the equilibrium between compounds **3a**−**c** and **4a**−**c** occurs when a mixture of these complexes in THF is treated at room temperature with 1 equiv of PMe_2Ph. As expected, the phosphonioalkynyl complexes **9a**−**c** are selectively formed (85−92% yield) as the result of the nucleophilic attack of the phosphine on the electrophilic C_γ atom of the allenylidene chain in **3a**−**c** (Scheme 4).[15,16] The formation of **9a**−**c** involves the total tautomerization of vinylvinylidenes **4a**−**c** into the allenylidenes **3a**−**c**. Since the nucleophilic addition, which generates a novel stereogenic center at C_γ, is not stereoselective, a nonseparable mixture of two diastereoisomers is obtained. NMR spectra show that they are formed in ca. ratios 4:1 (**9a**), 5:1 (**9b**), and 8:1 (**9c**).

Spectroscopic data for **9a**−**c** are in agreement with the proposed formulations, being comparable to those found for related indenyl−ruthenium(II) phosphonioalkynyl complexes [Ru{C≡CCR^{1}R^2(PR_3)}(η^5-C_9H_7)(PPh_3)$_2$]$^+$.[7g,10c,e] Thus, while the ^{31}P{^{1}H} NMR spectra exhibit the expected resonances for an ABM spin system, typical C_α (δ 113.48−114.72 (m)), C_β (δ 105.65−

(14) Synthesis of enynes **7a** and **7c** has been previously reported. **7a**: (a) Solyom, S.; Szilagyi, K.; Toldy, L. *J. Prakt. Chem.* **1988**, *330*, 309. **7c**: (b) Elsevier, C. J.; Meijer, J.; Tadema, G.; Stehouwer, P. M.; Bos, H. J. T.; Vermeer, P.; Runge, W. *J. Org. Chem.* **1982**, *47*, 2194. No spectroscopic data have been reported for **7c**.

(15) It is well-known that vinylidene complexes react with nucleophiles at the electrophilic C_α to afford σ-alkenyl derivatives (see ref 12).

(16) Mixtures containing complexes **3**−**4a**−**c** are unreactive toward bulkier phosphines, i.e., PPh_3 or $PMePh_2$, probably due to steric hindrance between the C_γ substituents of allenylidenes **3a**−**c** and the phosphine ligands.

106.69 (d, $^2J_{CP}$ = 5.1−5.7 Hz)), and C_γ (δ 54.35−57.42 (d, J_{CP} = 42.5−47.1 Hz)) resonances are observed in the $^{13}C\{^1H\}$ NMR spectra.

Theoretical Studies. The allenylidene−vinylvinylidene equilibrium involves a [1,3]-hydrogen sigmatropic rearrangement (see Chart 2). In thermal reactions of alkenes, this kind of rearrangement is forbidden in a suprafacial process due to orbital symmetry, and the geometrical requirements prevent the allowed antarafacial reaction.[17] However, the unique geometry and symmetry of the orbitals in an alkyl-substituted allene allow a net concerted [1,3]-hydrogen sigmatropic rearrangement, which involves both π bonds of the allene and a 90° rotation of the terminus.[18] This interesting fact prompted us to carry out theoretical calculations on such allenylidene−vinylvinylidene equilibrium.

The size of the complexes to be studied required the use of models for the calculations. Thus, [Ru{=C=C=C(H)CH_3}(η^5-C_5H_5)$(PH_3)_2]^+$ (**D**) was used for the allenylidene cation and [Ru{=C=C(H)CH=CH_2}(η^5-C_5H_5)-$(PH_3)_2]^+$ (**E**) for the vinylvinylidene one.[19] Searches for the transition state connecting **D**−**E** led to structure **F**. The relevant geometrical parameters of the optimized structures with the B3LYP/DZV(d,p) wave function are given in Figure 1. The **D** and **E** structures were characterized as minima, and **F** was characterized as a true transition structure (only one imaginary frequency) on the potential energy surface. By the intrinsic reaction coordinate (IRC) reaction path,[20] it was confirmed that **F** is the transition state for the interconversion between the two complexes **D** and **E**. The allenylidene group Ru=C_α=C_β=C_γ−C_δ in complex **D** shows distances of 1.904 (Ru=C_α), 1.268 (C_α=C_β), 1.336 (C_β=C_γ), and 1.492 (C_γ−C_δ) Å and a C_α=C_β=C_γ angle of 180.0°. The equilibrium distances for the vinylvinylidene moiety Ru=C_α=C_β−C_γ=C_δ in complex **E** are converted to 1.864 (Ru=C_α), 1.318 (C_α=C_β), 1.467 (C_β−C_γ), and 1.338 (C_γ=C_δ) Å together with a C_α=C_β−C_γ angle of 126.5°. All these structural parameters fit well with those obtained by X-ray crystal structure determinations for related species.[1,12] The values of the corresponding carbon−carbon bond distances (1.280, 1.398, and 1.406 Å) and angle (155.0°) in the transition state **F** are intermediate between those shown in complexes **D** and **E** (see Figure 1). Moreover, the hydrogen atom that migrates is bounded to both C_β (1.471 Å) and C_δ (1.494 Å), and a rotation of the organic group can be observed.

Table 1 shows the absolute and relative energies for **D**, **E**, and **F**. It is interesting to notice that the vinylvinylidene derivative is more stable than the allenylidene complex. The energy gap is −2.9 kcal/mol for T = 0 K [MP2/DZV(d,p)//B3LYP/DZV(d,p) level], but inclusion of thermal correction to Gibbs free energies[21] for T = 298 K places the energy gap at −2.1 kcal/mol.

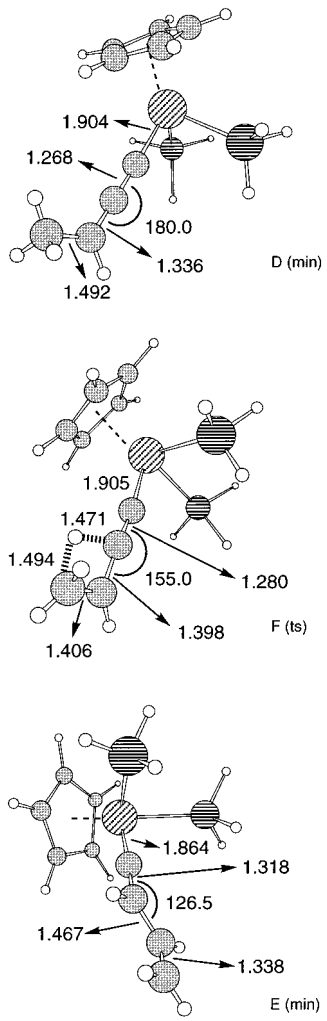


Figure 1. Computer plot of the B3LYP/DZV(d,p) optimized structures (lengths in Å, angles in deg) for the allenylidene (**D**) and vinylvinylidene (**E**) complexes and the transition structure for the interconversion between **D** and **E** (**F**).

Table 1. Calculated Total (hartrees) and Relative (kcal/mol) Energies for the Allenylidene (D) and Vinylvinylidene (E) Complexes and the Transition Structure for the Interconversion between D and E (F)[a]

	MP2/DZV(d,p)	MP2/DZV(d,p)+$G^{b,c}$	MP2/DZV(d,p)+$H^{b,d}$
D	−456.574879 (0.0)	−456.419643 (0.0)	−456.354490 (0.0)
E	−456.579433 (−2.9)	−456.422947 (−2.1)	−456.359287 (−3.0)
F	−456.462690 (70.4)	−456.313727 (66.5)	−456.249259 (66.0)

[a] Single-point calculations on the B3LYP/DZV(d,p)-optimized geometries. [b] Thermochemical analysis for T = 298 K at the B3LYP/DZV(d,p) level. [c] Including thermal correction to Gibbs free energy. [d] Including thermal correction to enthalpy.

To account for the activation energy, the thermal correction to enthalpies[21] is also included in Table 1. Since the Arrhenius activation energy is equated with the enthalpy of activation ($E_A = \Delta H^\ddagger + RT$),[22] the activation energy derived from our calculations should be 66.5 kcal/mol for T = 298 K (RT = 0.5 kcal/mol). This value seems quite high for a spontaneous reaction, which could indicate that the used level of theory overestimates the activation energy on the model sys-

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(19) We note that both allenylidene and vinylvinylidene complexes containing [Ru(η^5-C_5H_5)$(PR_3)_2]^+$ moieties have been prepared by activation of propargylic alcohols. See, for instance, refs 6, 7a, and: Bruce, M. I.; Low, P. J.; Tiekink, E. R. T. *J. Organomet. Chem.* **1999**, *572*, 3.

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(21) Foresman, J. B.; Frisch, *Æ. Exploring Chemistry with Electronic Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, 1996.

(22) See, for instance: Isaacs, N. S. *Physical Organic Chemistry*; Longman: Essex, U.K., 1987.

tems. Nevertheless, we note that comparable experimental activation parameters have been obtained for other spontaneous sigmatropic rearrangements.[23]

Conclusions

In this work we have described the activation of the biologically active propargylic alcohols ethisterone (**2a**), 17α-ethynylestradiol (**2b**), and mestranol (**2c**) by the ruthenium(II) complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$]. In contrast to the well-known behavior of conventional alkynols, which discloses selective synthetic approaches to either allenylidene or vinylvinylidene complexes, mixtures of both tautomers **3a**−**c** and **4a**−**c**, respectively, are achieved. However, it has been shown that the tautomeric equilibrium can be controlled by means of the typical reactivity of each of these species, which allows the selective displacement of the equilibrium. Thus, (a) enynyl complexes **5a**−**c** are selectively obtained via deprotonation of the vinylvinylidene tautomers by treatment of the equilibrium mixture with a base; (b) terminal 1,3-enynes **7a**−**c** are formed from the corresponding π-enyne derivatives, which are selectively generated from the vinylvinylidene complexes **4a**−**c** after heating under reflux the equilibrium mixture in acetonitrile; (c) phosphonio-alkynyl complexes **9a**−**c** are isolated via nucleophilic addition of PMe_2Ph to the C_γ atom of the cumulenic chain in allenylidene complexes **3a**−**c**.

Although Selegue's synthetic methodology of allenylidenes from alkynols has been largely shown as the most efficient route, the competitive formation of the vinylvinylidene tautomers has been a well-known drawback.[7] We have shown in this work a rationalization of this general behavior on the basis of theoretical calculations, which disclose that the vinylvinylidene tautomer is ca. 2.1 kcal/mol more stable than the allenylidene. It is likely that this energy gap would decrease in the case of 1-ethynyl-1-cyclopentanols since it is well-known[22] that endocyclic cyclopentenes (i.e., vinylvinylidenes **4a**−**c**) present a higher strain energy than their exocyclic counterparts (i.e., allenylidenes **3a**−**c**), giving rise to the observation of allenylidene complexes.[24] Moreover, for the first time an energy profile for the sigmatropic rearrangement accounting for the allenylidene−vinylvinylidene tautomerization is calculated. The activation energy value found for this spontaneous process of 66.5 kcal/mol at 298 K, although quite high, can be compared with those recently determined experimentally in other sigmatropic rearrangements.[23] These theoretical calculations are in agreement with our previously reported results in which the formation of allenylidene species as kinetic control intermediates is proposed.[7g]

Experimental Section

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification except compound [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**1**), which was prepared by following the method reported in the literature.[25] Infrared spectra were recorded on a Perkin-Elmer FT-1720-Y spectrometer. The C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported. Full NMR data for compounds **5**−**7a**−**c** and **9a**−**c** have been provided as Supporting Information.

Reactions of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (1) with Propargylic Alcohols 2a−c: General Procedure. To a solution of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**1**) (0.776 g, 1 mmol) in 50 mL of MeOH were added $NaPF_6$ (0.336 g, 2 mmol) and the corresponding propargylic alcohol **2a**−**c** (2 mmol). The reaction mixture was stirred at room temperature for 5 h. The solvent was then removed under vacuum, the crude product extracted with CH_2Cl_2, and the extract filtered. Concentration of the resulting solution to ca. 5 mL followed by the addition of 50 mL of diethyl ether precipitated a brown solid, which was washed with diethyl ether (3 × 20 mL) and dried in vacuo. **3a**/**4a**: Yield: 68% (0.802 g). Anal. Calcd for $C_{66}H_{63}F_6P_3ORu$ (1180.21): C, 67.16; H, 5.38. Found: C, 66.77; H, 5.16. Selected spectroscopic data for **3a**: IR (KBr, cm^{-1}) ν 839 (PF_6^-), 1950 (C=C=C); ^{31}P{^{1}H} ($CDCl_3$) δ 48.22 and 48.46 (d, $^2J_{PP}$ = 24.2 Hz) ppm; ^{13}C{^{1}H} ($CDCl_3$) δ 188.73 and 189.30 (s, C_β and C_γ), 307.27 (vt, $^2J_{CP}$ = 20.5 Hz, Ru=C_α) ppm. Selected spectroscopic data for **4a**: IR (KBr, cm^{-1}) ν 839 (PF_6^-); ^{31}P{^{1}H} ($CDCl_3$) δ 40.19 (br) ppm; ^{1}H ($CDCl_3$) δ 4.52 (br, 1H, Ru=C=CH) ppm; ^{13}C{^{1}H} ($CDCl_3$) δ 354.70 (vt, $^2J_{CP}$ = 16.4 Hz, Ru=C_α) ppm. **3b**/**4b**: Yield: 82% (0.954 g). Anal. Calcd for $C_{65}H_{59}F_6P_3ORu$ (1164.17): C, 67.06; H, 5.10. Found: C, 66.54; H, 5.31. Selected spectroscopic data for **3b**: IR (KBr, cm^{-1}) ν 841 (PF_6^-), 1953 (C=C=C); ^{31}P{^{1}H} ($CDCl_3$) δ 48.16 and 48.43 (d, $^2J_{PP}$ = 23.8 Hz) ppm; ^{13}C{^{1}H} ($CDCl_3$) δ 188.19 and 190.25 (s, C_β and C_γ), 307.18 (vt, $^2J_{CP}$ = 21.5 Hz, Ru=C_α) ppm. Selected spectroscopic data for **4b**: IR (KBr, cm^{-1}) ν 841 (PF_6^-); ^{31}P{^{1}H} ($CDCl_3$) δ 40.14 and 40.39 (d, $^2J_{PP}$ = 23.0 Hz) ppm; ^{1}H ($CDCl_3$) δ 4.56 (br, 1H, Ru=C=CH) ppm; ^{13}C{^{1}H} ($CDCl_3$) δ 354.77 (vt, $^2J_{CP}$ = 16.4 Hz, Ru=C_α) ppm. **3c**/**4c**: Yield: 79% (0.930 g). Anal. Calcd for $C_{66}H_{61}F_6P_3ORu$ (1178.20): C, 67.28; H, 5.21. Found: C, 66.84; H, 4.96. Selected spectroscopic data for **3c**: IR (KBr, cm^{-1}) ν 840 (PF_6^-), 1951 (C=C=C); ^{31}P{^{1}H} ($CDCl_3$) δ 48.45 and 48.74 (d, $^2J_{PP}$ = 23.0 Hz) ppm; ^{13}C{^{1}H} ($CDCl_3$) δ 188.33 and 190.04 (s, C_β and C_γ), 307.15 (vt, $^2J_{CP}$ = 18.9 Hz, Ru=C_α) ppm. Selected spectroscopic data for **4c**: IR (KBr, cm^{-1}) ν 840 (PF_6^-); ^{31}P{^{1}H} ($CDCl_3$) δ 40.48 and 40.70 (d, $^2J_{PP}$ = 20.4 Hz) ppm; ^{1}H ($CDCl_3$) δ 4.57 (br, 1H, Ru=C=CH) ppm; ^{13}C{^{1}H} ($CDCl_3$) δ 354.77 (vt, $^2J_{CP}$ = 16.5 Hz, Ru=C_α) ppm.

Synthesis of σ-Enynyl Complexes 5a−c: General Procedure. A solution containing a mixture of **3a**−**c**/**4a**−**c** (1 mmol) in 50 mL of dichloromethane was treated at room temperature with K_2CO_3 (1 g, 7.2 mmol) for 3 h. The solvent was then removed under vacuum, the solid residue extracted with diethyl ether (ca. 100 mL), and the resulting solution filtered over Kieselguhr. Evaporation of the solvent gave an orange solid, which was dried in vacuo. **5a**: Yield: 83% (0.858 g). Anal. Calcd for $C_{66}H_{62}P_2ORu$ (1034.24): C, 76.64; H, 6.04. Found: C, 76.42; H, 6.14. IR (KBr, cm^{-1}): ν 1674 (C=O), 2063 (C≡C). **5b**: Yield: 71% (0.723 g). Anal. Calcd for $C_{65}H_{58}P_2ORu$ (1018.19): C, 76.67; H, 5.74. Found: C, 76.54; H, 5.80. IR (KBr, cm^{-1}): ν 2062 (C≡C), 3554 (OH). **5c**: Yield: 73% (0.753 g). Anal. Calcd for $C_{66}H_{60}P_2ORu$ (1032.23): C, 76.79; H, 5.85. Found: C, 76.82; H, 5.77. IR (KBr, cm^{-1}): ν 2063 (C≡C).

Synthesis of Vinylvinylidene Complexes 6a−c: General Procedure. A solution of the corresponding σ-enynyl complex **5a**−**c** (0.3 mmol) in 20 mL of CH_2Cl_2 was treated at

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(24) We note that this energetic effect is higher in the case of strained polycyclic structures such as those derived from steroids **2a**−**c**.

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room temperature with $MeOSO_2CF_3$ (34 μL, 0.3 mmol) for 30 min. The solvent was then removed under vacuum and the orange solid residue washed with diethyl ether (3 × 20 mL) and dried in vacuo. **6a**: Yield: 79% (0.284 g). Anal. Calcd for $C_{68}H_{65}O_4F_3P_2SRu$ (1198.33): C, 68.15; H, 5.46. Found: C, 68.31; H, 5.23. IR (KBr, cm^{-1}): ν 1150, 1223, and 1272 ($CF_3SO_3^-$), 1665 (C═O). **6b**: Yield: 85% (0.301 g). Anal. Calcd for $C_{67}H_{61}O_4F_3P_2SRu$ (1182.30): C, 68.06; H, 5.20. Found: C, 68.12; H, 5.31. IR (KBr, cm^{-1}): ν 1155, 1224, and 1286 ($CF_3SO_3^-$), 3563 (OH). **6c**: Yield: 81% (0.291 g). Anal. Calcd for $C_{68}H_{63}O_4F_3P_2SRu$ (1196.33): C, 68.27; H, 5.30. Found: C, 68.32; H, 5.22. IR (KBr, cm^{-1}): ν 1150, 1223, and 1263 ($CF_3SO_3^-$).

Synthesis of Terminal 1,3-Enynes 7a−c: General Procedure. A solution containing a mixture of complexes **3a−c**/**4a−c** (0.5 mmol) in acetonitrile (30 mL) was heated under reflux for 30 min. The solution was then evaporated to dryness and the resulting solid residue extracted with diethyl ether (ca. 50 mL) and filtered. A yellow solid containing mainly the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**8**) remains insoluble. The extract was evaporated to dryness and the crude product purified by column chromatography on silica gel with a mixture of hexane/diethyl ether (3:1) as eluent. Evaporation of the solvents gave terminal enynes **7a−c** as white solids. **7a**: Yield: 74% (0.109 g). Anal. Calcd for $C_{21}H_{26}O$ (294.43): C, 85.66; H, 8.90. Found: C, 85.44; H, 9.02. IR (KBr, cm^{-1}): ν 1679 (C═O), 2090 (C≡C), 3272 (≡C−H). **7b**: Yield: 83% (0.115 g). Anal. Calcd for $C_{20}H_{22}O$ (278.39): C, 86.26; H, 7.96. Found: C, 86.32; H, 8.14. IR (KBr, cm^{-1}): ν 2082 (C≡C), 3254 (≡C−H), 3512 (OH). **7c**: Yield: 81% (0.118 g). Anal. Calcd for $C_{21}H_{24}O$ (292.42): C, 86.25; H, 8.27. Found: C, 86.43; H, 8.30. IR (KBr, cm^{-1}): ν 2085 (C≡C), 3293 (≡C−H).

Synthesis of Phosphonio-Alkynyl Complexes 9a−c: General Procedure. A solution containing a mixture of **3a−c**/**4a−c** (0.5 mmol) in 50 mL of tetrahydrofuran was treated at room temperature with PMe_2Ph (71 μL, 0.5 mmol) for 30 min. The solvent was then removed under vacuum and the yellow solid residue washed with diethyl ether (3 × 20 mL) and dried in vacuo. **9a**: Yield: 92% (0.606 g). Anal. Calcd for $C_{74}H_{74}F_6P_4ORu$: C, 67.42; H, 5.65. Found: C, 67.53; H, 5.59. IR (KBr, cm^{-1}): ν 839 (PF_6^-), 1669 (C═O), 2042 (C≡C). **9b**: Yield: 85% (0.553 g). Anal. Calcd for $C_{73}H_{70}F_6P_4ORu$: C, 67.32; H, 5.41. Found: C, 67.41; H, 5.33. IR (KBr, cm^{-1}): ν 839 (PF_6^-), 2042 (C≡C), 3534 (OH). **9c**: Yield: 86% (0.566 g). Anal. Calcd for $C_{74}H_{72}F_6P_4ORu$: C, 67.52; H, 5.51. Found: C, 67.31; H, 5.62. IR (KBr, cm^{-1}): ν 842 (PF_6^-), 2041 (C≡C).

Computational Details. All calculations were carried out with the Gaussian98 program package.[26] The molecular geometries were optimized, without any molecular symmetry constraint, using Schlegel's analytical gradient procedure[27] at the B3-LYP variant of density functional theory[28] with the standard split-valence 6-31G(d,p) basis set for C and H[29] and the pseudorelativistic effective core potential (ECP) by Hay and Wadt for Ru and P.[30] This basis set was referred to as DZV(d,p). The optimized structures were characterized as minima (representing equilibrium structures) or saddle points (representing transition structures) by analytic frequency calculations, which also yielded zero-point vibrational energy and thermochemical analysis. Single-point calculations on the DFT geometries were performed with incorporation of correlation energy using Møller−Plesset perturbation theory with second-order corrections (MP2).[31]

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Supporting Information Available: NMR spectroscopic data for compounds **5**−**7a**−**c** and **9a**−**c**. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (from rt to −60 °C) of **3**−**4a** in CD_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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