Reactivity of Indenyl–Ruthenium(II) Vinylidene Complexes: Selective Synthesis of Alkenyl–Phosphonio Derivatives via Nucleophilic Addition of Triphenylphosphine on Their η^2-Alkyne Tautomers. Theoretical Study of the η^1-Vinylidene–η^2-Alkyne Tautomerization

Victorio Cadierno, M. Pilar Gamasa, José Gimeno,* and
Covadonga González-Bernardo

*Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química
Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química,
Universidad de Oviedo, E-33071 Oviedo, Spain*

Enrique Pérez-Carreño and Santiago García-Granda

*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo,
E-33071 Oviedo, Spain*

The activation of terminal alkynes with the halide derivatives [RuX(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)-(PR$_3$)] (R = Me, X = Br, PR$_3$ = PPh$_3$ (**1**), P^{i}Pr$_3$ (**3**); R = H, X = I, PR$_3$ = P^{i}Pr$_3$ (**2**)) and AgBF$_4$ affords, in dichloromethane at room temperature, equilibrium mixtures containing the corresponding η^1-vinylidene and η^2-alkyne tautomers [Ru{=C=C(H)R'}(η^5-1,2,3-R$_3$C$_9$H$_4$)-(CO)(PR$_3$)][BF$_4$] (**4a**–**c**) and [Ru(η^2-HC≡CR')(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)][BF$_4$] (**5a**–**c**), respectively. The reaction of **1** with AgBF$_4$ and phenylacetylene has been studied by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy: at low temperature (−60 °C) the vinylidene complex [Ru{=C=C(H)Ph}(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] (**4a**) is initially observed which upon warming (14 °C) forms an equilibrium with the π-alkyne derivative [Ru(η^2-HC≡CPh)-(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] (**5a**). Treatment of this mixture with KO^{t}Bu, in dichloromethane at room temperature selectively yields the neutral σ-alkynyl derivative [Ru(C≡CPh)(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)] (**6**) by displacement of the aforementioned equilibrium via deprotonation of the acidic vinylidene proton in **4a**, while the addition of PPh$_3$ to this mixture stereoselectively affords the cationic alkenyl–phosphonio complex (*E*)-[Ru{C(H)=C(PPh$_3$)Ph}(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] [(*E*)-**7**] via the nucleophilic attack of PPh$_3$ on the coordinated π-alkyne in **5a**. In a similar fashion, compounds (*E*)-[Ru{C(H)=C(PPh$_3$)-R'}(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)][BF$_4$] (R = Me, PR$_3$ = PPh$_3$, R' = 1-cyclooctenyl [(*E*)-**13**]; R = H, PR$_3$ = P^{i}Pr$_3$, R' = Ph [(*E*)-**8**], 1-cyclooctenyl [(*E*)-**14**] can be selectively obtained by addition of PPh$_3$ to the corresponding reaction mixture. The monosubstituted alkenyl–vinylidene complexes [Ru{=C=C(H)CH=CRR'}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (R = R' = Ph (**11a**); R = H, R' = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) [(*E*)-**11b**], 4-OMe-C$_6$H$_4$ [(*Z*)-**11c**]) also react with triphenylphosphine, but in refluxing methanol, to afford the alkenyl–phosphonio derivatives (*EE*)-[Ru{C(H)=C(PPh$_3$)CH=CRR'}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**12a**–**c**) stereoselectively. The process also proceeds via an initial η^1-vinylidene–η^2-alkyne tautomerization followed by the nucleophilic attack of PPh$_3$ on the coordinated π-alkyne. The crystal structures of (*E*)-[Ru{C(H)=C(PPh$_3$)Ph}-(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] ((*E*)-**7**) and (*EE*)-[Ru{C(H)=C(PPh$_3$)CH=CH(η^5-C$_5$H$_4$)-Fe(η^5-C$_5$H$_5$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] ((*EE*)-**12b**) have been determined by X-ray diffraction methods. Ab initio molecular orbital calculations on the η^1-vinylidene to η^2-alkyne tautomerization on the models [Ru(η^5-C$_9$H$_7$)(PH$_3$)L(C$_2$H$_2$)]$^+$ (L = CO, PH$_3$) are also reported.

Introduction

A great deal of attention has been devoted to the chemistry of transition-metal vinylidene complexes [M]=C=CR$_2$ during the past 2 decades.[1] Thus, it is now

---

* To whom correspondence should be addressed. E-mail: jgh@sauron.quimica.uniovi.es.

(1) For comprehensive reviews see: (a) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev. (Engl. Transl.)* **1989**, *58*, 693. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) Werner, H. *Nachr. Chem. Technol. Lab.* **1992**, *40*, 435. (d) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45. (e) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (f) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193–195*, 977.

well-established that the stability and properties of such derivatives are essentially a function of the nature of both the metal center and its ancillary ligands.[1] In particular, electron-rich ruthenium(II) complexes have proven to be appropiate precursors for the preparation of stable vinylidene derivatives.[1] This fact has allowed the study in detail of their chemical behavior, and, by the aid of these studies, very useful synthetic applications have recently emerged.[2]

One of the most important reasons for the growing development of the chemistry of ruthenium(II)–vi-

nylidenes is that they are readily accessible from simple terminal alkynes.[1] The mechanism of this 1-alkyne to vinylidene rearrangement has been extensively studied both experimentally and theoretically, and it is now well-known that it depends on the nature of the ruthenium fragment. Nevertheless, as a common fact, the mechanism involves the initial side-on coordination of the alkyne to ruthenium, to form an intermediate η^2-alkyne complex.[3] Significantly, η^2-alkyne complexes [Ru-$(\eta^2$-HC≡CR)$(\eta^5$-C$_5$H$_5$)L$_2$]$^+$ (R = H, L = PMe$_2$Ph, L$_2$ = 1,2-bis(diisopropylphosphino)ethane; R = Me, L = PMe$_3$) have been isolated as stable intermediates in the formation of the corresponding vinylidene derivatives [Ru{=C=C(H)R}$(\eta^5$-C$_5$H$_5$)L$_2$]$^{+}$.[3b,4] Although it has not been extensively studied, the reverse process, i.e., interconversion of ruthenium(II)−vinylidenes into their corresponding η^2-alkyne tautomers, has been also shown to occur in a few cases.[5]

We have recently reported ab initio molecular orbital (MO) calculations on the η^1-vinylidene−η^2-alkyne tautomerization reaction path, back and forth of the equilibrium between [Ru(=C=CH$_2$)$(\eta^5$-C$_9$H$_7$)(PH$_3$)$_2$]$^+$ and [Ru(η^2-HC≡CH)$(\eta^5$-C$_9$H$_7$)(PH$_3$)$_2$]$^{+}$.[6] It is shown that (i) the vinylidene species is thermodinamically more stable

than the η^2-alkyne complex and (ii) the calculated energy barrier to reach the π-alkyne species from the vinylidene is low enough to be overcome under normal experimental reaction conditions (ca. 60 °C). In accordance with these expectations, we have found that the vinylidene moiety in monosubstituted complexes [Ru{=C=C(H)R}$(\eta^5$-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ is labile, being easily replaced by nitriles, at refluxing temperatures, to form [Ru(N≡CR′)$(\eta^5$-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ and the corresponding terminal alkyne which are generated by the displacement of the π-coordinated alkyne in the transient [Ru(η^2-HC≡CR)$(\eta^5$-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ species.[6,7]

Continuing with these studies herein we describe (i) the activation of terminal alkynes by the electrophilic carbonyl compounds [RuX$(\eta^5$-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)] (R = Me, X = Br, PR$_3$ = PPh$_3$, P^{i}Pr$_3$; R = H, X = I, PR$_3$ = P^{i}Pr$_3$) which leads to equilibrium mixtures containing both η^1-vinylidene and η^2-alkyne species; (ii) the synthesis of alkenyl−phosphonio derivatives (*E*)-[Ru{C(H)= C(PPh$_3$)R′}$(\eta^5$-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)]$^+$ obtained by addition of PPh$_3$ to the aforementioned equilibrium mixtures which are displaced easily at room temperature toward the formation of the π-alkyne complexes (this allows the selective nucleophilic attack of the phosphine to afford the alkenyl−phosphonio complexes); and (iii) the synthesis of analogous alkenyl−phosphonio complexes (*E*)-[Ru{C(H)=C(PPh$_3$)R}$(\eta^5$-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$, via the regioselective nucleophilic addition of PPh$_3$ on the π-alkyne complexes [Ru(η^2-C≡CR)$(\eta^5$-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ generated as transient species from the corresponding stable vinylidene derivatives [Ru{=C=C(H)R}$(\eta^5$-C$_9$H$_7$)- (PPh$_3$)$_2$]$^+$ in refluxing methanol. To study the electronic properties of the electrophilic indenyl−ruthenium(II) fragments [Ru$(\eta^5$-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)], which enable the easy tautomerization of the vinylidene moiety into the π-alkyne ligand, ab initio molecular orbital calcula-

(2) Ruthenium(II) vinylidene complexes have been shown to be excellent promoters for selective C−C coupling reactions. For recent references see: (a) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Am. Chem. Soc.* **1998**, *120*, 6175. (b) Jia, G.; Lau, C. P. *J. Organomet. Chem.* **1998**, *565*, 37, and references therein. (c) Yi, C. S.; Liu, N. *Organometallics* **1998**, *17*, 3158. (d) Huang, D.; Oliván, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 4700. (e) Yam, V. W. W.; Chu, B. W. K.; Cheung, K. K. *Chem. Commun.* **1998**, 2261. (f) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **1999**, 1141. (g) Jiménez Tenorio, M. A.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 1333. (h) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans.* **2000**, 2279. (i) Lin, Y. C. *J. Organomet. Chem.* **2001**, *617−618*, 141, and references therein. (j) Pavlik, S.; Gemel, C.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Organomet. Chem.* **2001**, *617−618*, 301, and references therein. They are also active catalysts for the ring-opening metathesis polymerization (ROMP) of olefines: (k) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (l) Katayama, H.; Ozawa, F. *Chem. Lett.* **1998**, 67. (m) Katayama, H.; Yoshida, T.; Ozawa, F. *J. Organomet. Chem.* **1998**, *562*, 203. (n) del Rio, I.; van Koten, G. *Tetrahedron Lett.* **1999**, *40*, 1401. (o) Katayama, H.; Urushima, H.; Ozawa, F. *J. Organomet. Chem.* **2000**, *606*, 16. (p) Saoud, M.; Romerosa, A.; Peruzzini, M. *Organometallics* **2000**, *19*, 4005.

(3) Following this initial step two different pathways have been proposed: (i) an intramolecular [1,2]-H shift to give the thermodynamically favored vinylidene isomer (for ab initio molecular orbital (MO) calculations on the rearrangement of [Ru(η^2-HC≡CH)Cl$_2$(PH$_3$)$_2$] to [Ru(=C=CH$_2$)Cl$_2$(PH$_3$)$_2$] supporting this intramolecular process see: (a) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105), and (ii) the formation of an intermediate hydride−alkynyl [Ru(H)(C≡CR)] complex, through the oxidative addition of the coordinated alkyne, followed by a hydrogen shift to the C$_\beta$ atom of the alkynyl group to afford the final vinylidene tautomer [Ru{=C=C(H)R}]: (b) de los Rios, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. (c) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. It should be noted that η^2-alkyne to η^1-vinylidene tautomerizations promoted by d^8 (Co(I), Rh(I), Ir(I)) metal complexes have been theoretically [(d) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360. (e) Pérez-Carreño, E.; Paoli, P.; Ienco, A.; Mealli, C. *Eur. J. Inorg. Chem.* **1999**, 1315.] and experimentally proved to occur also through this oxidative mechanism. See for example, the following. Co(I): (f) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697. Rh(I): (g) Windmüller, B.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *502*, 147. (h) Werner, H.; Gevert, O.; Steinert, P.; Wolf, J. *Organometallics* **1995**, *14*, 1786. (i) Wiedemann, R.; Fleischer, R.; Stalke, D.; Werner, H. *Organometallics* **1997**, *16*, 866. (j) Kovacik, I.; Laubender, M.; Werner, H. *Organometallics* **1997**, *16*, 5607, and references therein. Ir(I): (k) Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.* **1996**, *2*, 19. (l) Werner, H.; Lass, R. W.; Gevert, O.; Wolf, J. *Organometallics* **1997**, *16*, 4077, and references therein.

(4) (a) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165. (b) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518.

(5) The complex [Ru(=C=CH$_2$)Cl(κ^2-*P,O*-^{i}Pr$_2$PCH$_2$CH$_2$OMe)$_2$]$^+$ is stable only under an acetylene atmosphere indicating a reversible process: (a) Martín, M.; Gevert, O.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2275. The reaction of [Ru{=C=C(H)Ph}Cl(κ^2-*P,O*-^{i}Pr$_2$-PCH$_2$CH$_2$OMe)$_2$]$^+$, [Ru{=C=C(H)Ph}{=C(NHPh)(CH$_2$Ph)}Cl(PNP)]$^+$ (PNP = ^{n}PrN(CH$_2$CH$_2$PPh$_2$)$_2$) and [Ru{=C=C(H)R}$(\eta^5$-C$_5$H$_5$)(tmeda)]$^+$ (R = ^{t}Bu, SiMe$_3$; tmeda = Me$_2$N(CH$_2$)$_2$NMe$_2$) with CO which yields the free terminal alkyne and the carbonyl compounds [RuCl(CO)(κ^2-*P,O*-^{i}Pr$_2$PCH$_2$CH$_2$OMe)$_2$]$^+$, [Ru{=C(NHPh)(CH$_2$Ph)}Cl(CO)(PNP)]$^+$ and [Ru$(\eta^5$-C$_5$H$_5$)(CO)(tmeda)]$^+$, respectively, seems to proceed via an intermediate π-alkyne complex. See ref 5a and: (b) Bianchini, C.; Purches, G.; Zanobini, F.; Peruzzini, M. *Inorg. Chim. Acta* **1998**, *272*, 1. (c) Gemel, C.; Huffman, J. C.; Caulton, K. G.; Mauthner, K.; Kirchner, K. *J. Organomet. Chem.* **2000**, *593−594*, 342. Similarly, when complex [RuI$_2${=C=C(H)Ph}(κ^2-*P,O*-^{i}Pr$_2$PCH$_2$CH$_2$OMe)(κ-*P*-^{i}Pr$_2$-PCH$_2$CH$_2$OMe)] is heated at a high temperature, phenylacetylene is recovered with concomitant formation of *trans*-[RuI$_2$(κ^2-*P,O*-^{i}Pr$_2$PCH$_2$-CH$_2$OMe)$_2$] (see ref 5a). The vinylidene moiety is also displaced from the reaction of [Ru{=C=C(H)Me}$(\eta^5$-C$_5$H$_5$)(PMe$_3$)$_2$]$^+$, *trans*-[Ru(C≡CR)-{=C=C(H)R}{P(OR)$_3$}$_4$]$^+$ and [Ru{=C=C(H)R}Cl{HB(pz)$_3$}(PPh$_3$)] with two electron ligands (L = phosphines, phosphites, nitriles, isocyanides or CO) to give the free terminal alkyne and [Ru$(\eta^5$-C$_5$H$_5$)(L)(PMe$_3$)$_2$]$^+$, *trans*-[Ru(C≡CR)(L){P(OR)$_3$}$_4$]$^+$ or [RuCl{HB(pz)$_3$}(L)(PPh$_3$)], respectively. See ref 4a above. (d) Albertin, G.; Antoniutti, S.; Bordignon, E.; Cazzaro, F.; Ianelli, S.; Pellizi, G. *Organometallics* **1995**, *14*, 4114. (e) Slugovc, C.; Sapunov, V. N.; Wiede, P.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4209. Finally, the formation of [RuCl$(\eta^5$-C$_5$Me$_5$){P(OR)$_3$}$_2$] by treatment of vinylidene complexes [RuCl{=C=C(H)R}$(\eta^5$-C$_5$Me$_5$)(PPh$_3$)] with phosphites has been also reported: (f) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *522*, 307.

(6) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821.

(7) (a) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **2000**, 451. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *J. Organomet. Chem.* **2001**, *621*, 39. (c) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **2001**, *20*, 3175.

Scheme 1
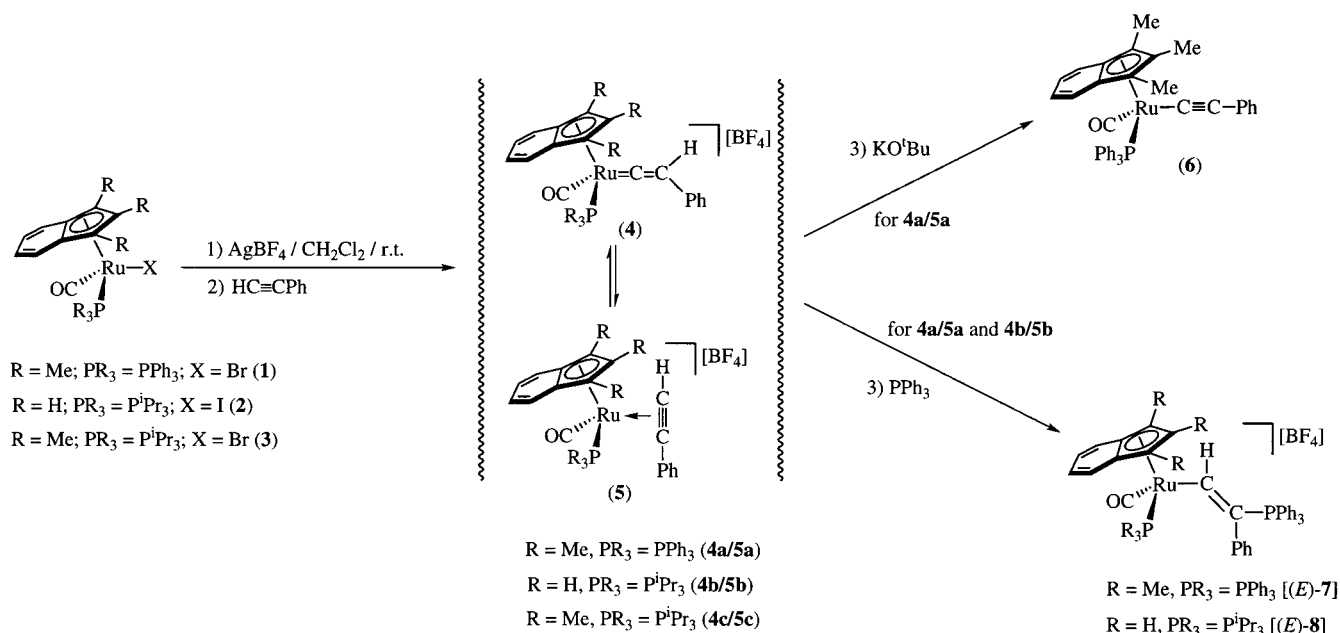
tions are also reported. This has allowed us a rational comparation of its chemical behavior with respect to that of the analogous fragment [Ru(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]. Part of this work has been preliminarily communicated.[8]

Results

Activation of Phenylacetylene by [RuX(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)] (R = Me, X = Br, PR$_3$ = PPh$_3$, P^{i}Pr$_3$; R = H, X = I, PR$_3$ = P^{i}Pr$_3$). The treatment of complexes [RuX(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)] (R = Me, X = Br, PR$_3$ = PPh$_3$ (**1**), P^{i}Pr$_3$ (**3**); R = H, X = I, PR$_3$ = P^{i}Pr$_3$ (**2**))[9] with an slight excess of AgBF$_4$ (ca. 1.1:1) in dichloromethane at room temperature leads, as monitored by IR spectroscopy, to the clean formation of the highly unstable tetrafluoroborate adducts [Ru(FBF$_3$)-(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)]. These species cannot be isolated and, when treated in situ with phenylacetylene, afford complicated reaction mixtures containing the corresponding vinylidene complexes [Ru{=C=C(H)Ph}-(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)][BF$_4$] (**4a**−**c**) in equilibrium with its η^2-alkyne tautomers [Ru(η^2-HC≡CPh)(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)][BF$_4$] (**5a**−**c**), as the major reaction products, as well as additional uncharacterized organometallic species (Scheme 1). To get information of the course of these processes, the reaction of **1** with AgBF$_4$ and phenylacetylene has been monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy at variable temperatures (details are given in the Experimental Section). Thus, at low temperature (−60 °C), the formation of the vinylidene complex **4a** is initially observed as inferred clearly from the apparition of a typical Ru=C=CH proton resonance at δ 4.76 ppm in the ^{1}H NMR spectrum. At this temperature, **4a** slowly forms an equilibrium with **5a** (ca. ratio **4a:5a** = 1:1.1). The formation of **5a** is supported by the presence in the ^{1}H NMR spectrum of a

new singlet resonance at δ 3.71 ppm assigned to the ≡CH proton of the π-coordinated phenylacetylene molecule.[10] When the solution is gradually warmed to 14 °C, the signals due to **4a** slowly decrease, while those assigned to **5a** increase to obtain a final ratio **4a:5a** of 1:1.5. The formation of minor uncharacterized species was also observed starting from −25 °C. This is confirmed by the ^{31}P{^{1}H} NMR spectrum which shows at room temperature the presence in solution of six different compounds, being **4a** and **5a** the major reaction products.[11]

The treatment of this reaction mixture with KO^{t}Bu at room temperature strongly support the existence of an η^1-vinylidene−η^2-alkyne equilibrium since the neutral σ-alkynyl derivative [Ru(C≡CPh)(η^5-1,2,3-Me$_3$C$_9$H$_4$)-(CO)(PPh$_3$)] (**6**) is generated in high yield (75%), via deprotonation of the acidic vinylidene proton of **4a** (Scheme 1).[8] Complex **6** has been characterized by IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopy and mass spectrometry (FAB) showing spectroscopic properties similar to those reported for other indenyl−ruthenium(II) σ-alkynyl derivatives (details are given in the Experimental Section).[7,12] In particular, the presence of the alkynyl group is confirmed by the appearance of (i) a ν(C≡C) absorption band at 2093 cm^{-1} in the IR spectrum (KBr), and (ii) a typical doublet resonance ($^2J_{CP}$ = 25.0 Hz) for the Ru−C$_\alpha$ in the ^{13}C{^{1}H} NMR spectra at δ 109.87 ppm, the C$_\beta$ carbon resonance falling within the aromatic region.

These results are in accordance with those recently reported by Lugan and co-workers who described that the protonation of [Ru(C≡CPh)(η^5-C$_5$H$_5$)(CO)(PPh$_3$)] at low temperature (−80 °C) selectively affords the vi-

(8) Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 2483.

(9) (a) Cadierno, V.; Díez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *Coord. Chem. Rev.* **1999**, *193−195*, 147. (b) Gamasa, M. P.; Gimeno, J.; González-Bernardo, C. Manuscript in preparation.

(10) The resonances assigned to the vinylidene [Ru]=C=C*H*Ph and π-alkyne [Ru](η^2-*H*C≡CPh) protons are in accordance with data reported in the literature. See refs 3b,c, 4 and: Nombel, P.; Lugan, N.; Mathieu, R. *J. Organomet. Chem.* **1995**, *503*, C22.

(11) We note that hydride−alkynyl ruthenium(IV) species were not detected by ^{1}H NMR spectroscopy. In agreement with this we have found that the calculated energy value for [Ru(H)(C≡CH)(η^5-C$_9$H$_7$)-(CO)(PH$_3$)] is 40.2 kcal/mol, similar to that found for the transition state **D** (L = PH$_3$) (Figure 5).

Scheme 2
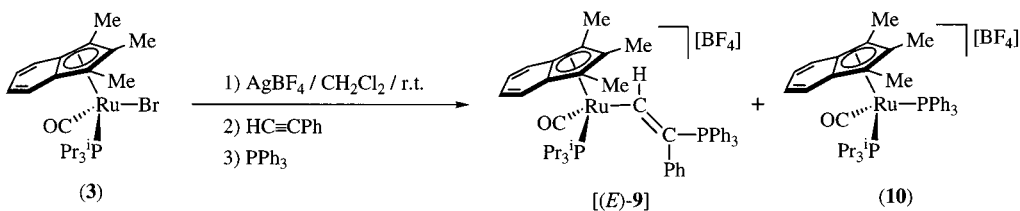
nylidene derivative [Ru{=C=C(H)Ph}(η^5-C$_5$H$_5$)(CO)-(PPh$_3$)]$^+$ which, upon warming to room temperature, readily isomerizes to give a mixture with its η^2-alkyne tautomer [Ru(η^2-HC≡CPh)(η^5-C$_5$H$_5$)(CO)(PPh$_3$)]$^+$.[10]

Synthesis of Alkenyl−Phosphonio Complexes (*E*)-[Ru{C(H)=C(PPh$_3$)Ph}(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)-(PR$_3$)][BF$_4$] (R = Me, PR$_3$ = PPh$_3$; R = H, PR$_3$ = P^{i}Pr$_3$). The formation of the transient π-alkyne species **5a** is also assessed by the addition at room temperature of 1 equiv of triphenylphosphine to a dichloromethane solution containing complexes **4a** and **5a**. The equilibrium between these species is readily displaced, via the regioselective nucleophilic attack of PPh$_3$ on the η^2-coordinated phenylacetylene molecule on **5a**, to form the cationic alkenyl−phosphonio derivative (*E*)-[Ru{C(H)=C(PPh$_3$)Ph}(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] [(*E*)-**7**; 60% yield; Scheme 1].[13] The NMR data are in agreement with the presence of an alkenyl−phosphonio chain (details are given in the Experimental Section) and can be compared to those reported for other indenyl−ruthenium(II) alkenyl complexes.[12e,14] Thus, the ^{31}P{^{1}H} NMR spectrum displays resonances consistent with an AM spin system (δ 16.70 (d, C−PPh$_3$) and 52.82 (d, Ru−PPh$_3$) ppm with $^4J_{PP}$ = 6.2 Hz), while the vinylic hydrogen appears, in the ^{1}H NMR spectrum, as a downfield doublet of doublets resonance ($^3J_{HP}$ = 32.5 and 7.5 Hz) at δ 9.43 ppm. The ^{13}C{^{1}H} NMR spectrum

displays the typical low-field resonance for the Ru−C$_\alpha$ atom in alkenyl complexes, as a doublet of doublets at δ 206.52 ppm ($^2J_{CP}$ = 13.9 and 2.8 Hz), as well as the doublet signal (J_{CP} = 85.1 Hz) due to the C$_\beta$ nucleus at δ 121.28 ppm. Furthermore, the *E* stereochemistry proposed for **7** was undoubtedly confirmed by means of X-ray diffraction methods (see below).

Under similar reaction conditions complex (*E*)-[Ru-{C(H)=C(PPh$_3$)Ph}(η^5-C$_9$H$_7$)(CO)(P^{i}Pr$_3$)][BF$_4$] [(*E*)-**8**] has also been prepared (70% yield; Scheme 1). In contrast, the addition of PPh$_3$ to the reaction mixture resulting from the treatment of **3** with AgBF$_4$ and phenylacetylene proceeds through a different way. Thus, IR and NMR (^{31}P{^{1}H} and ^{1}H) spectroscopies indicate the formation of a mixture containing the expected alkenyl-phosphonio derivative (*E*)-[Ru{C(H)=C(PPh$_3$)Ph}(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(P^{i}Pr$_3$)][BF$_4$] [(*E*)-**9**] and the bisphosphine complex [Ru(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)(P^{i}Pr$_3$)]-[BF$_4$] (**10**) (ca. ratio 1:1.6) (Scheme 2). Assuming that an equilibrium of the type shown in Scheme 1 is operative, the formation of **10** is probably the result of the competitive η^2-phenylacetylene substitution by PPh$_3$ vs the nucleophilic addition of the phosphine on the η^2-coordinated alkyne. It is apparent that the metallic fragment [Ru(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(P^{i}Pr$_3$)] is sterically more demanding toward the coordination of the alkyne than the analogous [Ru(η^5-C$_9$H$_7$)(CO)(P^{i}Pr$_3$)] and [Ru-(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)] moieties, increasing therefore its lability, which allows the partial substitution by PPh$_3$.

Synthesis of Alkenyl−Phosphonio Complexes (*EE*)-[Ru{C(H)=C(PPh$_3$)CH=CRR'}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]-[BF$_4$] (R = R' = Ph; R = H, R' = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$), 4-OMe-C$_6$H$_4$). Since the alkenyl−phosphonio complexes (*E*)-**7,8** are generated from the selective nucleophilic attack to the π-alkyne complexes **5a−b,** we believed it would be interesting to explore the scope of this reaction starting from stable vinylidene complexes [Ru{=C=C(H)R}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ for which we proved previously that a tautomerization to the corresponding π-alkyne can be achieved.[6,7] Thus, the monosubstituted alkenyl−vinylidene derivatives [Ru{=C=C(H)CH=CRR'}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (R = R' = Ph (**11a**);[6] R = H, R' = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) [(*E*)-**11b**],[12j] 4-OMe-C$_6$H$_4$ [(*Z*)-**11c**][6]) react with a large excess of PPh$_3$ (ca. 15:1) in refluxing methanol to give selectively the alkenyl−phosphonio complexes (*EE*)-[Ru{C(H)=C(PPh$_3$)CH=CRR'}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (R = R' = Ph (**12a**); R = H, R' = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) [(*EE*)-**12b**], 4-OMe-C$_6$H$_4$ [(*EE*)-**12c**]), which have been isolated in 66−73% yield (Scheme 3).
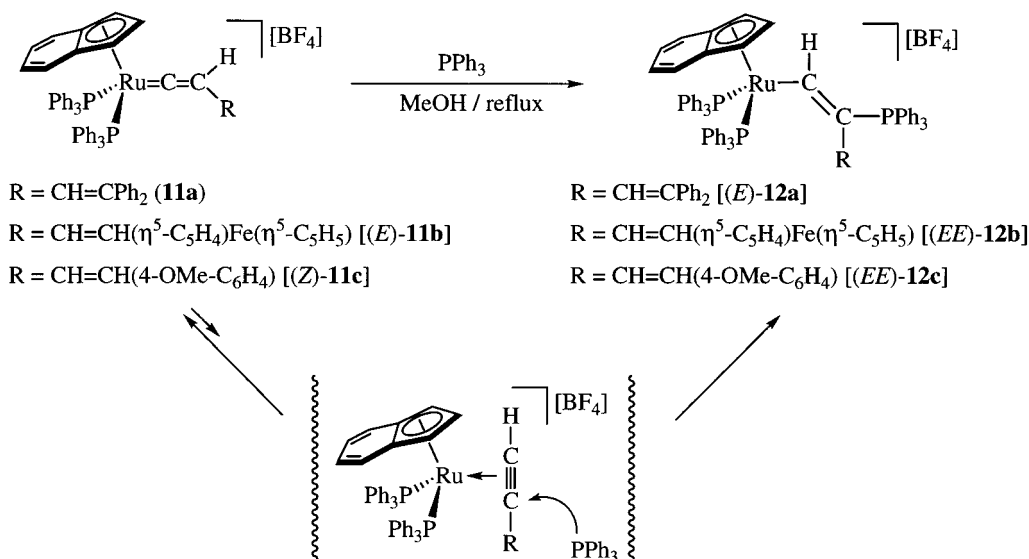
Compounds (*EE*)-**12a−c** have been characterized by elemental analyses, conductance measurements, and IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopies, being all data in accordance with the proposed formula-

(12) (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.; Borge, J.; García-Granda, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2495. (c) Gamasa, M. P.; Gimeno, J.; Godefroy, I.; Lastra, E.; Martín-Vaca, B. M.; García-Granda, S.; Gutierrez-Rodriguez, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1901. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S. *Organometallics* **1996**, *15*, 2137. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453. (g) Crochet, P.; Demerseman, B.; Vallejo, M. I.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 5406. (h) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Moretó, J. M.; Ricart, S.; Roig, A.; Molins, E. *Organometallics* **1998**, *17*, 697. (i) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; Ienco, A. *Organometallics* **1998**, *17*, 5216. (j) 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. (k) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1857. (l) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3235. (m) Sato, M.; Iawa, A.; Watanabe, M. *Organometallics* **1999**, *18*, 3208.

(13) Literature precedents for selective phosphine attack on coordinated alkynes to generate (*E*)-alkenyl−phosphonio complexes include: (a) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Chechulina, I. N.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1982**, *238*, 223. (b) Hoffman, D. M.; Huffman, J. C.; Lappas, D.; Wierda, D. A. *Organometallics* **1993**, *12*, 4312. (c) Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, *12*, 4560. (d) Jung, J. H.; Hoffman, D. M.; Lee, T. R. *J. Organomet. Chem.* **2000**, *599*, 112. (e) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, *19*, 4740.

(14) (a) Bassetti, M.; Casellato, P.; Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Martín-Vaca, B. *Organometallics* **1997**, *16*, 5470. (b) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M. *Organometallics* **1998**, *17*, 3707. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M. *J. Organomet. Chem.* **2001**, *617−618*, 261.

Scheme 3

R = CH=CPh$_2$ (**11a**)

R = CH=CH(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) [(*E*)-**11b**]

R = CH=CH(4-OMe-C$_6$H$_4$) [(*Z*)-**11c**]

R = CH=CPh$_2$ [(*E*)-**12a**]

R = CH=CH(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) [(*EE*)-**12b**]

R = CH=CH(4-OMe-C$_6$H$_4$) [(*EE*)-**12c**]

tions (details are given in the Experimental Section). In particular, the ^{1}H NMR spectra show the expected doublet of triplets resonance ($^3J_{HP}$ = 29.8−33.6 Hz, $^3J_{HP}$ = 9.7−10.0 Hz) for the vinylic RuCH= proton at ca. δ 10 ppm, while the C$_\alpha$ and C$_\beta$ atoms of the alkenyl chain appear, in the ^{13}C{^{1}H} NMR spectra, as a multiplet (δ 205.76−214.78 ppm) or a doublet signal (δ 121.06−122.09 ppm; J_{CP} = 85.0−88.7 Hz), respectively. It is interesting to note that complexes **12b,c** were obtained as the thermodynamically stable *EE* stereoisomers as inferred clearly from the values of the coupling constant for the olefinic CH=CH protons (J_{HH} = 17.1 Hz (**12b**), 16.7 Hz (**12c**)). In addition, the structure of (*EE*)-**12b** has been confirmed by X-ray diffraction methods (see below). Given the stereochemistry of the starting alkenyl−vinylidene complexes (*E*)-**11b** and (*Z*)-**11c**, an isomerization of the CH=CH double bond on **11c** has taken place. A similar isomerization has been previously observed in the reaction of **11c** with acetonitrile, which stereoselectively yields (*E*)-HC≡CCH=CH(4-OMe-C$_6$H$_4$) and [Ru(N≡CMe)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$].[6]

Synthesis of Alkenyl−Phosphonio Complexes (*E*)-[Ru{C(H)=C(PPh$_3$)R′}(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)-(PR$_3$)][BF$_4$] (R′ = 1-Cyclooctenyl; R = Me, PR$_3$ = PPh$_3$; R = H, PR$_3$ = P^{i}Pr$_3$). We have recently reported that 1-ethynyl-1-cycloalkanols HC≡CC(OH)CH$_2$CH$_2$-(CH$_2$)$_n$CH$_2$ (n = 1, 2, 3, 4), containing hydrogen atoms adjacent to the hydroxy group, react with indenyl−ruthenium(II) complexes [RuCl(η^5-C$_9$H$_7$)L$_2$] (L = PPh$_3$; L$_2$ = dppe) to give selectively alkenyl−vinylidene species of the type **C** (see Scheme 4). The process involves the initial formation of undetected π-alkyne and hydroxivinylidene derivatives (**A**), which spontaneously dehydrate to generate the final alkenyl−vinylidene species. Since allenylidene complexes **B** were never isolated, this fact indicates that the formation of vinylidene species **C** is thermodinamically favored.[12e,l]

With these precedents in mind, we wondered whether the modification of the electronic properties of the metal fragment would affect this reactivity. Thus, we explored the reactions of the tetrafluoroborate adducts [Ru-(FBF$_3$)(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)] (R = Me, PR$_3$ =

Scheme 4
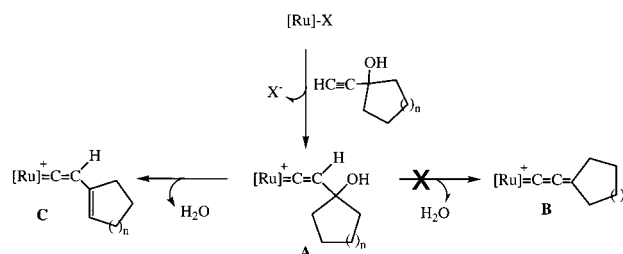
PPh$_3$; R = H, PR$_3$ = P^{i}Pr$_3$) (obtained in situ from complexes **1,2** in the presence of AgBF$_4$ in dichloromethane) with 1-ethynyl-1-cyclooctanol. In contrast to the analogous complexes [RuCl(η^5-C$_9$H$_7$)L$_2$], which are precursors of alkenyl−vinylidene derivatives **C**, the reactions of complexes **1,2** lead to complicated mixtures of products (observed by IR and ^{31}P{^{1}H} NMR spectroscopy) which could not be identified. To get information on the composition of these mixtures, 1 equiv of PPh$_3$ was added to the reaction media resulting in the formation of alkenyl−phosphonio derivatives (*E*)-[Ru{C(H)=C(PPh$_3$)R′}(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)][BF$_4$] (R′ = 1-cyclooctenyl; R = Me, PR$_3$ = PPh$_3$ [(*E*)-**13**]; R = H, PR$_3$ = P^{i}Pr$_3$ [(*E*)-**14**]) as the main reaction products (60 and 50% isolated yields, respectively) (Scheme 5).

Analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) are in accordance with the proposed formulations (see the Experimental Section for details). In particular, the ^{13}C{^{1}H} NMR spectra strongly support the presence of an alkenyl−phosphonio chain showing four low-field doublet resonances assigned to the Ru−C$_\alpha$ ((*E*)-**13**, δ 205.61 ($^2J_{CP}$ = 13.9 Hz) ppm; (*E*)-**14**, δ 206.52 ($^2J_{CP}$ = 12.0 Hz) ppm)), the C$_\beta$ ((*E*)-**13**, δ 122.35 (J_{CP} = 84.2 Hz) ppm; (*E*)-**14**, δ 122.61 (J_{CP} = 84.2 Hz) ppm)), the =C ((*E*)-**13**, δ 124.35 ($^2J_{CP}$ = 56.4 Hz) ppm; (*E*)-**14**, δ 126.16 ($^2J_{CP}$ = 57.3 Hz) ppm)), and the =CH ((*E*)-**13**, δ 135.04 ($^3J_{CP}$ = 9.2 Hz) ppm; (*E*)-**14**, δ 137.75 ($^3J_{CP}$ = 8.3 Hz) ppm)) carbons.

The formation of complexes (*E*)-**13,14** can be easily explained as the result of the regioselective nucleophilic attack of PPh$_3$ on the π-coordinated 1,3-enyne on intermediates [Ru(η^2-HC≡CR′)(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)-

Scheme 5

R = Me; PR$_3$ = PPh$_3$; X = Br (**1**)

R = H; PR$_3$ = P^{i}Pr$_3$; X = I (**2**)

R = Me; PR$_3$ = PPh$_3$ [(*E*)-**13**]

R = H; PR$_3$ = P^{i}Pr$_3$ [(*E*)-**14**]
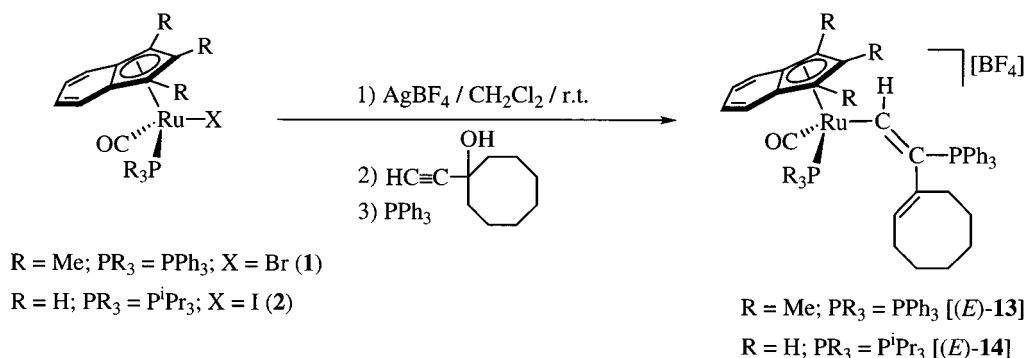
(PR$_3$)][BF$_4$] (R′ = 1-cyclooctenyl). Nevertheless, an alternative mechanism involving the initial formation of alkenyl−phosphonio derivatives (*E*)-[Ru{C(H)=C-(PPh$_3$)R′}(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)][BF$_4$] (R′ = cyclooctyl-1-ol) followed by the spontaneous dehydration of the cyclooctyl-1-ol moiety cannot be discarded.

X-ray Crystal Structures of (*E*)-[Ru{C(H)=C-(PPh$_3$)Ph}(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] and (*EE*)-[Ru{C(H)=C(PPh$_3$)CH=CH(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$]. Crystals of (*E*)-**7** and (*EE*)-**12b** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into saturated solutions of the complexes in dichloromethane. The crystal structure of (*EE*)-**12b** consists of one molecule of the complex together with two CH$_2$Cl$_2$ molecules of crystallization. ORTEP views of the molecular geometries of (*E*)-**7** and (*EE*)-**12b** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are listed in the captions. Both molecules exhibit the usual pseudooctahedral three-legged piano stool geometry with the corresponding indenyl ligand in the usual η^5 coordination mode. The interligand angles ((*E*)-**7**, C(3)−

Ru−P(1), C(1)−Ru−P(1), and C(1)−Ru−C(3); (*EE*)-**12b**, P(1)−Ru−P(2), C(1)−Ru−P(1), and C(1)−Ru−P(2)) and those between the centroid C* and the legs show values typical of a pseudooctahedron (see captions for Figures 1 and 2). The most interesting features of the structures are those related to the alkenyl−phosphonio ligands. An *E* configuration for this moiety (the ruthenium atom is located trans with respect to the triphenylphosphine group) is in both cases observed. In accordance with the NMR data, an *E* stereochemistry is also found for the CH=CH unit in complex (*EE*)-**12b**. The dihedral angle (DA) between the pseudo mirror plane of the metallic moiety (containing the ruthenium atom, the C(1) atom, and the centroid C* of the five-carbon ring of the indenyl ligands) and the mean phosphonio−alkenyl plane (containing the Ru, C(1), C(2) atoms) is 107.0(6) [(*E*)-**7**] and 100.7(6)° [(*EE*)-**12b**], showing a deviation from the orthogonal relationship calculated by theoretical studies.[15] The Ru−C(1) bond length ((*E*)-**7**, 2.039(7) Å; (*EE*)-
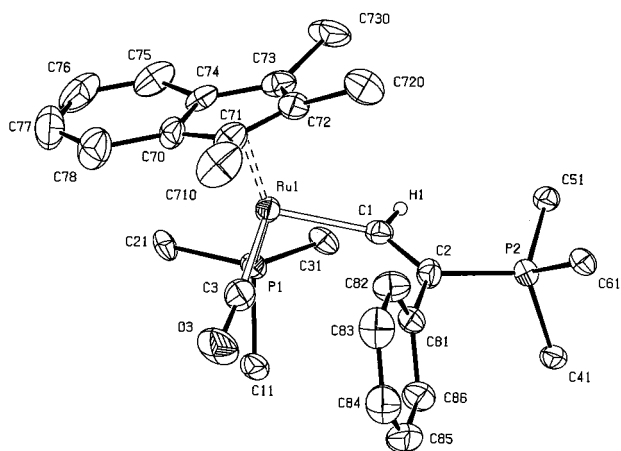
Figure 1. ORTEP view of the structure of the cation (*E*)-**7** (thermal ellipsoids at 30% probability). Aryl groups of the triphenylphosphine ligands have been omitted for clarity (C* = centroid of the indenyl ring). Selected bond lengths (Å) and angles (deg): Ru1−C* = 1.953(5); Ru1−P1 = 2.323-(2); Ru1−C1 = 2.039(7); Ru1−C3 = 1.831(9); C3−O3 = 1.170(9); C1−C2 = 1.344(10); C2−P2 = 1.801(7); C2−C81 = 1.513(10); C*−Ru1−P1 = 130.4(2); C*−Ru1−C1 = 119.5-(2); C*−Ru1−C3 = 121.4(3); C3−Ru1−P1 = 92.0(3); C1−Ru1−P1 = 86.7(2); C1−Ru1−C3 = 97.8(3); Ru1−C1−C2 = 135.6(6); C1−C2−P2 = 120.5(6); C1−C2−C81 = 124.9-(7); Ru1−C1−H1 = 113.1.
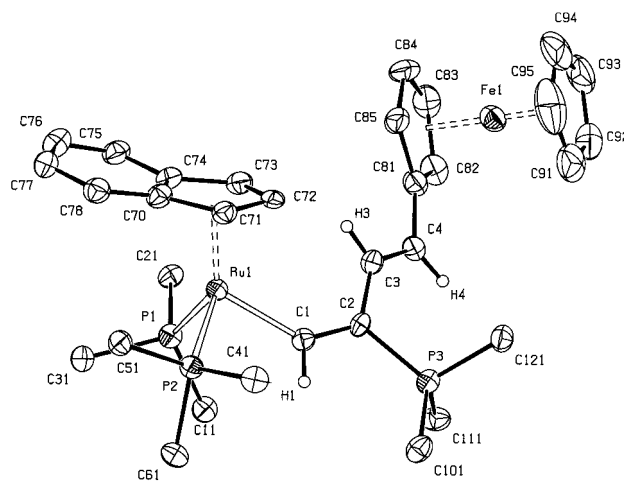

Figure 2. ORTEP view of the structure of the cation (*EE*)-**12b** (thermal ellipsoids at 30% probability). Aryl groups of the triphenylphosphine ligands have been omitted for clarity (C* = centroid of the indenyl ring). Selected bond lengths (Å) and angles (deg): Ru1−C* = 1.986(1); Ru1−P1 = 2.341(2); Ru1−P2 = 2.315(3); Ru1−C1 = 2.039(8); C1−C2 = 1.354(11); C2−P3 = 1.783(8); C2−C3 = 1.481-(11); C3−C4 = 1.334(12); C4−C81 = 1.465(13); C*−Ru1−P1 = 123.78(6); C*−Ru1−P2 = 119.47(8); C*−Ru1−C1 = 123.7(2); P1−Ru1−C1 = 90.1(2); P2−Ru1−C1 = 88.8(3); P1−Ru1−P2 = 102.70(10); Ru1−C1−C2 = 133.5(7); C1−C2−P3 = 120.4(6); C1−C2−C3 = 125.2(7); C2−C3−C4 = 130.4(8); C3−C4−C81 = 121.7(9); Ru1−C1−H1 = 113.2; P3−C2−C3 = 114.4(6).

**12b**, 2.039(8) Å) can be compared to that shown by the analogous indenyl−ruthenium(II) alkenyl−phosphonio complex (*E*)-[Ru{C(H)=C(PPh$_3$)R}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = 1-cyclohexenyl; 2.045(6) Å),[12e] but is slightly shorter than those reported for other alkenyl−ruthenium(II) complexes, i.e., (*E*)-[Ru{C(CO$_2$Me)=CH(CO$_2$-Me)}(η^5-C$_5$H$_5$)(dppe)] (2.07(1) Å),[16] (*Z*)-[Ru{C(CO$_2$Me)=CH(CO$_2$Me)}(η^5-C$_5$H$_5$)(CO)(PPh$_3$)] (2.080(8) Å),[16] (*E*)-[Ru{C(H)=CH(R)}Cl(CO)(Me$_2$Hpz)(PPh$_3$)$_2$] (R = ^{n}Pr (2.05(1) Å),[17] ^{t}Bu (2.063(7) Å)[18]), (*E*)-[Ru{C(H)=CH(^{t}-Bu)}(CO){NH=C(Me)(Me$_2$Hpz)}(PPh$_3$)$_2$][PF$_6$] (2.067(8) Å),[19] and (*E*)-[Ru{C(H)=CH(Ph)}(CH$_3$)(CO)$_2$(P^{i}Pr$_3$)$_2$] (2.141(3) Å).[20] The C−C bond lengths of the dienyl chain C(1)−C(4) in complex (*EE*)-**12b** are consistent with the typical sequence of double, single, and double bonds, i.e., 1.354(11), 1.481(11), and 1.334(12) Å, respectively. Similarly, the C(1)−C(2) distance in complex (*E*)-**7** (1.344(10) Å) shows also the expected value for a double carbon−carbon bond.

Theoretical Calculations. The η^2-alkyne to η^1-vinylidene tautomerization in the coordination sphere of transition metals is at present well-documented by theoretical studies which show that this process is energetically favored.[3a,d,e,6,21] When this transformation takes place in d^6 metal complexes, the [1,2]-H shift mechanism has been found to be the most favored.[3a] In a previous work we have reported a theoretical study on the tautomerization of the indenyl−ruthenium(II) complexes [Ru(η^5-C$_9$H$_7$)(PH$_3$)$_2$(C$_2$H$_2$)]$^+$ (C$_2$H$_2$ = η^2-HC≡CH, η^1-=C=CH$_2$).[6] As previously mentioned, the replacement in the metallic fragment of one of the PPh$_3$ ligands by CO seems to determine the tautomerization control, since, as shown for the moieties [Ru(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PR$_3$)]$^+$ (L = PPh$_3$, P^{i}Pr$_3$), the process leads to an equilibrium of the η^2-alkyne and the η^1-vinylidene complexes. To explain this behavior, we have performed a DFT study of the two reaction paths using as models the complexes [Ru(η^5-C$_9$H$_7$)(PH$_3$)L(C$_2$H$_2$)]$^+$ (L = CO, PH$_3$). Geometry optimization and vibrational analysis on the C$_2$H$_2$ unit with the [Ru(η^5-C$_9$H$_7$)(PH$_3$)L]$^+$ moieties were performed. The optimized structures and main geometric parameters are shown in Figures 3 (L = CO) and 4 (L = PH$_3$), while their relative energies are summarized in Figure 5.

In the previous theoretical study on [Ru(η^5-C$_9$H$_7$)(PH$_3$)$_2$(C$_2$H$_2$)]$^+$, following Wakatsuki's previous studies on Ru(II) complexes,[3a] we have assumed that the 1,2-hydrogen migration proceeds with C_s symmetry.[6] However, in this work we have examined an alternative process without restriction of symmetry which allows us to compare the results with the model [Ru(η^5-C$_9$H$_7$)(CO)(PH$_3$)(C$_2$H$_2$)]$^+$ in which the symmetry plane is not present. Similar reaction paths were found (Figure 5)
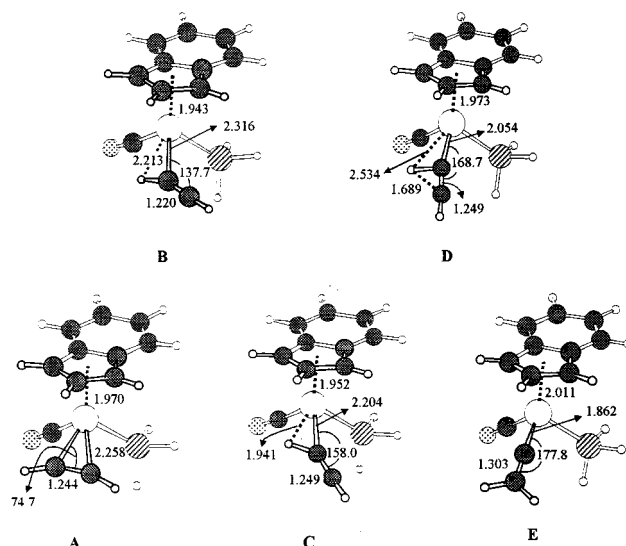
Figure 3. Optimized ab initio (B3LYP) structures (Å, deg) of reactants, products, and transition states for the formation of [Ru(η^5-C$_9$H$_7$)(=C=CH$_2$)(CO)(PH$_3$)]$^+$ from [Ru(η^5-C$_9$H$_7$)(CO)(PH$_3$)]$^+$ and C$_2$H$_2$.
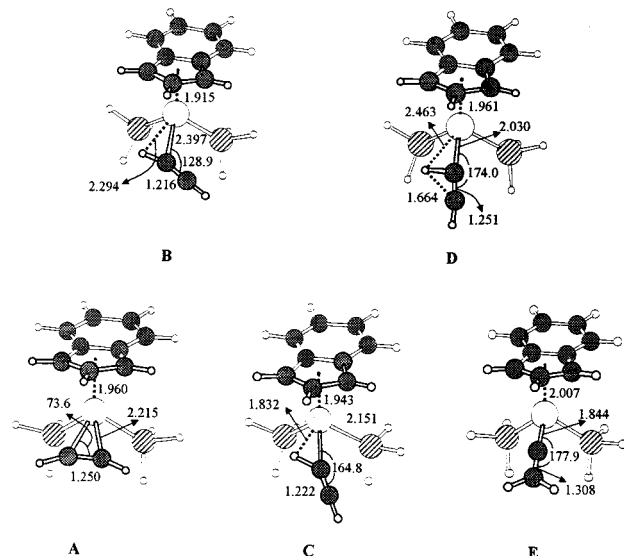
Figure 4. Optimized ab initio (B3LYP) structures (Å, deg) of reactants, products, and transition states for the formation of [Ru(η^5-C$_9$H$_7$)(=C=CH$_2$)(PH$_3$)$_2$]$^+$ from [Ru(η^5-C$_9$H$_7$)-(PH$_3$)$_2$]$^+$ and C$_2$H$_2$.

in the potential energy surface for the two types of complexes [Ru(η^5-C$_9$H$_7$)(PH$_3$)L(C$_2$H$_2$)]$^+$ (L = CO, PH$_3$), with five stationary points for each of them: three minima **A**, **C**, and **E** and two transition states **B** and **D**. The indenyl ligand is located in a trans orientation relative to the η^2-alkyne or vinylidene groups in agreement with the preferred conformation found in our reported theoretical and crystallographic studies.[12a] The structure of the η^2-alkyne complexes **A** and of the η^1-vinylidene complexes **E**, where the alkyne and vinylidene groups are located perpendicular to the pseudomolecular plane (containing the ruthenium atom and both indenyl centroids C* and C**) are more stable than the corresponding rotamers, where both groups are contained in the pseudomolecular plane.[6] MO calculations reported earlier indicate that the most efficient π-back-bonding from the metal to the π-alkyne or

(15) Kostic, N. M.; Fenske, R. J. *Organometallics* **1982**, *1*, 974.
(16) Bruce, M. I.; Catlow, A.; Humphrey, M. G.; Koutsantonis, G. A.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *338*, 59.
(17) Torres, M. R.; Santos, A.; Perales, A.; Ros, J. *J. Organomet. Chem.* **1988**, *353*, 321.
(18) Romero, A.; Santos, A. Vegas, A. *Organometallics* **1988**, *7*, 1988.
(19) López, J.; Santos, A.; Romero, A.; Echevarren, A. M. *J. Organomet. Chem.* **1993**, *443*, 221.
(20) Bohanna, C.; Esteruelas, M.; A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685.
(21) (a) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461. (b) Stegmann, R.; Frenking, G. *Organometallics* **1998**, *17*, 2089. (c) García-Yebra, C.; López-Mardomingo, C.; Fajardo, M.; Antiñolo, A.; Otero, A.; Rodríguez, A.; Vallat, A.; Lucas, D.; Mugnier, Y.; Carbó, J. J.; Lledós, A.; Bo, C. *Organometallics* **2000**, *19*, 1749.
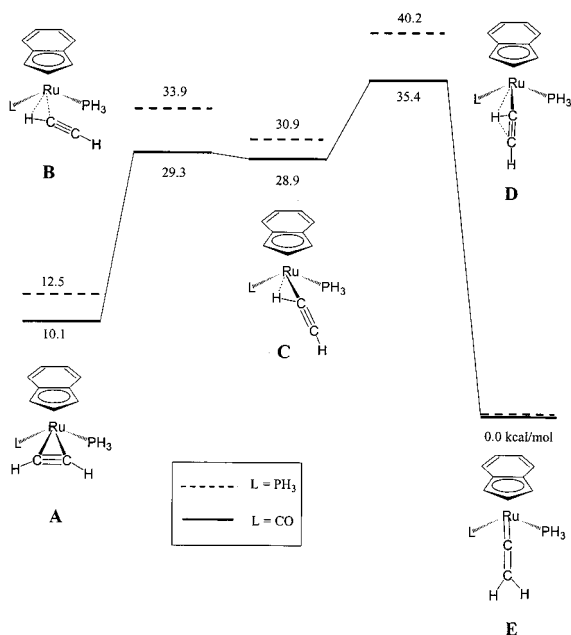
Figure 5. Energy diagram (kcal/mol) for the formation of $[Ru(\eta^5\text{-}C_9H_7)(=C=CH_2)L(PH_3)]^+$ (L = CO, PH$_3$) from [Ru-$(\eta^5\text{-}C_9H_7)L(PH_3)]^+$ and C$_2$H$_2$. To compare the energy values for each case the origins have been fixed at 0.0 kcal/mol for the vinylidene complexes.

vinylidene group is found for this orientation.[15,22] X-ray crystal structure determinations[4b,12a,e] of both complexes are in agreement with these theoretical calculations.

Figures 3 and 4 show the geometrically optimized structures and the main geometric parameters. In **E**, the calculated bond distances Ru$-$C$_\alpha$ (1.862 (L = CO) and 1.844 Å (L = PH$_3$)) and C$_\alpha$$-C_\beta$ (1.303 (L = CO) and 1.308 Å (L = PH$_3$)) are very close to those experimentally determined by X-ray diffraction in the vinylidene complexes $[Ru\{=C=C(R^1)R^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (R^1 = Me, R^2 = Me, 1-cyclohexenyl; R^1 = H, R^2 = Ph; the average values are 1.834(5) and 1.290(6) Å, respectively).[12a,e,23] The calculated Ru$-$P (2.395 and 2.375 Å) and Ru$-$C* (2.011 and 2.007 Å) bond lengths are also in agreement with the observed values (average values, 2.364(3) and 1.97(1) Å, respectively).

The calculated energies (Figure 5) indicate that the vinylidene complexes **E** are the structures with a global minimum energy. It is also found that the rearrangement of **A** to **E** is an exothermic process, being slightly more favored for the bis-phosphine than for the carbonyl complex (12.5 vs 10.1 kcal/mol). In the reaction pathway, which connects the η^2-alkyne with the vinylidene complexes, there have been located the structures of the intermediates **C** at 28.9 (L = CO) and 30.9 kcal/mol (L = PH$_3$) above the vinylidene complexes. The calculated geometries of **C** shown in Figures 3 (L = CO) and 4 (L = PH$_3$) display values for Ru$-$C$_\alpha$ of 2.204 and 2.151 Å and for Ru$-$H$_\alpha$ of 1.941 and 1.832 Å, respectively. The relative stabilization of the intermediate complexes **C** with respect to species **B** seems to be a result of the stronger σ-C$-$H metal bonding.[3a,d,e,6,21,24]

(22) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292.
(23) Pérez-Carreño, E. Doctoral Thesis, University of Oviedo, 1996.
(24) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091.

The transition states **B** and **D** connect the three minima found in each reaction channel, giving rise to the activation barrier of the two-step mechanism involved in the 1,2-hydrogen migration. The species **B** lie above complexes **E** at 29.3 (L = CO) and 33.9 kcal/mol (L = PH$_3$), only slightly destabilized from the intermediate energy values. The internal geometry parameters of the C$_2$H$_2$ group in **B** do not significantly change with respect to **A**, although the angle Ru$-$C$_\alpha$$_-C_\beta$ increases from 74.7 (L = CO) and 73.6° (L = PH$_3$) in the η^2-alkyne species to 137.7 and 128.9°, respectively, in the transition states. This is in agreement with a slippage of the η^2-CC alkyne complex to the η^2-CH found in the intermediates **C**. The species **D**, which are located at the highest energies of the reaction path with values of 35.4 (L = CO) and 40.2 kcal/mol (L = PH$_3$), are generated as transition states in the migration of the hydrogen atom from C$_\alpha$ to C$_\beta$. For L = CO there is a lengthening of the Ru$-$H$_\alpha$ distance and a shortening of the C$_\beta$$-H_\alpha$ distance with respect to the intermediate **C** (2.534 vs 1.941 Å and 1.689 vs 2.209 Å, respectively). Similar differences are found for the bis-phosphine derivative (L = PH$_3$).

As far as the back and forth η^1-vinylidene$-\eta^2$-alkyne tautomerization process is concerned, it is interesting to note that the calculated activation energy for each reaction path reveals higher values for the bis-phosphine complex: 25.3 and 35.4 kcal/mol (L = CO) vs 27.7 and 40.2 kcal/mol (L = PH$_3$). These data, in addition to the relative stability of the vinylidene tautomer with respect to the η^2-alkyne, which is lower for the carbonyl$-$phosphine complex 10.11 (L = CO) vs 12.52 kcal/mol (L = PH$_3$), indicate that the vinylidene to alkyne tautomerization is more accessible both thermodynamically and kinetically for the carbonyl species. Although the difference in the energy values is not critical, this is in agreement with the experimental observations which show that at room temperature an η^2-alkyne$-$ η^1-vinylidene equilibrium is only observed for the carbonyl derivatives.

It is noteworthy that the actual presence in the complexes of PR$_3$ (R = Ph, ^{i}Pr) instead of the PH$_3$ used in the models should increase the steric effects notably. If this fact is considered, the calculations would lead to (i) a higher stabilization of the vinylidene species with respect to the η^2-alkyne precursors for both cases, because the former are less influenced by steric effects caused by the presence of bulky phosphine ligands; and (ii) due to the fact the structures of the species involved in the reaction pathways show the C$_2$H$_2$ moiety near the preferred perpendicular orientation, where this position has greater steric hindrance, in particular for the bis-phosphine complex, the energy profile of the reaction paths must be higher than those calculated in the absence of steric effects.

In conclusion, it is apparent that the substitution of one PPh$_3$ by a CO ligand has a greater effect on the releasing of the steric hindrance in the η^2-alkyne coordination with respect to the bis-phosphine complex. Nevertheless, the electronic effect is also operative, and therefore the control of the tautomerization process will be the result of both steric and electronic contributions.

Discussion

The tautomerization of terminal alkynes HC≡CR into a vinylidene group =C=C(H)R in the presence of transition metal complexes has been specially studied for ruthenium(II) derivatives.[1] It is nowadays well-established both experimentally and theoretically that the first step in the mechanism of this process involves the formation of a π-alkyne ruthenium complex, which in most cases undergoes a thermodynamically favored transformation to the vinylidene complex.[3] In this work examples of the existence of an equilibrium mixture involving both tautomers, i.e., between the η^1-vinylidenes **4a−c** and the η^2-alkynes **5a−c**, are shown. These equilibria are easily achieved from the classical treatment of the chloride precursor complexes **1−3** with AgBF$_4$ in the presence of the terminal alkyne. This behavior contrasts with that shown in analogous reactions using the electron-rich complexes [RuCl(η^5-C$_9$H$_7$)-L$_2$] (L = PPh$_3$; L$_2$ = dppe, dppm) which yield stable vinylidene derivatives.[12a,d,e,j,l] This type of equilibrium have been also observed in the activation of HC≡CPh with the related ruthenium fragment [Ru(η^5-C$_5$H$_5$)(CO)-(PPh$_3$)]$^+$ at room temperature[10] and in the isomerization of [Fe{=C=C(R)R′}(η^5-C$_5$H$_5$)(CO)$_2$)]$^+$ (R = R′ = Me, Ph; R = Me, R′ = Ph) to internal π-alkyne complexes [Fe-(η^2-RC≡CR′)(η^5-C$_5$H$_5$)(CO)$_2$)]$^+$ which is readily established above −50 °C.[25] All of these examples seem to indicate that the conversion of η^2-alkyne derivatives into the corresponding η^1-vinylidene tautomers depends mainly on the electronic properties of the metal fragment. However, we have found that along with the electronic effect associated to the substitution of one PPh$_3$ by a more π-accepting CO ligand the η^1-vinylidene−η^2-alkyne tautomerization process is also dependent on the steric properties of both ligands.

The competitive reactivity toward nucleophiles of the π-alkyne vs vinylidene complexes in these tautomerization equilibria has been also studied. Thus, it has been shown that the presence of the electrophilic fragments [Ru(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)] (R = Me, PR$_3$ = PPh$_3$; R = H, PR$_3$ = P^{i}Pr$_3$) allows the nucleophilic addition of PPh$_3$ on the π-coordinated alkyne to give selectively alkenyl−phosphonio complexes (*E*)-**7** and (*E*)-**8** (Scheme 1). It is apparent that the selective formation of these species is favored vs the potential addition of the phosphine at the electrophilic C$_\alpha$ atom of the tautomeric vinylidene species.[1] The synthesis of the analogous alkenyl−phosphonio complexes (*EE*)-

12a−c, obtained by addition of PPh$_3$ to the stable alkenyl−vinylidene complexes **11a−c** (Scheme 3) clearly demonstrates that this nuceophilic addition is thermodinamically favored since the process proceeds through the transient formation of π-alkyne complexes. This is consistent with our previous experimental and theoretical studies on the tautomerization of stable vinylidene complexes [Ru{=C=C(H)R}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ to the corresponding π-alkyne derivatives.[6,7] In accordance, related nucleophilic additions on cationic iron(II) η^2-alkyne complexes [Fe(η^2-RC≡CR′)(η^5-C$_5$H$_5$)(CO)L][BF$_4$] (L = PPh$_3$, P(OPh)$_3$) have been reported to yield *E*-alkenyl derivatives regioselectively.[26] Although the nucleophilic addition of phosphines to vinylidene complexes to give α-phosphonio−alkenyl species [M]−C-(PR$_3$)=CR$_2$ are scarce, probably on steric hindrance grounds, several examples are known.[27]

The selectivity of the coordinated π-alkyne species for undergoing nucleophilic addition of PPh$_3$ is also achieved for the equilibrium established in the activation of 1-ethynyl-1-cyclooctanol with the electrophilic ruthenium precursors **1** and **2**. Thus, the addition of PPh$_3$, as described above for the reactions with terminal alkynes, gives also alkenyl−phosphonio complexes (*E*)-**13** and (*E*)-**14** (Scheme 5). It is interesting to note that the simple activation of the alkynol by **1** and **2**, which leads to an unidentified mixture of products, also contrasts with the behavior shown by the ruthenium derivatives [RuCl(η^5-C$_9$H$_7$)L$_2$] (L = PPh$_3$; L$_2$ = dppe), which gives selectively alkenyl−vinylidene complexes **C** (Scheme 4).[12e,l] Moreover, no allenylidene species are apparently present in these reaction mixtures since otherwise allenyl−phosphonio [Ru]−C(PPh$_3$)=C=CR$_2$ or alkynyl−phosphonio complexes [Ru]−C≡CC(PPh$_3$)R$_2$, generated from the nucleophilic addition of PPh$_3$ on the electrophilic C$_\alpha$ or C$_\gamma$ atoms of the allenylidene chain, respectively, would have to be formed.[28] In fact, we have reported that related allenylidene complexes [Ru{=C=C=C(R)R′}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = R′ = Ph; R = H,

(25) (a) Bly, R. S.; Zhong, Z.; Kane, C.; Bly, R. K. *Organometallics* **1994**, *13*, 899, and references therein. Equilibriums between π-coordinated terminal alkynes and their vinylidene tautomers have been also proposed in Cr(CO)$_5$ and W(CO)$_5$ complexes. See for example: (b) Abd-Alzaher, M. M.; Fischer, H. *J. Organomet. Chem.* **1999**, *588*, 235. (c) Abd-Alzaher, M. M.; Froneck, T.; Roth, G.; Gvozdev, V.; Fischer, H. *J. Organomet. Chem.* **2000**, *599*, 288, and references therein. The spontaneous isomerization of [Nb{=C=C(H)R}(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CO)]$^+$ (R = Ph, ^{t}Bu) into [Nb(η^2-HC≡CR)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CO)]$^+$ has been recently reported: see ref 21c. The rearrangement of vinylidenes [M{=C=C(R)SiMe$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (M= Mo, W; R = Ph, ^{t}Bu, Me, SiMe$_3$) into η^2-alkyne complexes [M(η^2-RC≡CSiMe$_3$)(η^5-C$_5$H$_5$)(CO)(NO)] has been also described: (d) Ipaktschi, J.; Demuth-Eberle, G. J.; Mirzaei, F.; Müller, B. G.; Beck, J.; Serafin, M. *Organometallics* **1995**, *14*, 3335. Vinylidene ligands in complexes [Re{=C=C(H)Ph}(CO)$_2$P$_3$]$^+$ (P = P(OMe)$_3$, PPh(OEt)$_2$, PPh$_2$OEt) and [OsX{=C=C(H)Ph}P$_4$]$^+$ (X = Cl, Br, I; P = PPh(OEt)$_2$, PPh$_2$OEt) are rather labile the dissociation of which gives the free alkyne: (e) Albertin, G.; Antoniutti, S.; Bordignon, E.; Bresolin, D. *J. Organomet. Chem.* **2000**, *609*, 10. (f) Albertin, G.; Antoniutti, S.; Bordignon, E.; Pegoraro, M. *J. Chem. Soc., Dalton Trans.* **2000**, 3575.

(26) Reger, D. L. *Acc. Chem. Res.* **1988**, *21*, 229, and references therein.

(27) Cationic iron(II) vinylidene complexes [Fe{=C=C(H)R}(η^5-C$_5$H$_5$)(CO)(PPh$_3$)]$^+$ react with phosphines to afford the α-phosphonio−alkenyl derivatives [Fe{C(PR$_3$)=C(H)R}(η^5-C$_5$H$_5$)(CO)(PPh$_3$)]$^+$ (R = H, PR$_3$ = PPh$_3$, PMe$_2$Ph; R = Ph, PR$_3$ = PPh$_3$): (a) Kolobova, N. Y.; Stripkin, V. V.; Alexandrof, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1979**, *169*, 293. (b) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628. Similarly, complexes [Re{C(PMe$_3$)=CMe$_2$}(η^5-C$_5$H$_5$)(NO)(PPh$_3$)]$^+$ and [W{C-(PPh$_3$)=C(H)Ph}(η^5-C$_5$H$_5$)(CO)$_3$]$^+$ have been obtained by addition of the corresponding phosphine on vinylidenes [Re(=C=CMe$_2$)(η^5-C$_5$H$_5$)-(NO)(PPh$_3$)]$^+$ and [W{=C=C(H)Ph}(η^5-C$_5$H$_5$)(CO)$_3$]$^+$, respectively: (c) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096. (d) Kolobova, N. E.; Skripkin, V. V.; Rozantseva, T. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2393. Neutral vinylidenes [Mn{=C=C(H)R}(η^5-C$_5$H$_5$)(CO)$_2$] also react with phosphines to yield α-phosphonio−alkenyl complexes [Mn{C(PR$_3$)=C(H)R}(η^5-C$_5$H$_5$)(CO)$_2$] (PR$_3$ = PPh$_3$, R = Me, Ph, C^{t}Bu$_2$OH·; PMe$_2$Ph; PR$_3$ = PMePh$_2$, R = Ph): (e) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55. (f) Nesmeyanov, A. N.; Kolobova, N. E.; Antonova, A. B.; Obezyuk, N. S.; Anisimov, K. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 948. (g) Antonova, A. B.; Gubin, S. P.; Kovalenko, S. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 953. The reaction of [W{=C=C(H)R}-(η^5-C$_5$H$_5$)(CO)(NO)] with Ph$_2$PCl has been reported to yield metalla-cyclopropanes [WCl{C̅=C(H)R}(P̅Ph$_2$)(η^5-C$_5$H$_5$)(NO)] (R = H, Me, Ph) by the nucleophilic attack of the phosphine on the C$_\alpha$ carbon of the vinylidene fragment: (h) Ipaktschi, J.; Klotzbach, T.; Dülmer, A. *Organometallics* **2000**, *19*, 5281. The intramolecular version of a phosphine attack at a vinylidene C$_\alpha$ is also known. See for example: (i) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241.

R′ = Ph; RR′ = $-CH_2(CH_2)_nCH_2-$) readily react with phosphines to afford cationic alkynyl−phosphonio derivatives $[Ru\{C\equiv CC(R)(PR_3)R'\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ selectively.[12e,f,j]

In summary, in this paper a systematic approach for the selective synthesis of indenyl−ruthenium(II) alkenyl−phosphonio complexes is reported. It is shown by theoretical calculations that the tautomerization equilibrium between η^2-alkyne and η^1-vinylidene complexes is dependent not only on the electronic properties but also on the steric requirements of the ruthenium fragment. The nucleophilic attack of PPh_3 takes place selectively on the coordinated π-alkyne molecule being favored vs the addition at the electrophilic C_α atom of the corresponding η^1-vinylidene tautomers.

Experimental Section

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds **1**,[9] **3**,[9] **2**,[9] **11a**,[6] (*E*)-**11b**,[12j] and (*Z*)-**11c**[6] were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C and H analyses were carried out with a Perkin-Elmer 240-B microanalyzer (uncompleted combustions were systematically observed for most of the complexes reported). Mass spectra (FAB) were recorded using a VG Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol was used as the matrix. 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$_3$PO$_4$ as standards. DEPT experiments have been carried out for all the complexes. The abbreviations used are as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt, doublet of triplets; m, multiplet.

The numbering for the indenyl skeleton is as follows:
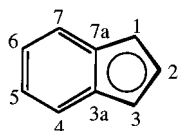
Spectroscopic Characterization of [Ru{=C=C(H)Ph}-(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] (4a) and [Ru(η^2-HC≡CPh)(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)][BF$_4$] (5a). A mixture of **1** (0.015 g, 0.024 mmol) and AgBF$_4$ (0.005 g, 0.026 mmol) in CD$_2$Cl$_2$ (0.6 mL) was stirred for 15 min at room temperature in the absence of light. After the AgBr formed was filtered, the solution was transferred into a NMR tube and phenylacetylene (0.004 mL, 0.036 mmol) was then added at −60 °C. The reaction was followed by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy from −60 to +14 °C. The NMR data reported here were obtained at −43 °C when a mixture of complexes **4a** and **5a** is present in ca. ratio 1:1.3. Compound **4a**. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 41.51 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.17, 1.60, and 2.26 (s, 3H each one, Me-1, Me-2, and Me-3), 4.76 (s broad, 1H, Ru=C=CH), 5.82−7.80 (m, 24H, Ph, H-4, H-5, H-6, and H-7) ppm. Compound **5a**. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 44.65 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.41, 1.98, and 2.55 (s, 3H each

one, Me-1, Me-2, and Me-3), 3.71 (s broad, 1H, HC≡), 5.82−7.80 (m, 24H, Ph, H-4, H-5, H-6, and H-7) ppm.

Synthesis of [Ru(C≡CPh)(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(PPh$_3$)] (6). A mixture of **1** (0.628 g, 1 mmol) and AgBF$_4$ (0.214 g, 1.1 mmol) in CH$_2$Cl$_2$ (50 mL) was stirred for 15 min at room temperature in the absence of light. After the AgBr formed was filtered, phenylacetylene (0.165 mL, 1.5 mmol) was added to the solution. The reaction mixture was stirred for 5 min and then treated with KO^{t}Bu (0.168 g, 1.5 mmol) at room temperature for 40 min. The solvent was then evaporated in vacuo and the resulting solid residue extracted with diethyl ether (50 mL) and filtered. Evaporation of the diethyl ether gave complex **6** as a yellow solid; yield, 75% (0.487 g). IR (KBr, cm^{-1}): 1935 ν(CO), 2093 ν(C≡C). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 54.78 (s) ppm. ^{1}H NMR (C$_6$D$_6$): δ 1.53 and 2.04 (s, 3H each one, Me-1, Me-2, or Me-3), 1.94 (d, 3H, $^4J_{HP}$ = 1.7 Hz, Me-1, Me-2, or Me-3), 6.63, 6.71, and 6.82 (m, 1H each one, H-4, H-5, H-6, or H-7), 6.96−7.40 (m, 21H, Ph and H-4, H-5, H-6, or H-7) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 8.59, 9.95, and 11.16 (s, Me-1, Me-2, and Me-3), 85.56 (s, C-1 or C-3), 86.23 (d, $^2J_{CP}$ = 5.0 Hz, C-1 or C-3), 105.24 and 109.01 (s, C-2, C-3a, or C-7a), 110.50 (d, $^2J_{CP}$ = 8.1 Hz, C-2, C-3a, or C-7a), 109.87 (d, $^2J_{CP}$ = 25.0 Hz, Ru−C$_\alpha$), 121.78−134.82 (m, Ph, C$_\beta$, C-4, C-5, C-6, and C-7), 207.25 (d, $^2J_{CP}$= 18.6 Hz, CO) ppm. MS (FAB) for RuC$_{39}$H$_{33}$-OP: m/z 650 [M$^+$], 622 [M$^+$ − CO], 550 [M$^+$ − C≡CPh + 1], 522 [M$^+$ − C≡CPh − CO + 1], 465 [M$^+$ − Me$_3$C$_9$H$_4$ − CO]. Complex **6** was too sensitive to moisture and oxygen to give satisfactory elemental analysis.

Synthesis of (*E*)-[Ru{C(H)=C(PPh$_3$)R′}(η^5-1,2,3-R$_3$C$_9$H$_4$)-(CO)(PR$_3$)][BF$_4$] (R = Me, PR$_3$ = PPh$_3$, R′ = Ph [(*E*)-7], 1-Cyclooctenyl [(*E*)-13]; R = H, PR$_3$ = P^{i}Pr$_3$, R′ = Ph [(*E*)-8], 1-Cyclooctenyl [(*E*)-14]). General Procedure. A mixture of **1,2** (1 mmol) and AgBF$_4$ (0.214 g, 1.1 mmol) in CH$_2$Cl$_2$ (100 mL) was stirred for 15 min at room temperature in the absence of light. After the unsoluble salts formed were filtered, the corresponding alkyne or 1-ethynyl-1-cyclooctanol (1.5 mmol) was added to the solution. The reaction mixture was stirred for 10 min and then treated with PPh$_3$ (0.262 g, 1 mmol) at room temperature for 10 min. The solvent was then evaporated in vacuo, and the resulting yellow solid washed with diethyl ether (2 × 30 mL) and vacuum-dried. Yield (%), IR (KBr, ν(CO), ν(BF$_4^-$), cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), analytical data, NMR spectroscopic data, and mass spectra are as follows. Compound (*E*)-**7**: 60 (0.599 g); 1937, 1055; 119. ^{31}P{^{1}H} (CDCl$_3$): δ 16.70 (d, $^4J_{PP}$ = 6.2 Hz, C−PPh$_3$), 52.82 (d, $^4J_{PP}$ = 6.2 Hz, Ru−PPh$_3$) ppm. ^{1}H (CDCl$_3$): δ 1.52, 1.83, and 1.93 (s, 3H each one, Me-1, Me-2, and Me-3), 6.67−7.78 (m, 39H, Ph, H-4, H-5, H-6, and H-7), 9.43 (dd, 1H, $^3J_{HP}$ = 32.5 Hz, $^3J_{HP}$ = 7.5 Hz, RuCH) ppm. ^{13}C{^{1}H} (CD$_2$Cl$_2$): δ 8.65, 9.99, and 10.74 (s, Me-1, Me-2, and Me-3), 83.02 (d, $^2J_{CP}$ = 3.7 Hz, C-1 or C-3), 88.16 (d, $^2J_{CP}$ = 3.7 Hz, C-1 or C-3), 105.42, 110.65, and 112.91 (s, C-2, C-3a, and C-7a), 119.53, 123.35, 125.74, and 127.80 (s, C-4, C-5, C-6, and C-7), 121.28 (d, J_{CP} = 85.1 Hz, C$_\beta$), 128.74−139.82 (m, Ph), 206.52 (dd, $^2J_{CP}$ = 13.9 Hz, $^2J_{CP}$ = 2.8 Hz, Ru−C$_\alpha$), 207.27 (d, $^2J_{CP}$ = 17.6 Hz, CO) ppm. MS (FAB) for RuC$_{57}$H$_{49}$F$_4$P$_2$BO: m/z 913 [M$^+$], 651 [M$^+$ − PPh$_3$], 621 [M$^+$ − Ph − CO − Me$_3$C$_9$H$_4$], 549 [M$^+$ − C(H)=CPh(PPh$_3$)], 521 [M$^+$ − C(H)=CPh(PPh$_3$) − CO] ppm. Compound (*E*)-**8**: 70 (0.598 g); 1941, 1056; 128. Anal. Calcd for RuC$_{45}$H$_{49}$F$_4$P$_2$BO: C, 63.16; H, 5.77. Found: C, 61.61; H, 5.83. ^{31}P{^{1}H} (CDCl$_3$): δ 16.15 (d, $^4J_{PP}$ = 3.5 Hz, PPh$_3$), 63.91 (d, $^4J_{PP}$ = 3.5 Hz, P^{i}Pr$_3$) ppm. ^{1}H (CDCl$_3$): δ 0.73 (m, 9H, P(CH*Me*$_a$Me$_b$)$_3$), 0.99 (m, 9H, P(CHMe$_a$*Me*$_b$)$_3$), 1.77 (m, 3H, P(C*H*Me$_a$Me$_b$)$_3$), 5.03, 5.44, and 5.68 (s, 1H each one, H-1, H-2, and H-3), 6.97−7.79 (m, 24H, Ph, H-4, H-5, H-6, and H-7), 9.85 (dd, 1H, $^3J_{HP}$ = 30.9 Hz, $^3J_{HP}$ = 8.3 Hz, RuCH) ppm. ^{13}C{^{1}H} (CD$_2$Cl$_2$): δ 19.32 (s, P(CH*Me*$_a$Me$_b$)$_3$), 19.54 (s, P(CHMe$_a$*Me*$_b$)$_3$), 27.70 (d, J_{CP} = 22.2 Hz, P(*C*HMe$_a$Me$_b$)$_3$), 70.62 (d, $^2J_{CP}$ = 4.6 Hz, C-1 or C-3), 71.22 (s, C-1 or C-3), 97.73 (s, C-2), 111.26 and 111.55 (s, C-3a and C-7a), 120.41 and 122.10 (s, C-4, C-5, C-6, or C-7), 122.82−139.41 (m, Ph, C$_\beta$ and

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

C-4, C-5, C-6, or C-7), 198.28 (dd, $^2J_{CP}$ = 10.1 Hz, $^2J_{CP}$ = 3.9 Hz, Ru−C$_\alpha$), 207.14 (d, $^2J_{CP}$ = 15.7 Hz, CO) ppm. $\Delta\delta$(C-3a,-7a)= −19.29 (average). MS (FAB): m/z 769 [M$^+$], 479 [M$^+$ − CO − PPh$_3$], 405 [M$^+$ − C(H)=CPh(PPh$_3$)], 377 [M$^+$ − C(H)= CPh(PPh$_3$) − CO], 319 [M$^+$ − CO − P^{i}Pr$_3$ - PPh$_3$]. Compound (*E*)-**13**: 60 (0.619 g); 1932, 1053; 96. Anal. Calcd for RuC$_{59}$H$_{57}$-F$_4$P$_2$BO: C, 68.67; H, 5.57. Found: C, 67.88; H, 4.72. ^{31}P{^{1}H} (CDCl$_3$): δ 15.84 (d, $^4J_{PP}$ = 3.3 Hz, C−PPh$_3$), 51.65 (d, $^4J_{PP}$ = 3.3 Hz, Ru−PPh$_3$) ppm. ^{1}H (CDCl$_3$): δ 0.65−2.14 (m, 10H, CH$_2$), 1.70 (s, 6H, Me-1, Me-2, or Me-3), 1.88 (s, 3H, Me-1, Me-2, or Me-3), 2.67 (m, 2H, CH$_2$), 5.41 (m, 1H, C=CH), 6.55−7.81 (m, 34H, Ph, H-4, H-5, H-6, and H-7), 9.43 (dd, 1H, $^3J_{HP}$ = 34.0 Hz, $^3J_{HP}$ = 6.9 Hz, RuCH) ppm. ^{13}C{^{1}H} (CD$_2$Cl$_2$): δ 9.27, 9.71, and 10.76 (s, Me-1, Me-2, and Me-3), 25.79, 26.12, 27.57, 28.84, 28.90, and 29.50 (s, CH$_2$), 84.19 (d, $^2J_{CP}$ = 5.5 Hz, C-1 or C-3), 87.39 (s, C-1 or C-3), 107.66, 110.40, and 111.96 (s, C-2, C-3a, and C-7a), 120.43, 122.80, 126.20, and 127.21 (s, C-4, C-5, C-6, and C-7), 122.35 (d, J_{CP} = 84.2 Hz, C$_\beta$), 124.35 (d, $^2J_{CP}$ = 56.4 Hz, *C*=CH), 128.62−140.31 (m, Ph), 135.04 (d, $^3J_{CP}$ = 9.2 Hz, C=*C*H), 205.61 (d, $^2J_{CP}$ = 13.9 Hz, Ru−C$_\alpha$), 208.57 (d, $^2J_{CP}$ = 19.4 Hz, CO) ppm. MS (FAB): m/z 945 [M$^+$], 807 [M$^+$ − CO − C$_8$H$_{13}$ − 1], 654 [M$^+$ − CO − PPh$_3$], 549 [M$^+$ − C(H)=C(C$_8$H$_{13}$)(PPh$_3$)], 521 [M$^+$ − C(H)=C(C$_8$H$_{13}$)-(PPh$_3$) − CO]. Compound (*E*)-**14**: 50 (0.444 g); 1936, 1054; 118. ^{31}P{^{1}H} (CDCl$_3$): δ 13.38 (d, $^4J_{PP}$ = 3.6 Hz, PPh$_3$), 64.11 (d, $^4J_{PP}$ = 3.6 Hz, P^{i}Pr$_3$) ppm. ^{1}H (CDCl$_3$): δ 0.78 (m, 9H, P(CH*Me*$_a$Me$_b$)$_3$), 0.94−2.18 (m, 24H, P(CHMe$_a$*Me*$_b$)$_3$, P(C*H*Me$_a$-Me$_b$)$_3$, and CH$_2$), 5.38 and 5.66 (s broad, 1H, H-1, H-2, or H-3), 5.58 (m, 2H, C=CH and H-1, H-2, or H-3), 7.11−7.67 (m, 19H, Ph, H-4, H-5, H-6, and H-7), 9.77 (dd, 1H, $^3J_{HP}$ = 28.1 Hz, $^3J_{HP}$ = 5.5 Hz, RuCH) ppm. ^{13}C{^{1}H} (CD$_2$Cl$_2$): δ 19.49−33.47 (m, P(CH*Me*$_a$Me$_b$)$_3$, P(CHMe$_a$*Me*$_b$)$_3$, P(C*H*Me$_a$Me$_b$)$_3$ and CH$_2$), 70.83 (d, $^2J_{CP}$ = 3.7 Hz, C-1 or C-3), 71.51 (d, $^2J_{CP}$ = 1.8 Hz, C-1 or C-3), 96.98 (s, C-2), 111.87 and 112.07 (s, C-3a and C-7a), 122.61 (d, J_{CP}= 84.2 Hz, C$_\beta$), 123.22 and 126.26 (s, C-4, C-5, C-6, or C-7), 126.16 (d, $^2J_{CP}$ = 57.3 Hz, *C*=CH), 128.92−140.00 (m, Ph and C-4, C-5, C-6, or C-7), 137.75 (d, $^3J_{CP}$ = 8.3 Hz, C=*C*H), 206.52 (d, $^2J_{CP}$ = 12.0 Hz, Ru−C$_\alpha$), 208.16 (d, $^2J_{CP}$ = 12.0 Hz, CO) ppm. $\Delta\delta$(C-3a,7a) = −18.73 (average). Complexes (*E*)-**7a** and (*E*)-**14** were too sensitive to moisture and oxygen to give satisfactory elemental analyses.

Reaction of [RuI(η^5-1,2,3-Me$_3$C$_9$H$_4$)(CO)(P^{i}Pr$_3$)] with Phenylacetylene and Triphenylphosphine. A mixture of **3** (0.525 g, 1 mmol) and AgBF$_4$ (0.214 g, 1.1 mmol) in CH$_2$Cl$_2$ (100 mL) was stirred for 15 min at room temperature in the absence of light. After the AgI formed was filtered, phenylacetylene (0.165 mL, 1.5 mmol) was added to the solution. The reaction mixture was stirred for 10 min and then treated with PPh$_3$ (0.262 g, 1 mmol) at room temperature for 10 min. The solvent was then evaporated in vacuo, and the resulting yellow solid washed with diethyl ether (2 × 30 mL) and vacuum-dried. IR, ^{31}P{^{1}H}, and ^{1}H NMR spectroscopic data are in agreement with the presence of a mixture of (*E*)-**9** and **10** in ca. ratio 1:1.6. Compound (*E*)-**9**: IR (KBr, cm^{-1}): 1928 ν(CO), 1054 ν(BF$_4^-$). ^{31}P{^{1}H} (CDCl$_3$): δ 15.54 (d, $^4J_{PP}$ = 4.6 Hz, PPh$_3$), 58.50 (d, $^4J_{PP}$ = 4.6 Hz, P^{i}Pr$_3$) ppm. ^{1}H (CDCl$_3$): δ 0.71−2.32 (m, 30H, P(CH*Me*$_a$Me$_b$)$_3$, P(CHMe$_a$*Me*$_b$)$_3$, P(C*H*Me$_a$-Me$_b$)$_3$, Me-1, Me-2, and Me-3), 6.51−7.82 (m, 24H, Ph, H-4, H-5, H-6, and H-7), 10.20 (dd, 1H, $^3J_{HP}$ = 32.6 Hz, $^3J_{HP}$ = 5.0 Hz, RuCH) ppm. Compound **10**: IR (KBr, cm^{-1}): 1946 ν(CO), 1054 ν(BF$_4^-$). ^{31}P{^{1}H} (CDCl$_3$): δ 44.01 (d, $^2J_{PP}$ = 21.3 Hz, PPh$_3$), 53.20 (d, $^2J_{PP}$ = 21.3 Hz, P^{i}Pr$_3$) ppm. ^{1}H (CDCl$_3$): δ 0.71−2.32 (m, 30H, P(CH*Me*$_a$Me$_b$)$_3$, P(CHMe$_a$*Me*$_b$)$_3$, P(C*H*Me$_a$-Me$_b$)$_3$, Me-1, Me-2, and Me-3), 6.51−7.82 (m, 19H, Ph, H-4, H-5, H-6, and H-7) ppm.

Synthesis of (*EE*)-[Ru{C(H)=C(PPh$_3$)CH=CRR′}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (R = R′ = Ph [(*E*)-12a; R = H, R′ = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) [(*EE*)-12b], 4-OMe-C$_6$H$_4$ [(*EE*)-12c]). General Procedure. A solution of the corresponding vinylvinylidene complex **11a**−**c** (1 mmol) and PPh$_3$ (3.934 g, 15 mmol) in MeOH (50 mL) was heated under reflux for 90 min. The

solvent was then evaporated in vacuo and the resulting yellow solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield (%), IR (KBr, ν(BF$_4^-$), cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), analytical, and NMR spectroscopic data are as follows. Compound (*E*)-**12a**: 66 (0.854 g); 1048; 115. Anal. Calcd for RuC$_{79}$H$_{64}$F$_4$P$_3$B: C, 73.32; H, 4.98. Found: C, 73.48; H, 4.81. ^{31}P{^{1}H} ((CD$_3$)$_2$CO): δ 23.55 (s broad, C−PPh$_3$), 45.63 (s broad, Ru−PPh$_3$) ppm. ^{1}H ((CD$_3$)$_2$CO): δ 4.85 (s broad, 2H, H-1,3), 5.26 and 7.04 (m, 2H each one, H-4,7 and H-5,6), 5.92 (s broad, 1H, H-2), 6.85−7.89 (m, 56H, Ph and =CH), 10.88 (dt, 1H, $^3J_{HP}$ = 33.6 Hz, $^3J_{HP}$ = 9.9 Hz, RuCH) ppm. ^{13}C{^{1}H} ((CD$_3$)$_2$CO): δ 79.10 (s, C-1,3), 100.50 (s, C-2), 112.36 (s, C-3a,7a), 121.06 (d, J_{CP} = 88.7 Hz, C$_\beta$), 124.11 (s, C-4,7 or C-5,6), 124.87−136.23 (m, Ph, =CH, =C, and C-4,7 or C-5,6), 205.76 (m, Ru−C$_\alpha$) ppm. $\Delta\delta$(C-3a,7a) = −18.34. Compound (*EE*)-**12b**: 68 (0.901 g); 1062; 118. Anal. Calcd for FeRuC$_{77}$-H$_{64}$F$_4$P$_3$B: C, 69.74; H, 4.86. Found: C, 68.81; H, 4.94. ^{31}P-{^{1}H} (CD$_2$Cl$_2$): δ 15.58 (s broad, C−PPh$_3$), 48.24 (s broad, Ru−PPh$_3$) ppm. ^{1}H (CD$_2$Cl$_2$): δ 3.89 (s, 5H, C$_5$H$_5$), 4.30 (m, 4H, C$_5$H$_4$), 5.10 (s broad, 2H, H-1,3), 5.55 (m, 2H, H-4,7 or H-5,6), 5.64 (d, 1H, J_{HH} = 17.1 Hz, =CH), 5.82 (s broad, 1H, H-2), 6.97−7.83 (m, 48H, Ph, =CH and H-4,7 or H-5,6), 10.21 (dt, 1H, $^3J_{HP}$ = 29.8 Hz, $^3J_{HP}$ = 9.7 Hz, RuCH) ppm. ^{13}C{^{1}H} (CD$_2$-Cl$_2$): δ 66.67 and 69.78 (s, CH of C$_5$H$_4$), 69.36 (s, C$_5$H$_5$), 73.54 (s, C-1,3), 84.06 (s, C of C$_5$H$_4$), 96.13 (s, C-2), 112.72 (s, C-3a,-7a), 122.09 (d, J_{CP} = 85.1 Hz, C$_\beta$), 123.39 and 127.09 (s, C-4,7 and C-5,6), 128.36−137.44 (m, Ph and 2=CH), 212.36 (m, Ru−C$_\alpha$) ppm. $\Delta\delta$(C-3a,7a) = −17.98. Compound (*EE*)-**12c**: 73 (0.911 g); 1056; 128. Anal. Calcd for RuC$_{74}$H$_{62}$F$_4$P$_3$OB: C, 71.21; H, 5.00. Found: C, 70.75; H, 4.88. ^{31}P{^{1}H} (CD$_2$Cl$_2$): δ 15.82 (s broad, C−PPh$_3$), 48.17 (s broad, Ru−PPh$_3$) ppm. ^{1}H ((CD$_3$)$_2$CO): δ 3.80 (s, 3H, OCH$_3$), 5.14 (s broad, 2H, H-1,3), 5.61 (m, 2H, H-4,7 or H-5,6), 5.92 (d, 1H, J_{HH} = 16.7 Hz, =CH), 6.16 (s broad, 1H, H-2), 7.09−8.12 (m, 37H, Ph, C$_6$H$_4$, =CH and H-4,7 or H-5,6), 10.36 (dt, 1H, $^3J_{HP}$ = 30.4 Hz, $^3J_{HP}$ = 10.0 Hz, RuCH) ppm. ^{13}C{^{1}H} (CD$_2$Cl$_2$): δ 55.77 (s, OCH$_3$), 73.51 (s, C-1,3), 96.41 (s, C-2), 112.90 (s, C-3a,7a), 114.69 (s, CH of C$_6$H$_4$), 121.92 (d, J_{CP} = 85.0 Hz, C$_\beta$), 123.41 (s, C-4,7 or C-5,6), 127.25−135.75 (m, Ph, 2=CH, CH of C$_6$H$_4$, C of C$_6$H$_4$ and C-4,7 or C-5,6), 159.68 (s, C of C$_6$H$_4$), 214.78 (m, Ru−C$_\alpha$) ppm. $\Delta\delta$(C-3a,7a) = −17.80.

X-ray Diffraction Studies. Data collection, crystal, and refinement parameters for complexes (*E*)-**7** and (*EE*)-**12b** are collected in Table 1. A Mo Kα radiation was used with a graphite crystal monochromator on an Enraf-Nonius CAD4 single-crystal diffractometer (λ = 0.71073 Å). The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 15 and 18° for (*E*)-**7** and between 6 and 13° for (*EE*)-**12b**). The intensity data were measured with the $\omega−2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s/reflection. The final drift correction factors were between 0.98 and 1.05 for (*E*)-**7** and between 0.99 and 1.08 for (*EE*)-**12b**. On all reflections, profile analysis was performed.[29,30] Lorentz and polarization corrections were applied, and the data were reduced to F_o^2 values. The structures were solved by Patterson methods using the program DIRDIF.[31] Isotropic least-squares refinement on F^2 was made using SHELXL93.[32] Hydrogen atoms were geometrically placed. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-H-atoms were refined (except the high disordered CH$_2$Cl$_2$ and BF$_4^-$ molecules on (*EE*)-**12b** which were

(29) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.
(30) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.
(31) Beurkens, P. T.; Admiraal, G.; Beurkens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report; Crystallographic Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1992.
(32) Sheldrick, G. M. SHELXL93. In *Crystallographic Computing 6*; Flack, P., Parkanyi, P., Simon, K., Eds.; IUCr/Oxford University Press: Oxford, U.K., 1993.

Table 1. Crystallographic Data for Complexes (*E*)-7 and (*EE*)-12b

	*complex (E)-*7	*complex (EE)-*12b
empirical formula	$C_{57}H_{49}BF_4OP_2Ru$	$C_{77}H_{64}BF_4FeP_3Ru\cdot2CH_2Cl_2$
fw	999.78	1495.86
temp, K	293(2)	200(2)
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	15.145(2)	16.212(10)
b, Å	15.228(4)	23.551(16)
c, Å	20.986(5)	18.143(9)
β, deg	98.99(2)	94.39(6)
Z	4	4
V, Å^3	4780.5(17)	6907(7)
D_{calcd}, g cm^{-3}	1.389	1.436
μ, mm^{-1}	0.451	0.708
F(000)	2056	3052
cryst size, mm	$0.33 \times 0.30 \times 0.13$	$0.36 \times 0.33 \times 0.20$
θ range, deg	1.36–24.97	1.42–25.97
index ranges for data collecn	$17 \leq h \leq 17$	$19 \leq h \leq 19$
	$0 \leq k \leq 18$	$0 \leq k \leq 29$
	$0 \leq l \leq 24$	$0 \leq l \leq 22$
no. of rflns measd	9086	13961
no. of indep rflns	8380	13526
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	8380/0/599	13526/3/778
goodness-of-fit on F^2	1.003	1.023
final *R* factors (I > 2σ(I))	$R_1 = 0.0534$, $wR_2 = 0.1147$	$R_1 = 0.0854$, $wR_2 = 0.2010$
final *R* factors (all data)	$R_1 = 0.2164$, $wR_2 = 0.1569$	$R_1 = 0.1781$, $wR_2 = 0.2529$
largest diff. peak and hole, e Å^{-3}	0.594 and −1.069	0.982 and −0.866

isotropically refined). The hydrogen atoms were isotropically refined with a common thermal parameter.

(a) Complex (*E*)-7. The function minimized was $[\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$, where $\omega = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 5.0778P]$ with $\sigma(F_o^2)^2$ from counting statistics and $P = (max(F_o^2,0) + 2F_c^2)/3$. The maximum shift-to-estimated ratio in the last full-matrix least-squares cycle was 0.001. The final difference Fourier map showed no peaks higher than 0.59 e Å^{-3} nor deeper than −1.07 e Å^{-3}.

(b) Complex (*EE*)-12b. The function minimized was $[\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$, where $\omega = 1/[\sigma^2(F_o^2) + (0.1074P)^2 + 10.32P]$ with $\sigma(F_o^2)^2$ from counting statistics and $P = (max(F_o^2,0) + 2F_c^2)/3$. The maximum shift-to-estimated ratio in the last full-matrix least-squares cycle was 0.027. The final difference Fourier map showed no peaks higher than 0.98 e Å^{-3} nor deeper than −0.87 e Å^{-3}.

Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974).[33] Geometrical calculations were made with PARST.[34] The crystallographic plots were drawn by EUCLID[35] (for (*E*)-7) or PLATON[36] (for (*EE*)-12b). All calculations were performed at the University of Oviedo on the Scientific Computer Center and X-ray group VAX and DEC-ALPHA computers.

Computational Details. Ab initio calculations were carried out with the Gaussian 98 set of programs[37] within the

framework of DFT at the B3LYP level.[38] LANL2DZ effective core potentials (quasi relativistic for the metal centers) were used to replace the 28 innermost electrons of Ru, as well as the 10 core electrons of P.[39] The associated double ζ basis set of P atoms was augmented by a *d* function.[40] The rest of the atoms were represented by a 6-31G(d,p) basis set.[41] PH$_3$ and indenyl hydrogen atoms were represented at the STO-3G level.[42] In our calculations we have replaced the PPh$_3$ ligand and the monosubtituted acetylene by PH$_3$ and HC≡CH, respectively.

Full geometry optimization and frequency calculations were performed without any symmetry constraints. The stationary points were classified as a minimun or transition state according to vibrational analysis. The transition-state structures were relaxed after introducing small perturbations to ensure that they are actually connected to the corresponding reactants and products.

Supporting Information Available: Crystal structure data for (*E*)-7 and (*EE*)-12b, including tables of atomic parameters, anisotropic thermal parameters, bond distances, and bond angles, and figures showing $^{13}C\{^1H\}$ NMR spectra for complexes 6, (*E*)-7, (*E*)-8, (*EE*)-12b, (*E*)-13, and (*E*)-14 and FAB spectra for complexes 6, (*E*)-7, (*E*)-8, and (*E*)-13. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010308E

(33) *International Tables for X-ray Crystallography*; Kynoch Press: Birminghan, U.K., 1974; Vol. IV.

(34) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(35) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, U.K., 1982; p 528.

(36) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuk, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98* (Revision A.7); Gaussian Inc.: Pittsburgh, PA, 1998.

(38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(39) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(40) Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237.

(41) Hariharan, P. C.; Pople, J. *Theor. Chim. Acta* **1973**, *28*, 213.

(42) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.