A Novel Route to Functionalized Terminal Alkynes through η^1-Vinylidene to η^2-Alkyne Tautomerizations in Indenyl−Ruthenium(II) Monosubstituted Vinylidene Complexes: Synthetic and Theoretical Studies

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Heating under reflux solutions of the monosubstituted vinylidene complex [Ru{=C=C(H)-Ph}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**) in nitriles yields the complexes [Ru(N≡CR)(η^5-C_9H_7)(PPh_3)$_2$]-[PF_6] (R = Me (**2a**), Et (**2b**), Ph (**2c**)) and phenylacetylene. The process proceeds via an initial η^1-vinylidene-η^2-alkyne tautomerization followed by the displacement of the coordinated π-alkyne by the solvent. Vinylidene complexes [Ru{=C=C(H)R}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R = (η^5-C_5H_4)Fe(η^5-C_5H_5) (**3**), 4-NO_2-C_6H_4 (**4**)) also react with acetonitrile to yield the nitrile derivative **2a** and the corresponding terminal alkynes HC≡CR. Cationic alkenyl−vinylidene derivatives [Ru{=C=C(H)CH=CR^1R^2}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (R^1 = R^2 = Ph (**7a**), R^1 = H; R^2 = 4-OMe-C_6H_4 [(*Z*)-**7b**], 4-NO_2-C_6H_4 [(*E*,*Z*)-**7c**], (η^5-C_5H_4)Fe(η^5-C_5H_5) [(*E*)-**7d**]) behave similarly. Thus, the treatment of **7a**−**d** with acetonitrile at reflux results in the formation of complex **2a** and the liberation of the corresponding terminal 1,3-enyne HC≡CCH=CR^1R^2 (**8a**−**d**). The formation of the enynes **8b**−**d** is stereoselective, giving rise to the *E* stereoisomer. The allenylidene complex [Ru{=C=C=C($C_{13}H_{20}$)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**9**), containing the bicyclic [3.3.1]non-2-en-9-ylidene moiety $C_{13}H_{20}$, reacts with NaC≡CH in THF at −20 °C to yield the neutral σ-alkynyl derivative [Ru{C≡CC(C≡CH)$C_{13}H_{20}$}(η^5-C_9H_7)(PPh_3)$_2$] (**10**) in a regioselective manner. Protonation of **10** with HBF_4·Et_2O, in diethyl ether at −20 °C, affords the vinylidene complex [Ru{=C=C(H)C(C≡CH)$C_{13}H_{20}$}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**11**), which can be easily demetalated by heating in refluxing acetonitrile to give **2a** and the unprecedented diyne (HC≡C)$_2$C$C_{13}H_{20}$ (**12**). These demetalation processes allow the quantitative recovery of the metal auxiliary as the labile complex **2a,** which can be used as starting material for further reactions. Ab initio molecular orbital calculations on the η^1-vinylidene to η^2-alkyne tautomerization have been performed. It is shown that the process proceeds through a 1,2-[H] shift mechanism showing that the conversion requires an energy barrier of 29.9 kcal/mol. This is a value low enough to be overcome under the experimental reaction conditions allowing the formation of the labile η^2-alkyne complex and the subsequent exchange of the coordinated alkyne by acetonitrile.

Introduction

Transition metal vinylidene complexes [M]=C=CR_2 have attracted increasing attention in recent years since they display a rich and versatile reactivity of potential utility in organic synthesis.[1] In this respect, ruthenium(II) vinylidene derivatives have proven to be appropriate promoters for selective carbon−heteroatom[2] and carbon−carbon[2a,3] coupling reactions, and they have been also proposed as key intermediates in a number of catalytic transformations involving terminal alkynes.[4] Although several methods are known for the preparation of

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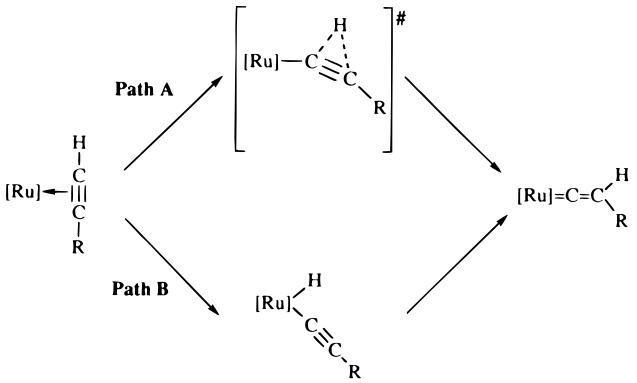
Chart 1



transition metal vinylidene derivatives, the most general approach is the addition of electrophiles to the nucleophilic C_β atom of σ-alkynyl complexes.[1] An alternative procedure widely used in the chemistry of ruthenium(II) complexes is the direct activation of terminal alkynes, which proceeds through the initial formation of the corresponding η^2-alkyne complex. The subsequent tautomerization via either the 1,2-[H] shift (see Chart 1; path A) or formation of the hydride−alkynyl ruthenium(IV) complex (see Chart 1; path B)[5] gives rise to the thermodynamically favored vinylidene isomer.[1]

Theoretical studies[6] support both mechanisms which have been also experimentally proved through the spectroscopic characterization or isolation of the corresponding intermediate complexes. As far as the η^2-terminal alkyne species are concerned, derivatives such as $[Ru(\eta^2\text{-HC}{\equiv}CR)(\eta^5\text{-}C_5H_5)L_2]^+$ (R = H, L = PMe_2Ph; R = Me, L = PMe_3)[7] and $[Ru(\eta^2\text{-HC}{\equiv}CH)(\eta^5\text{-}C_5H_5)$(dippe)]$^+$ (dippe = 1,2-bis(diisopropylphosphino)ethane)[5] have been isolated as stable intermediates in the formation of the corresponding vinylidene complexes. Moreover, both tautomers have been found to be in equilibrium at room temperature in complexes containing the ruthenium(II) fragments $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]^+$ [2d] and $[Ru(\eta^5\text{-}C_9H_4Me_3)(CO)(PPh_3)]^+$,[8] showing that the conversion of the η^2-alkyne into the vinylidene complexes depends on the electronic properties of the metallic fragment. Although the reverse process, i.e., the transformation of the vinylidene complex into the corresponding η^2-alkyne, has not been so extensively studied, it has also been described in a few cases. Thus, the reaction of $[Ru\{{=}C{=}C(H)Ph\}Cl(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2]^+$[9a] and $[Ru\{{=}C{=}C(H)Ph\}\{{=}C(NHPh)(CH_2Ph)\}Cl(PNP)]^+$[9b] (PNP = $Pr^nN(CH_2CH_2PPh_2)_2$) with CO in THF leads to the elimination of HC≡CPh and formation of the carbonyl compounds $[RuCl(CO)(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2]^+$ and $[Ru\{{=}C(NHPh)(CH_2Ph)\}Cl(CO)(PNP)]^+$, respectively. Similarly, the terminal alkyne is obtained when $[RuI_2\{{=}C{=}C(H)Ph\}(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)(\kappa P\text{-}Pr^i_2PCH_2CH_2OMe)]$ is heated at a high temperature.[9a] The vinylidene moiety is also displaced from the reaction of $[Ru(C{\equiv}CR)\{{=}C{=}C(H)R\}P_4]^+$ (P = phosphites) with $P(OMe)_3$ and isocyanides[3a] as well as in half-sandwich ruthenium(II) complexes of the type $[Ru\{HB(pz)_3\}Cl(PPh_3)\{{=}C{=}C(H)R\}]$ by nucleophiles (L) such as PMe_3, PPh_3, MeCN, pyridine, and CO to give $[Ru\{HB(pz)_3\}Cl(PPh_3)L]$ and the free terminal alkyne.[10]

It is, therefore, apparent that the transformation of the vinylidene moiety into the corresponding terminal alkyne in ruthenium(II) complexes is a feasible process which is accessible in ordinary reaction conditions. Although in the above-mentioned examples there is no valuable synthetic approach of alkynes (the resulting terminal alkynes are themselves the precursors of the vinylidene complexes), we believed it to be of interest to investigate the utility of these processes as a synthetic methodology for the preparation of functionalized terminal alkynes.

As part of our continuing studies on the reactivity patterns of unsaturated carbene ruthenium(II) complexes,[11] here we report that functionalized indenyl−

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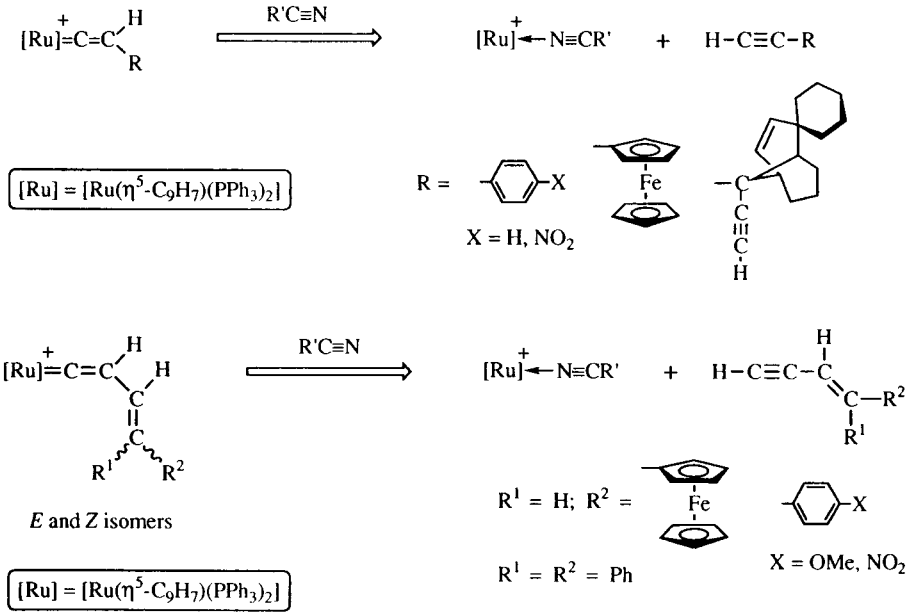
Chart 2



ruthenium(II) vinylidene derivatives [Ru{=C=C(H)R}-(η^5-C_9H_7)$(PPh_3)_2]^+$ react with nitriles to give the cationic complexes [Ru(η^5-C_9H_7)(N≡CR′)$(PPh_3)_2]^+$ (R′ = Me, Et, Ph) and the corresponding functionalized terminal alkyne HC≡CR (R = C_6H_5, 4-NO_2-C_6H_4, (η^5-C_5H_4)Fe-(η^5-C_5H_5), C(C≡CH)$C_{13}H_{20}$) (see Chart 2). Similarly terminal (*E*)-1,3-enynes HC≡CCH=CR^1R^2 (R^1 = R^2 = Ph; R^1 = H, R^2 = 4-OMe-C_6H_4, 4-NO_2-C_6H_4, (η^5-C_5H_4)-Fe(η^5-C_5H_5)) can be obtained starting from the alkenyl−vinylidene complexes [Ru{=C=C(H)CH=CR^1R^2}(η^5-C_9H_7)$(PPh_3)_2]^+$, which have been synthesized by protonation of the neutral σ-enynyl derivatives [Ru(C≡CCH=CR^1R^2)(η^5-C_9H_7)$(PPh_3)_2$].

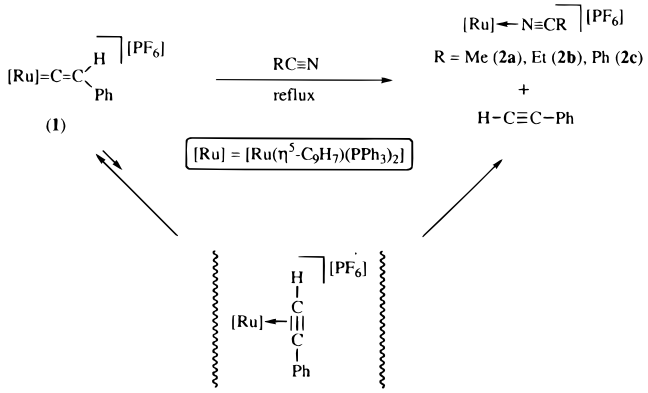
To study the electronic properties of the indenyl−ruthenium(II) fragment [Ru(η^5-C_9H_7)$(PPh_3)_2$] which enable the lability of the vinylidene moiety via conversion to the η^2-alkyne complex, ab initio molecular orbital calculations are also reported.

Results and Discussion

Reactions of Monosubstituted Vinylidene Ruthenium(II) Complexes with Nitriles. Although the monosubstituted vinylidene derivative [Ru{=C=C(H)-Ph}(η^5-C_9H_7)$(PPh_3)_2$][PF_6] (**1**)[11a] is obtained from phenylacetylene itself, we have first explored the feasibility of the vinylidene to π-alkyne transformation using the easily accessible complex **1** as precursor. Thus, the treatment of **1** with nitriles at high temperature results in the formation of the cationic nitrile complexes [Ru-(N≡CR)(η^5-C_9H_7)$(PPh_3)_2$][PF_6] (R = Me (**2a**), Et (**2b**), Ph (**2c**)), which were isolated in 75−85% yield, via phenylacetylene elimination (Scheme 1). Compounds **2a**−**c** have been characterized by elemental analysis, conductance measurements, and IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopy (details are given in the Experimental Section). The presence of the nitrile ligands is unambiguosly confirmed by the appearance in the IR spectra (KBr) of a ν(C≡N) absorption in the range 2226−2271 cm^{-1}.

The formation of **2a**−**c** may be understood assuming that the vinylidene complex **1** is in equilibrium with its

Scheme 1

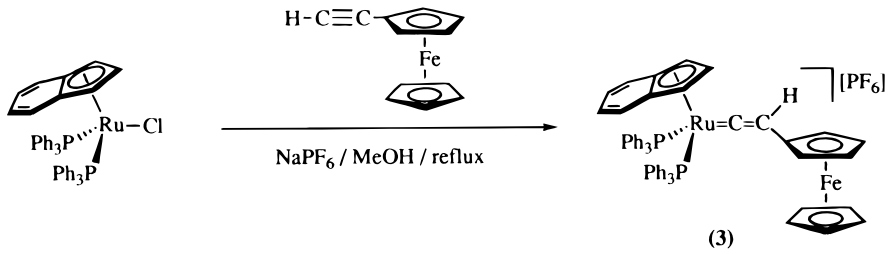


η^2-alkyne tautomer [Ru(η^2-HC≡CPh)(η^5-C_9H_7)$(PPh_3)_2$]-[PF_6] under the reaction conditions (ca. temperature 65−97 °C). Although at room temperature complex **1** is more stable (see Theoretical Calculations below), the rapid substitution in the transient π-alkyne species of the labile coordinated phenylacetylene by the more basic nitrile ligands favors the displacement of the equilibrium to afford complexes **2a**−**c** and the free alkyne. To get information on the existing species in solution, the reaction of complex **1** with CD_3CN has been monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy (from 20 to 70 °C). However, the presence of the π-alkyne species is not observed[12,13] since the spectra show only the resonances of the precursor complex **1** along with those assigned to the nitrile complex [Ru(N≡CCD_3)(η^5-C_9H_7)-$(PPh_3)_2$][PF_6].

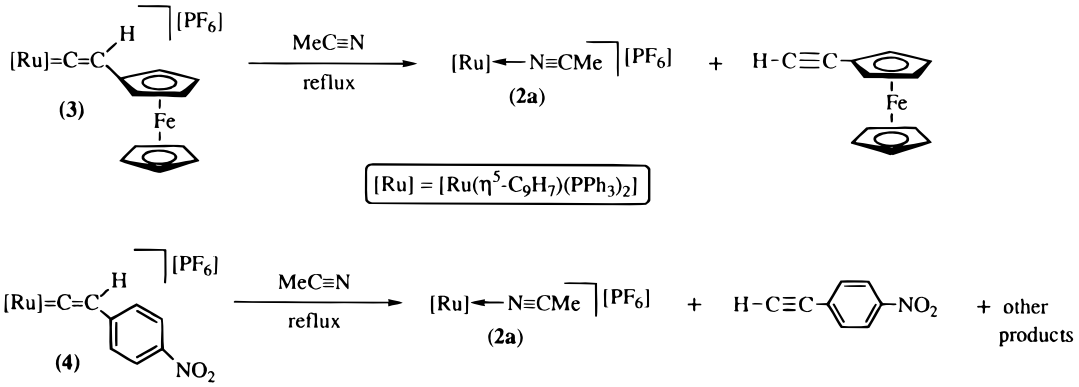
(12) The existence of this equilibrium is confirmed in the reaction of the analogous vinylidene complex [Ru{=C=C(H)R}(η^5-C_9H_7)$(PPh_3)_2$]-[PF_6] (R = 1-cyclohexenyl) with triphenylphosphine in refluxing methanol, which leads to the formation of the alkenyl−phosphonio complex (*E*)-[Ru{CH=C(PPh_3)R}(η^5-C_9H_7)$(PPh_3)_2$][PF_6] (R = 1-cyclohexenyl) via nucleophilic addition of PPh_3 to the coordinated π-alkyne (see ref 11d). Similarly, complex **1** reacts with PPh_3 in refluxing methanol to give the analogous alkenyl−phosphonio complex [Ru{CH=C(PPh_3)Ph}(η^5-C_9H_7)$(PPh_3)_2$][PF_6] (Unpublished results).

(13) Variable-temperature ^{31}P{^{1}H} and ^{1}H NMR experiments were also carried out with both CD_3OD and CD_3NO_2 solutions of the vinylidene complex **1**. No products other than **1** could be detected.

Scheme 2



Scheme 3



To find out to what extent the electronic density of the vinylidene ligand may affect this η^1-vinylidene−η^2-alkyne tautomerization, the behavior of the vinylidene derivatives [Ru{=C=C(H)(η^5-C_5H_4)Fe(η^5-C_5H_5)}(η^5-C_9H_7)-(PPh_3)$_2$][PF_6] (**3**) and [Ru{=C=C(H)-4-NO_2-C_6H_4}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**4**)[14] toward acetonitrile was explored. Compound **3** containing the electron-donor ferrocenyl fragment was prepared (82%) by reaction of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] with ethynylferrocene and $NaPF_6$ in refluxing methanol (Scheme 2), as previously described for analogous indenyl−ruthenium(II) vinylidene complexes.[11a,14] Analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) are in agreement with the proposed formulation. In particular, the presence of the vinylidene moiety was identified, as usual, on the basis of the low-field triplet resonance in ^{13}C-{^{1}H} NMR of the carbene carbon Ru=C_α (δ 352.30 ppm, $^2J_{CP}$ = 13.4 Hz).[11]

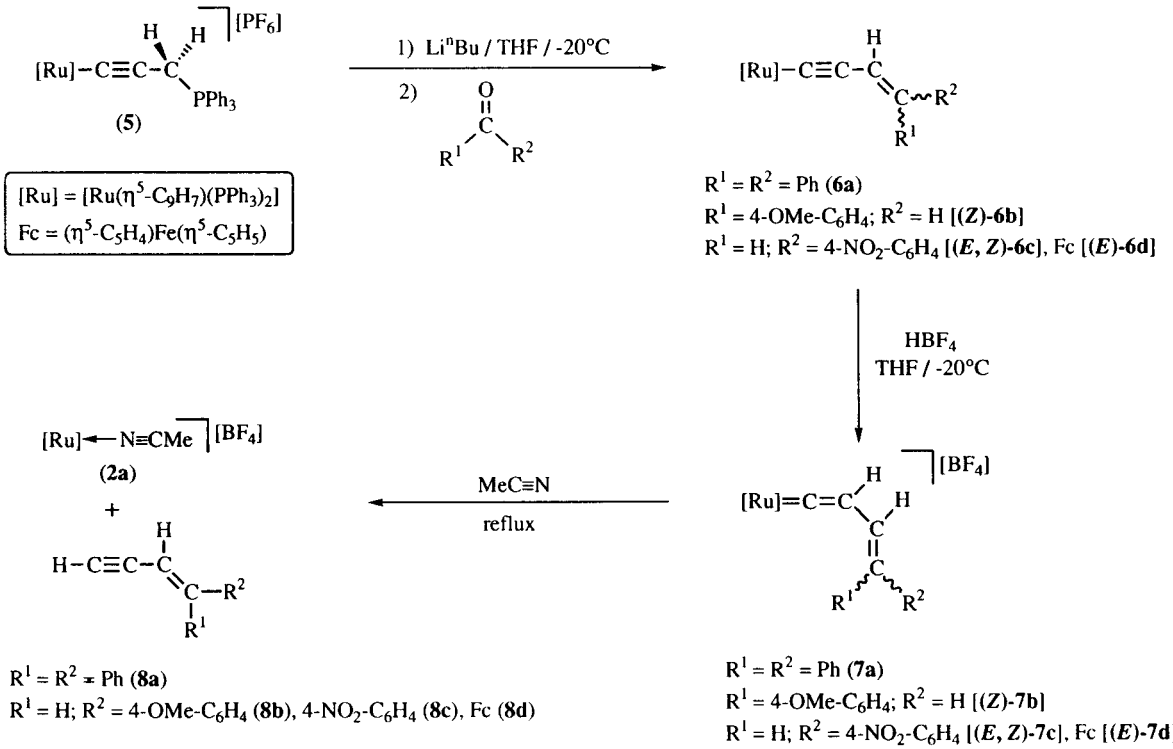
Complex **3** readily reacts with acetonitrile at reflux (ca. 1 h), like the vinylidene derivative **1**, to yield the expected nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$]-[PF_6] (**2a**) and ethynylferrocene in almost quantitative yield (Scheme 3). In contrast, vinylidene complex **4**, containing the electron-withdrawing *p*-nitrophenyl group, reacts slowly with acetonitrile at reflux to afford after 6 h a complicated mixture of products including **2a** and PPh_3, along with *p*-nitroethynylbenzene and additional uncharacterized organic and organometallic species. It is likely that competitive processes occur in the course of the long reaction period, among others the substitution of the coordinated PPh_3 ligands by acetonitrile. Although it is apparent that the η^1-vinylidene−η^2-alkyne tautomerization takes place, since for both reactions the free alkyne is obtained, these results seem to indicate that the process is kinetically favorable for the vinylidene groups bearing electron-releasing substituents.

Reactions of Monosubstituted Alkenyl−Vinylidene Ruthenium(II) Complexes with Acetonitrile: Synthesis of Terminal 1,3-Enynes. Since the vinylidene ligand in complexes **1**, **3,** and **4** has been found to be easily converted into the corresponding terminal alkyne in refluxing acetonitrile, we became interested in extending this reactivity to functionalized vinylidene derivatives. Providing that these derivatives are not accessible from the corresponding terminal alkyne, this approach could lead to a new route of terminal functionalized alkynes. We have previously shown[11b,g,14] that alkynyl−phosphonio complexes [Ru-{C≡CCH(R^1)(PR_3)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R^1 = H, PR_3 = PPh_3; R^1 = Ph, PR_3 = PMe_3) are excellent substrates for Wittig reactions, leading to the formation of new carbon−carbon double bonds. Thus, functionalized neutral σ-enynyl derivatives such as [Ru(C≡C−C(Ph)=CR^1R^2)(η^5-C_9H_7)(PPh_3)$_2$] (R^1 = R^2 = Ph; R^1 = H, R^2 = Me)[11b] and [Ru(C≡C−CH=CH−C≡CPh)(η^5-C_9H_7)-(PPh_3)$_2$][11g] can be obtained in good yields. Following this synthetic methodology novel σ-enynyl derivatives have been prepared in order to use them as potential precursors of the corresponding alkenyl−vinylidene complexes.

The treatment of a THF solution of the alkynyl−phosphonio complex [Ru{C≡CCH_2(PPh_3)}(η^5-C_9H_7)-(PPh_3)$_2$][PF_6][14b] (**5**) with 1 equiv of Li^{n}Bu at −20 °C, adding the corresponding aldehyde or ketone and warming the mixture up to room temperature resulted in the formation of the σ-enynyl complexes **6a,b** (98% and 62% yield, respectively) (Scheme 4). IR and NMR (^{1}H, ^{31}P-{^{1}H}, and ^{13}C{^{1}H}) spectroscopic data (see Experimental Section) support the proposed formulations and are in accordance with the presence of the novel carbon−carbon double bonds. It is worth mentioning that complex **6b** was stereoselectively obtained as the pure

(14) (a) Houbrechts, S.; Clays, K.; Persoons, A.; Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Organometallics* **1996**, *15*, 5266. (b) 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.

Scheme 4



Z stereoisomer, as clearly indicated by the coupling constant (J_{HH} = 13.0 Hz) for the olefinic protons in the ^{1}H NMR spectrum. The presence of the enynyl moiety was identified on the basis of (i) the presence of a ν(C≡C) absorption band in the IR spectra (KBr) at 2049 (**6a**) and 2045 (**6b**) cm^{-1} and (ii) the triplet resonance of the Ru−C$_\alpha$ atom (**6a**: δ 123.96 ($^2J_{CP}$ = 24.2 Hz) ppm; **6b**: δ 116.90 ($^2J_{CP}$ = 25.0 Hz) ppm), the singlet resonance of the C$_\beta$ atom (δ 116.36 (**6a**) and 115.77 (**6b**) ppm), and the olefinic carbon resonances (ca. δ 114−145 ppm) observed in the ^{13}C{^{1}H} NMR spectra.

As expected, the protonation of **6a,b** with HBF$_4$·Et$_2$O in THF at −20 °C leads to the formation of the alkenyl−vinylidene derivatives **7a,b** (98% and 88% yield, respectively) (Scheme 4). The analytical and spectroscopic data of **7a,b**, which are similar to those reported for other indenyl−ruthenium(II) alkenyl−vinylidene complexes,[11b,d,g,14] are consistent with the proposed formulations (see Experimental Section). Since no isomerization of the C=C bond takes place in the course of these protonations, complex **7b** has been isolated as the pure *Z* stereoisomer. Similarly, complex **7c** has been obtained from the previously reported σ-enynyl complex **6c**[14] and isolated (73% yield) as a mixture of the corresponding *E* and *Z* stereoisomers in accordance with the isomeric mixture of the precursor derivative **6c** (ca. 2:1 ratio).

Complexes **7a**−**c** react rapidly with refluxing MeCN, resulting in the quantitative formation of the nitrile complex **2a**, isolated as an unsoluble tetrafluoroborate salt, and the elimination of the 1,3-enynes **8a**−**c**, which are readily isolated from the reaction mixture by extraction with diethyl ether (Scheme 4). If we compare the behavior of the vinylidene complexes **4** and **7c**, both containing the strong acceptor *p*-nitrophenyl group, we can conclude that the presence of a conjugated C=C double bond in the vinylidene group of the latter seems to favor the initial η^1-vinylidene−η^2-alkyne tautomerization. The enyne HC≡C−CH=CH−(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) (**8d**) has been similarly obtained following an analogous sequence of reactions from the known σ-enynyl (*E*)-**6d** and alkenyl−vinylidene (*E*)-**7d** complexes.[14b] Enynes **8a**−**d** were easily purified by column chromatography on silica gel (60−77% isolated yield) and spectroscopically characterized (see Experimental Section).[15] Thus, the IR spectra show the expected ν(C≡C) absorptions in the range 2092−2106 cm^{-1}. The acetylenic C≡CH proton resonances appear, in the ^{1}H NMR spectra, as doublets (J_{HH} = 2.1−2.5 Hz) at δ 2.80−3.22 ppm, and the C≡CH carbons resonate, in ^{13}C{^{1}H} NMR, in the ranges δ 78.42−83.94 (≡CH) and 81.49−89.92 (≡C) ppm, respectively.

The most remarkable feature of this synthesis is that 1,3-enynes **8b**−**d** were stereoselectively obtained as the thermodynamically stable *E* stereoisomers, as inferred clearly from the values of the coupling constant for the olefinic protons (ca. J_{HH} = 16 Hz). Given the stereochemistry of the starting vinylidene complexes, (*Z*)-**7b** and (*E*,*Z*)-**7c**, it is probable that during the demetalation process, the isomerization of the C=C double bond takes place in the intermediate coordinated enyne derivatives.

Despite the plethora of methods that have been used for the preparation of terminal 1,3-enynes,[16] those based on a simple Wittig reaction for the generation of the

(15) Enynes **8a,b** have been previously reported. **8a:** (a) Jasiobedzki, W.; Zimniak, A.; Glinka, T. *Rocz. Chem.* **1975**, *49*, 111. **8b:** (b) Gibson, A. W.; Humphrey, G. R.; Kennedy, D. J.; Wright, S. H. B. *Synthesis* **1991**, 414.

(16) See for example: (a) Pattenden, G. In *Comprehensive Organic Chemistry, Vol 1*; Stoddart, J. F., Ed.; Pergamon: Oxford, 1979; p 205. (b) Yamamoto, H. In *Comprehensive Organic Synthesis, Vol 2*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; p 91. (c) Cheshire, D. R. In *Comprehensive Organic Synthesis, Vol 3*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; p 217. (d) Sonogashira, K. In *Comprehensive Organic Synthesis, Vol 3*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; p 521. (e) Coveney, D. J. In *Comprehensive Organic Synthesis, Vol 3*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; p 878.

Scheme 5

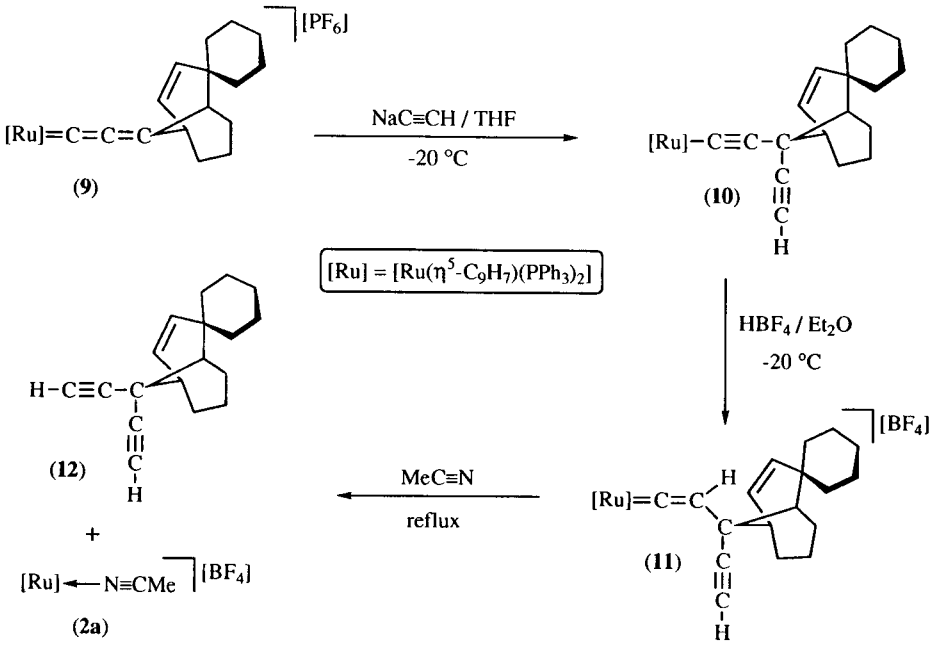
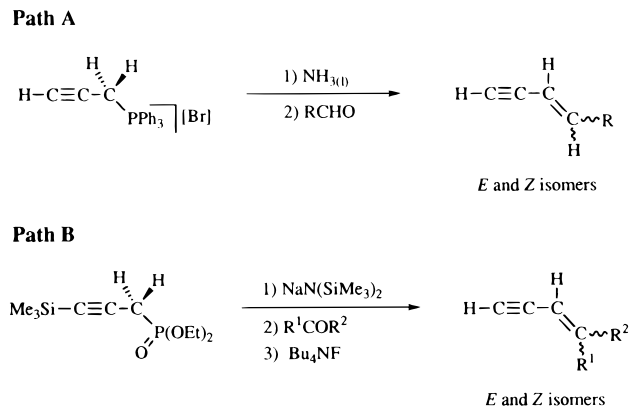


Chart 3



carbon−carbon double bond are scarce (see Chart 3). Thus, it is known that the phosphorus ylide derived from triphenyl (2-propynyl)phosphonium bromide reacts with aldehydes to produce largely (*Z*)-1,3-enynes in poor yields (path A).[17] The Horner−Wadsworth−Emmons variant of the Wittig reaction, starting from (3-trimethylsilyl-2-propynyl)phosphonate and aldehydes or ketones, has been also reported and gives terminal 1,3-enynes in excellent yields but as mixtures of the *E* and *Z* stereoisomers (path B).[15b] With these precedents in mind, the results reported here provide a useful methodology for the stereoselective generation of terminal (*E*)-1,3-enynes based on the Wittig reaction. Furthermore, taking into account that the precursor alkynyl−phosphonio complex **5** is obtained in a one-pot synthesis by treatment of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with 2-propyn-1-ol and $NaPF_6$ in the presence of PPh_3,[14b] this synthetic route of enynes can be regarded as a formal ruthenium-mediated coupling of 2-propyn-1-ol with aldehydes or ketones without precedent in the literature.[18]

Synthesis of the Diyne $(HC{\equiv}C)_2CC_{13}H_{20}$. In the search for the versatility and potential utility of this methodology for the synthesis of functionalized terminal alkynes, we have investigated the reactivity of other types of σ-alkynyl ruthenium(II) derivatives. Thus, we have recently reported that the activation of 1-ethynyl-1-cyclohexanol by $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ gives the allenylidene complex $[Ru\{{=}C{=}C{=}C(C_{13}H_{20})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**9**), which contains the bicyclic [3.3.1]non-2-en-9-ylidene moiety $C_{13}H_{20}$ (Scheme 5). This spiro bicycle results from the formal addition of two molecules of the 1-alkyn-3-ol via an unprecedent metal-promoted double dehydration of 1-ethynyl-1-cyclohexanol.[19] Since all attempts to liberate the organic fragment in **9** through the cleavage of the Ru=C bond using standard oxidative reagents (e.g., DMSO, ammonium cerium(IV) nitrate (CAN)) were unsuccessful, we decided to transform the allenylidene chain into a vinylidene ligand, which would enable the subsequent elimination of the terminal alkyne by the treatment with acetonitrile, as has been described above. The overall transformations which are based on the initial generation of a σ-alkynyl derivative and subsequent conversion into a vinylidene complex are shown in Scheme 5. The allenylidene complex **9** reacts in THF with a large excess of NaC≡CH at −20 °C to generate, via the typical regioselective nucleophilic addition[11b−i] at the C_γ of the allenylidene group, the σ-alkynyl complex **10** isolated as an air-stable orange solid (61% yield). Elemental analyses and spectroscopic data are in accordance with the formulation as an σ-yninyl derivative. The IR spectrum (KBr) of **10** shows the expected ν(C≡C) absorption bands at 2082 and 2275 cm^{-1} assigned to the coordinated and terminal C≡C bonds, respectively. The most remarkable features

(17) Eiter, K.; Oediger, H. *Liebigs Ann. Chem.* **1965**, *682*, 62. The use of the trimethylsilyl-protected phosphonium salt and $LiBu^n$ as base has been reported to yield trimethylsilyl-protected (*E*)-1,3-enynes in good yields. Corey, E. J.; Ruden, R. A. *Tetrahedron Lett.* **1973**, 1495.

(18) The related coupling of propargyl alcohols with ketones containing α-hydrogens, via $[Co_2(CO)_6]$-stabilized propargylium ions, is known to yield γ-keto-substituted alkynes. (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (b) Smit, W. A.; Caple, R.; Smoliakova, I. P. *Chem. Rev.* **1994**, *94*, 2359.

(19) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; García-Granda, S. *Organometallics* **1994**, *13*, 745.

of the NMR spectra are (i) (^{1}H NMR) the singlet resonance at δ 2.02 ppm of the C≡CH proton and (ii) (^{13}C{^{1}H} NMR) the Ru−C_α resonance, which appears as a virtual triplet at δ 89.41 ppm ($^2J_{CP} = {}^2J_{CP'} = 24.9$ Hz) due to the coupling with the two unequivalent phosphorus atoms, as well as the expected C_β and C≡CH singlet resonances (δ 113.65 (C_β), 90.48 (≡C), 71.20 (≡CH) ppm). As expected, the treatment of a diethyl ether solution of complex **10** with $HBF_4 \cdot Et_2O$ at −20 °C leads to the formation of the monosubstituted vinylidene derivative **11** (79% yield). Analytical and spectroscopic data are fully consistent with the proposed structure (see Experimental Section).

The demetalation of complex **11** by reaction with acetonitrile at 60 °C proceeds smoothly and gives, besides the nitrile complex **2a**, the diyne **12,** which was isolated after column chromatography as a colorless oil in 70% yield. Spectroscopic data of this unprecedented alkyne supports this formulation (see Experimental Section). The most significant spectroscopic features are (a) (^{1}H NMR) two unequivalent ≡CH proton resonances at δ 2.22 and 2.50 ppm and (b) (^{13}C{^{1}H} NMR) acetylenic carbon resonances at δ 69.88 (≡C), 72.55 (≡C), 87.00 (≡CH), and 89.29 (≡CH) ppm.

Theoretical Calculations. The 1-alkyne to vinylidene tautomerization in the coordination sphere of a transition metal is at present well-documented by theoretical studies which show that the process is energetically favorable.[6] This transformation takes place after the coordination of the terminal alkyne and may proceed via two mechanisms: (a) the initial formation of an intermediate hydrido−alkynyl species, through the oxidative addition of the coordinated alkyne, followed by a hydrogen shift to the β carbon atom of the alkynyl group to afford the vinylidene complex (Chart 1; path B), and (b) a direct 1,2-hydrogen shift from the α to β carbon in the η^2-coordinated terminal alkyne (Chart 1; path A). The former mechanism has been experimentally supported by the identification of hydrido−alkynyl species in a series of Co, Rh, Ir,[20] and Ru[5] complexes. Recent ab initio calculations and kinetic studies have shown that these transformations proceed either by a bimolecular hydrogen shift (i.e., $[RhCl(PH_3)_2(H)(C{\equiv}CH)]$)[6c] or by an intramolecular 1,3-hydrogen shift (i.e., $[Co(H)(C{\equiv}CH)(P(CH_2CH_2PPh_2)_3)]$.[20a] The 1,2-hydrogen shift mechanism seems to be more favorable for d^6 metal complexes such as $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2\text{-}C_2H_2)]$[6a] and $[RuCl_2(PH_3)_2(\eta^2\text{-}C_2H_2)]$,[6b] as it was found by extended Hückel or ab initio calculations, respectively.[21]

Since these studies are relevant for the knowledge of energy barriers, it seemed therefore of interest to carry out theoretical simulations on the isomerization processes described in this paper. In accord with Wakatsuki's previous studies on Ru(II) complexes,[6b] we have assumed that the isomerizations in our indenyl−ruthenium(II) complexes proceed through the 1,2-hydrogen shift mechanism. In fact, no hydrido−alkynyl complexes were detected under the experimental conditions used in the described vinylidene to η^2-alkyne conversions.

Geometry optimization and vibrational analysis on the C_2H_2 unit with the $[Ru(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$ moiety were performed. The optimized structures and main geometric parameters are shown in Figure 1, while their relative energies are summarized in Figure 2. Minimum energies for complexes **A** and **E** and three transition states **B**, **C,** and **D** were found. The indenyl ligands were located in a trans orientation with respect to the η^2-alkyne or vinylidene groups, in accord with the preferred conformation found in our previous reported theoretical studies.[11a] The X-ray structures of the vinylidene indenyl−ruthenium(II) complexes $[Ru\{{=}C{=}C(R^1)R^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (R^1 = Me, R^2 = 1-cyclohexenyl, Me; R^1 = H, R^2 = Ph) are known.[11a,d,j] The calculated Ru−C_α (1.844 Å) and the C_α−C_β (1.308 Å) distances in **E** are very close to those experimentally determined (average values: 1.834(5) and 1.290(6) Å, respectively). The Ru−P (2.375 Å) and Ru−C* (2.007 Å) (C* = centroid of the five-membered ring of the indenyl group) bond lengths in **E** are also in agreement with the observed values (average values: 2.364(3) and 1.97(1) Å, respectively).

The η^2-HC≡CH complexes **A** and **B** are rotational isomers with the alkyne group either perpendicular to the molecular plane characteristic of the C_s symmetry or in the same plane, respectively. Analogously, the vinylidene complexes **D** and **E** are rotational isomers (by rotation around the ruthenium−C_α bond) in which the vinylidene group is also contained or perpendicular to the molecular plane, respectively. Finally complex **C** is the transition state associated with the transformation of **A** to **E**.

As shown in Figure 2 rotamers **A** and **E**, in which the alkyne and vinylidene groups are located perpendicular to the molecular plane, are more stable than rotamers **B** and **D** (4.3 and 5.8 kcal/mol, respectively). This is in accord with previous molecular orbital calculations[23] which showed for these orientations the most efficient π-back-bonding from the metal to the π-alkyne or vinylidene ligand. Therefore, the less stable rotational isomers **B** and **D**, generated from the rotation of the η^2-alkyne and the vinylidene groups, may be considered as transition states in the isomerization process.

Although the calculated energy difference between **D** and **E** is 5.8 kcal/mol, as shown in Figure 2, this value

(20) [Co]: (a) Bianchini, C.; Peruzzini, M.; Vacca A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697. [Rh]: (b) Wolf, J.; Werner, H.; Sehadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414. (c) Werner, H.; García Alonso, F. J.; Otto, H.; Wolf, J. *Z. Naturforsch.* **1988**, *43b*, 722. (d) Werner, H.; Brekau, U. *Z. Naturforsch.* **1989**, *44b*, 1438. (e) Rappert, T.; Nurnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156. (f) Werner, H.; Baum, M.; Schneider, D.; Windmuller, B. *Organometallics* **1994**, *13*, 1089. (g) Werner, H.; Rappert, T.; Baum, M.; Stark, A. *J. Organomet. Chem.* **1993**, *459*, 319. [Ir]: (h) Hoehn, A.; Otto, H.; Dziallas, M.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406. (i) Hoehn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852. (j) Hoehn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255. (k) Werner, H.; Hoehn, A.; Schulz, M. *J. Chem. Soc., Dalton Trans.* **1991**, 777.

(21) In the experimental studies on the mechanism of the isomerization of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}HC{\equiv}CH)(dippe)]^+$ to the vinylidene complex $[Ru(\eta^5\text{-}C_5Me_5)(=C{=}CH_2)(dippe)]^+$ (dippe = 1,2-bis(diisopropylphosphino)ethane) C. Puerta and co-workers have also isolated a metastable hydrido−alkynyl intermediate (see ref 5). However, since this reaction is inhibited in solution by strong acids, the mechanism seems to be dissociative in contrast to the usual 1,3-[H] shift, indicating that the isomerization proceeds in a nonconcerted fashion.

(22) We have explored the alternative mechanism (path B; Chart 1) with a single calculation of the optimized structure energy of the corresponding hydrido−alkynyl species, and we have found an energy comparable to the transition state **C**. This fact allows us to predict that the energy barrier needed for this mechanism should be higher than that of the [1, 2]-H shift process and could explain why this intermediate was not detected.

(23) (a) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292. (b) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

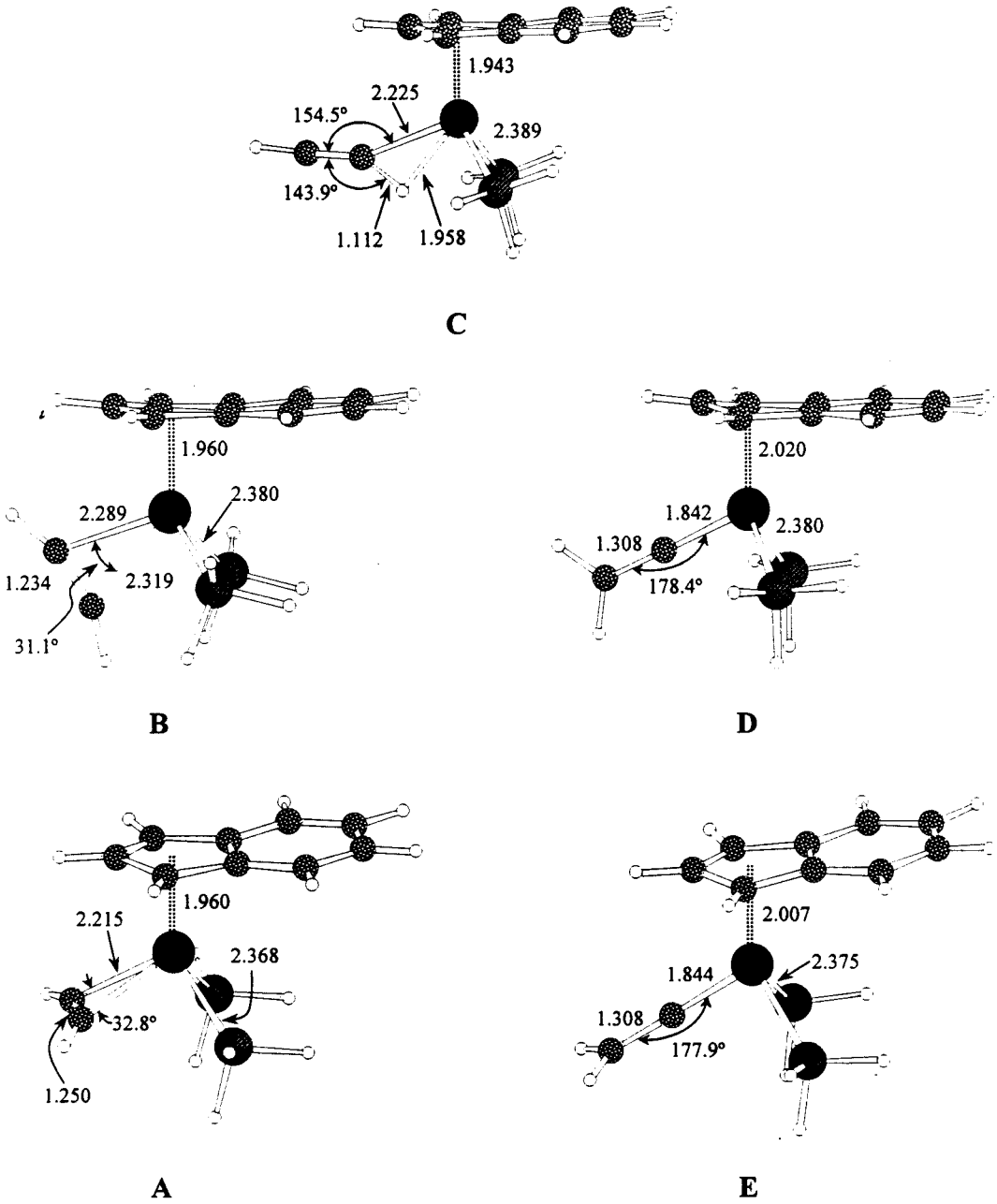


Figure 1. Optimized ab initio (B3LYP) structures (Å, deg) of reactants, products, and transition states for the formation of $[Ru(\eta^5\text{-}C_9H_7)(=C=CH_2)(PH_3)_2]^+$ from $[Ru(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$ and C_2H_2.

should be less in the actual complexes since a maximum steric repulsion between the vinylidene substituents and the triphenylphosphine ligands should be expected for **E**. In fact, the X-ray structures of $[Ru\{=C=C(R^1)R^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (R^1 = Me, R^2 = 1-cyclohexenyl, Me; R^1 = H, R^2 = Ph)[11a,d,j] show orientations of the vinylidene group that deviate more than 18° away from the preferred perpendicular orientation. Similarly, an important steric repulsion can be predicted for the rotamer $\eta^2\text{-}C_2H_2$ complex **A,** which therefore should lead to a less stable energy level than that shown in Figure 2. Providing the existence of these steric repulsions and the small differences in the energy values of the rotational isomers (which may be easily overcome in solution), it can be assumed that **B** and **D** are the acting species in the 1,2-[H] shift mechanism.

In this migration only the transition state **C** has been found along the reaction path. The calculated optimized structure and the energy (18.9 kcal/mol less stable than **B**) are shown in Figures 1 and 2, respectively. The distances Ru−C_α (2.225 Å), C_α−C_β (1.220 Å), Ru−H (1.958 Å), and C_α−H (1.112 Å) and the angles Ru−C_α−C_β (154.5°) and C_β−C_α−H (143.9°) are very similar to those found by Wakatsuki[6b] in the analogous intermediate complex $[RuCl_2(\eta^2\text{-}H-C_2H)(PH_3)_2]$ (distances: Ru−C_α (2.087 Å), C_α−C_β (1.225 Å), Ru−H (1.763 Å), and C_α−H (1.130 Å); angles: Ru−C_α−C_β (154.9°) and C_β−C_α−H (147.5°)). Nevertheless, this complex in the Wakatsuki's model is a relative minimum state with respect to two close transition states, while in our case the structure **C** is a transition state itself.

The following interesting features are relevant in the η^1-vinylidene−η^2-alkyne tautomerization reaction path, back and forth (Figure 2): (i) The vinylidene species are thermodynamically more stable than the η^2-alkyne complexes (11.0 kcal/mol), (ii) the calculated activation

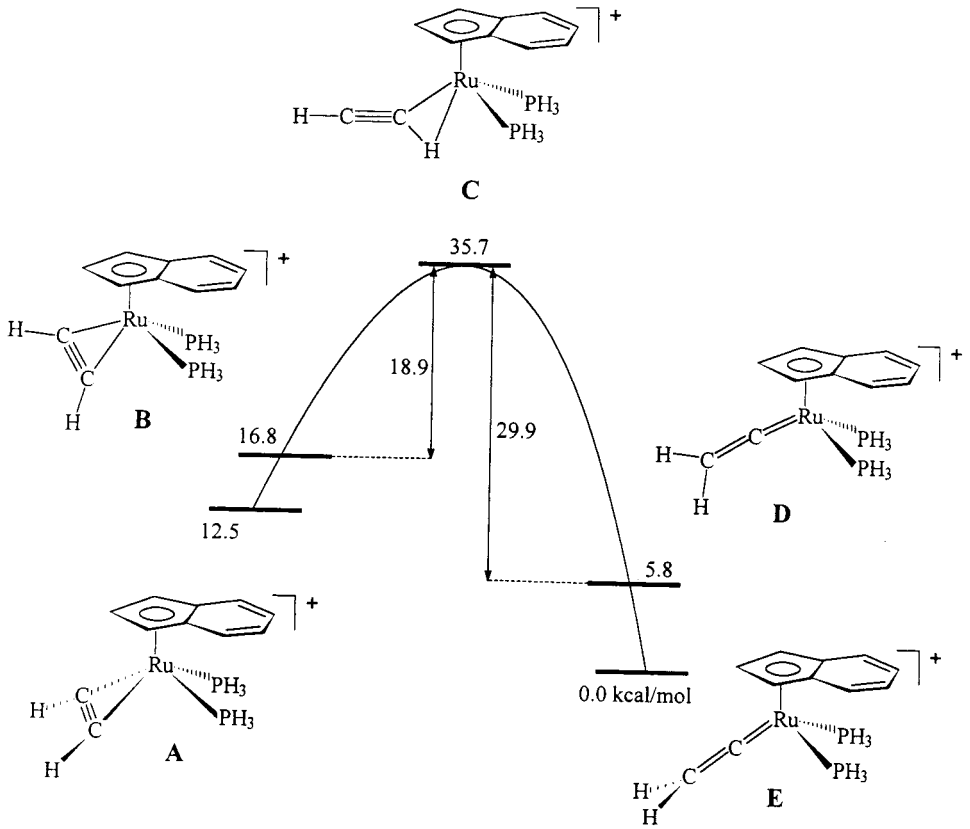


Figure 2. Energy diagram (kcal/mol) for the formation of $[Ru(\eta^5\text{-}C_9H_7)(=C=CH_2)(PH_3)_2]^+$ from $[Ru(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$ and C_2H_2.

energy to reach **C** from **B** is 18.9 kcal/mol, and (iii) the reverse process from **D** requires 29.9 kcal/mol. Therefore, since the energy barrier to reach the η^2-alkyne species from the stable vinylidene complex can be overcome under the experimental reaction conditions, the transformation to the kinetically labile π-alkyne complexes may be readily achieved.

Concluding Remarks

As part of our continuing interest in studying the reactivity of allenylidene ruthenium(II) complexes, we have recently reported the synthesis of a wide series of functionalized indenyl−ruthenium(II) vinylidene derivatives.[11,14] The synthetic methodology is based on the nucleophilic additions at the C_γ of the allenylidene chain in the cationic complexes $[Ru(=C=C=CRR')(\eta^5\text{-}C_9H_7)L_2]^+$ to give the corresponding neutral σ-alkynyl derivatives $[Ru\{C{\equiv}CC(Nu)RR'\}(\eta^5\text{-}C_9H_7)L_2]$, which can be easily converted into the corresponding vinylidene complexes $[Ru\{=C=C(H)C(Nu)RR'\}(\eta^5\text{-}C_9H_7)L_2]^+$ after typical proton additions. In addition, we have reported the synthesis of a large series of alkenyl−vinylidene complexes $[Ru\{=C=C(H)C(R)=CRR'\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$, which can be obtained in high yields from the reaction of alkynyl−phosphonio complexes with ketones or aldehydes, via Wittig type processes, and subsequent protonation of the corresponding σ-enynyl $[Ru\{C{\equiv}CC(R)=CRR'\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ intermediates. This paper illustrates for the first time the utility of these processes in stoichiometric organic synthesis. Thus, it is shown that the readily accessible indenyl−ruthenium(II) alkenyl−vinylidene complexes are able to undergo demetalation reactions by heating in CH_3CN under reflux to afford stereoselectively terminal (*E*)-1,3-enynes HC≡C−CH=CRR′. They are formed in good yields through the initial tautomerization at the ruthenium center of the η^1-vinylidene group to the η^2-terminal alkyne and subsequent elimination from the ruthenium center (Scheme 4) by exchange with CH_3CN. These syntheses can be regarded as a formal metal-mediated coupling of 2-propyn-1-ol with aldehydes or ketones without precedent in the literature.

$$HC{\equiv}CCH_2OH + RCOR' \xrightarrow{[Ru]} (E)\text{-}HC{\equiv}CCH{=}CRR'$$

Since these processes take place under mild reaction conditions and have proven to be general for other vinylidene complexes (Schemes 1 and 3−5), they provide a useful synthetic methodology of functionalized alkynes and diynes. Furthermore, it should be mentioned that the metal auxiliary is recovered as the acetonitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (**2a**), which can be used as starting material for further reactions, taking into account the well-known lability of the nitrile ligands.

In this paper we also describe a theoretical simulation of the η^1-vinylidene to η^2-alkyne tautomerization in these indenyl−ruthenium(II) complexes, which is shown to proceed through the classical 1,2-[H] shift mechanism. Although the η^2-alkyne to η^1-vinylidene tautomerization is well-known to occur for several transition metal complexes[1] and has been calculated to be thermodynamically favorable,[6] the reverse transformation has hardly been described experimentally.[9,10] It is apparent from the processes described above that the energy barrier associated in the conversion of η^1-

vinylidene to η^2-alkyne can be readily overcome in the reaction conditions (refluxing acetonitrile). Ab initio molecular orbital calculations are consistent with the experimental results and show that the energy barrier is 29.9 kcal/mol, allowing the formation of the kinetically labile π-alkyne complex under relatively mild reaction conditions.

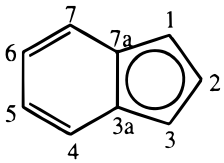
In summary, this work reports theoretical and experimental studies on the tautomerization of indenyl−ruthenium(II) vinylidene complexes in the corresponding η^2-alkyne derivatives which readily undergo exchange of the coordinated alkyne by nitriles. It is shown that this process discloses a new entry for the synthesis of functionalized terminal alkynes, which are obtained in good yields and stereoselectively. This synthetic methodology also allows the quantitative recovery of the metal fragment, which may be used for further transformations. Studies directed to the extension of this methodology are currently in progress.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk tube 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 [RuCl(η^5-C_9H_7)(PPh_3)$_2$],[24] [Ru{=C=C(H)R}(η^5-C_9H_7)(PPh_3)$_2$][X] (R = Ph,[11a] 4-NO_2-C_6H_4,[14] −CH=CH−(η^5-C_5H_4)Fe(η^5-C_5H_5)[14b]), [Ru(C≡CCH=CHR)(η^5-C_9H_7)(PPh_3)$_2$] (R = 4-NO_2-C_6H_4,[14] (η^5-C_5H_4)Fe(η^5-C_5H_5)[14b]), [Ru{C≡CCH_2(PPh_3)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6],[14] [Ru{=C=C=C$C_{13}H_{20}$}(η^5-C_9H_7)(PPh_3)$_2$][PF_6][19] and (η^5-C_5H_5)Fe(η^5-C_5H_4−C≡CH)[25] 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, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. High-resolution mass spectra were recorded using a MAT-95 spectrometer. 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. Abbreviations used: s, singlet; bs, broad singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet.

Legend for indenyl skeleton



Synthesis of [Ru(N≡CR)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R = Me (2a), Et (2b), Ph (2c)). A solution of complex **1** (0.987 g, 1 mmol) in the corresponding nitrile (50 mL) (for **2a,b**), or in methanol (50 mL) and in the presence of PhC≡N (1.010 mL, 10 mmol) (for **2c**), was heated under reflux for 90 min. The solution was then evaporated to dryness and the resulting yellow solid washed with diethyl ether (2 × 20 mL) and vacuum-dried. **2a:** yield 0.723 g (78%); IR (KBr) ν = 835 cm^{-1} (PF_6^-), 2270 cm^{-1} (C≡N); Λ (acetone, 20 °C) = 104 Ω^{-1} cm^2 mol^{-1}; ^{31}P{^{1}H} ($CDCl_3$, 121.5 MHz) δ = 48.16 (s); ^{1}H ($CDCl_3$, 300 MHz) δ = 2.20 (s, 3H, CH_3), 4.49 (d, 2H, J_{HH} = 1.7 Hz, H-1,3), 4.73 (t, 1H, J_{HH} = 1.7 Hz, H-2), 6.89−7.37 (m, 34H, Ph, H-4,7 and H-5,6); ^{13}C{^{1}H} ($CDCl_3$, 75.4 MHz) δ = 4.14 (s, CH_3), 67.90 (s, C-1,3), 93.64 (s, C-2), 109.60 (s, C-3a,7a), 124.63 and 129.43 (s, C-4,7 and C-5,6), 128.08−135.01 (m, Ph and C≡N). $RuC_{47}H_{40}F_6P_3N$ (926.8): calcd C 60.91, H 4.35, N 1.51; found C 60.40, H 4.49, N 1.48. **2b:** yield 0.705 g (75%); IR (KBr) ν = 840 cm^{-1} (PF_6-), 2271 cm^{-1} (C≡N); Λ (acetone, 20 °C) = 108 Ω^{-1} cm^2 mol^{-1}; ^{31}P{^{1}H} ($CDCl_3$, 121.5 MHz) δ = 47.93 (s); ^{1}H ($CDCl_3$, 300 MHz) δ = 0.91 (t, 3H, J_{HH} = 7.6 Hz, CH_3), 2.64 (d, 2H, J_{HH} = 7.6 Hz, CH_2), 4.51 (bs, 2H, H-1,3), 4.75 (bs, 1H, H-2), 6.90−7.45 (m, 34H, Ph, H-4,7 and H-5,6); ^{13}C{^{1}H} ($CDCl_3$, 75.4 MHz) δ = 9.55 (s, CH_3), 13.09 (s, CH_2), 67.95 (s, C-1,3), 93.52 (s, C-2), 109.55 (s, C-3a,7a), 124.55 and 129.32 (s, C-4,7 and C-5,6), 127.96−134.91 (m, Ph and C≡N). $RuC_{48}H_{42}F_6P_3N$ (940.8): calcd C 61.28, H 4.50, N 1.49; found C 61.54, H 4.66, N 1.57. **2c:** yield 0.840 g (85%); IR (KBr) ν = 834 cm^{-1} (PF_6^-), 2226 cm^{-1} (C≡N); Λ (acetone, 20 °C) = 112 Ω^{-1} cm^2 mol^{-1}; ^{31}P{^{1}H} ($CDCl_3$, 121.5 MHz) δ = 47.83 (s); ^{1}H ($CDCl_3$, 300 MHz) δ = 4.59 (d, 2H, J_{HH} = 2.1 Hz, H-1,3), 4.83 (t, 1H, J_{HH} = 2.1 Hz, H-2), 6.86−7.61 (m, 39H, Ph, H-4,7 and H-5,6); ^{13}C{^{1}H} ($CDCl_3$, 75.4 MHz) δ = 68.75 (s, C-1,3), 93.80 (s, C-2), 109.54 (s, C-3a,7a), 110.88 (s, C≡N), 124.28 (s, C-4,7 or C-5,6), 128.13−134.56 (m, Ph and C-4,7 or C-5,6). $RuC_{52}H_{42}F_6P_3N$ (988.8): calcd C 63.16, H 4.28, N 1.41; found C 63.02, H 4.32, N 1.44.

Synthesis of [Ru{=C=C(H)Fc}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (Fc = (η^5-C_5H_4)Fe(η^5-C_5H_5)) (3). A mixture of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (0.776 g, 1 mmol), $NaPF_6$ (0.336 g, 2 mmol), and ethynylferrocene (0.273 g, 1.3 mmol) in MeOH (50 mL) was heated under reflux for 1 h. The solvent was then removed under vacuum, and the solid residue was extracted with dichloromethane (ca. 25 mL) and filtered. The resulting solution was then concentrated (ca. 5 mL), and diethyl ether (100 mL) was added, yielding a brown solid, which was washed with diethyl ether (3 × 20 mL) and vacuum-dried: yield 0.898 g (82%); IR (KBr) ν = 833 cm^{-1} (PF_6^-); Λ (acetone, 20 °C) = 106 Ω^{-1} cm^2 mol^{-1}; ^{31}P{^{1}H} ($CDCl_3$, 121.5 MHz) δ = 41.27 (s); ^{1}H ($CDCl_3$, 300 MHz) δ = 4.44 (m, 10H, C_5H_5, C_5H_4 and Ru=C=CH), 5.47 (m, 3H, H-1,3 and H-2), 6.24 (m, 2H, H-4,7 or H-5,6), 6.89−7.68 (m, 32H, Ph and H-4,7 or H-5,6); ^{13}C{^{1}H} ($CDCl_3$, 75.4 MHz) δ = 67.58 and 69.92 (s, CH of C_5H_4), 71.58 (s, C_5H_5), 73.42 (s, C of C_5H_4), 83.81 (s, C-1,3), 98.63 (s, C-2), 113.59 (s, C_β), 114.73 (s, C-3a,7a), 122.97 and 130.06 (s, C-4,7 and C-5,6), 126.93−142.43 (m, Ph), 352.30 (t, $^2J_{CP}$ = 13.4 Hz, Ru=C_α). $FeRuC_{57}H_{47}F_6P_3$ (1095.8): calcd C 62.47, H 4.32; found C 62.21, H 4.18.

Synthesis of [Ru(C≡CCH=CR^1R^2)(η^5-C_9H_7)(PPh_3)$_2$] (R^1 = R^2 = Ph (6a); R^1 = 4-OMe-C_6H_4, R^2 = H [(*Z*)-6b]). LiBu^n (1.6 M in hexane; 0.625 mL, 1 mmol) was added at −20 °C to a solution of complex **5** (1.186 g, 1 mmol) in THF (30 mL). The reaction mixture was stirred for 10 min., and benzophenone (0.546 g, 3 mmol) or *p*-anisaldehyde (0.365 mL, 3 mmol) was then added. Upon warming to room temperature, the solution was stirred for an additional 30 min. The solvent was then removed under vacuum and the orange solid residue dissolved in dichloromethane (ca. 5 mL) and transferred to an Al_2O_3 (neutral; activity grade I) chromatography column. Elution with a mixture hexane/diethyl ether (3:1) gave an orange band, which was collected and evaporated to give the desired compounds. Complex **6b** was obtained as the *Z* stereoisomer only. **6a:** yield 0.925 g (98%); IR (KBr) ν = 2049 cm^{-1} (C≡C); ^{31}P{^{1}H} (C_6D_6, 121.5 MHz) δ = 51.33 (s); ^{1}H (C_6D_6, 300 MHz) δ = 4.68 (d, 2H, J_{HH} = 2.1 Hz, H-1,3), 5.59 (t, 1H, J_{HH} = 2.1 Hz, H-2), 6.25 and 6.68 (m, 2H each one, H-4,7 and H-5,6), 6.73 (s, 1H, =CH), 6.86−8.21 (m, 40H, Ph); ^{13}C{^{1}H} (C_6D_6, 75.4 MHz) δ = 75.51(s, C-1,3), 96.28 (s, C-2), 110.26 (s, C-3a,7a), 115.81 (s, =CH), 116.36 (s, C_β), 123.79 and 126.46

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(s, C-4,7 and C-5,6), 123.96 (t, $^2J_{CP}$ = 24.2 Hz, Ru−C_α), 126.93−145.04 (m, Ph and =C). $RuC_{61}H_{48}P_2$ (944.0): calcd C 77.60, H 5.12; found C 77.01, H 5.20. **6b:** yield 0.556 g (62%); IR (KBr) ν = 2045 cm^{-1} (C≡C); $^{31}P\{^1H\}$ (C_6D_6, 121.5 MHz) δ = 51.88 (s); ^1H (C_6D_6, 300 MHz) δ = 3.30 (s, 3H, OCH_3), 4.75 (d, 2H, J_{HH} = 1.9 Hz, H-1,3), 5.72 (t, 1H, J_{HH} = 1.9 Hz, H-2), 6.34 and 6.69 (m, 2H each one, H-4,7 and H-5,6), 6.77 and 7.33 (d, 2H each one, J_{HH} = 8.7 Hz, 4-OMe-C_6H_4), 6.82 (d, 1H, J_{HH} = 13.0 Hz, =CH), 6.92−7.49 (m, 31H, Ph and =CH); $^{13}C\{^1H\}$ (C_6D_6, 75.4 MHz) δ = 55.42 (s, OCH_3), 75.71 (s, C-1,3), 96.19 (s, C-2), 110.22 (s, C-3a,7a), 114.55 and 132.51 (s, =CH), 115.02 and 127.20 (s, CH of 4-OMe-C_6H_4), 115.77 (s, C_β), 116.90 (t, $^2J_{CP}$ = 25.0 Hz, Ru−C_α), 123.83 and 126.63 (s, C-4,7 and C-5,6), 128.10−139.75 (m, Ph), 133.32 and 159.53 (s, C of 4-OMe-C_6H_4). $RuC_{56}H_{46}P_2O$ (897.9): calcd C 74.90, H 5.16; found C 73.98, H 5.22.

Synthesis of [Ru{=C=C(H)CH=CR^{1}R^2}(η^5-C_9H_7)(PPh_3)$_2$]-[BF_4] (R^1 = R^2 = Ph (7a); R^1 = 4-OMe-C_6H_4, R^2 = H [(*Z*)-7b]; R^1 = H, R^2 = 4-NO_2-C_6H_4 [(*E*, *Z*)-7c]). A solution of HBF_4·Et_2O (1.9 mL, 1.5 mmol) in diethyl ether (10 mL) was added dropwise, at −20 °C, to a solution of the corresponding σ-enynyl complex **6a**−**c** (1 mmol) in THF (30 mL). The reaction mixture was gradually warmed to room temperature and then concentrated (ca. 5 mL). Addition of diethyl ether (100 mL) gave a brown solid, which was washed with diethyl ether (3 × 20 mL) and vacuum-dried. Quantities used: **6a**, 0.944 g (1 mmol); **6b**, 0.898 g (1 mmol); **6c**, 0.913 g (1 mmol). **7a:** yield 1.011 g (98%); IR (KBr) ν = 1059 cm^{-1} (BF_4^-); Λ (acetone, 20 °C) = 127 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$ ($CDCl_3$, 121.5 MHz) δ = 39.34 (s); ^1H ($CDCl_3$, 300 MHz) δ = 5.22 (dt, 1H, J_{HH} = 10.6 Hz, $^4J_{HP}$ = 1.7 Hz, Ru=C=CH), 5.50 (d, 2H, J_{HH} = 2.4 Hz, H-1,3), 5.98 (m, 3H, H-2 and H-4,7 or H-5,6), 6.51 (d, 1H, J_{HH} = 10.6 Hz, =CH), 6.79−7.52 (m, 42H, Ph and H-4,7 or H-5,6); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 83.92 (s, C-1,3), 98.62 (s, C-2), 109.37 and 115.11 (s, C_β and =CH), 115.22 (s, C-3a,7a), 122.94 (s, C-4,7 or C-5,6), 127.12−141.30 (m, Ph, =C and C-4,7 or C-5,6), 358.48 (t, $^2J_{CP}$ = 16.8 Hz, Ru=C_α). $RuC_{61}H_{49}F_4P_2B$ (1031.8): calcd C 71.00, H 4.78; found C 70.82, H 4.70. **7b:** yield 0.945 g (88%) as pure (*Z*) product; IR (KBr) ν = 1060 cm^{-1} (BF_4-); Λ (acetone, 20 °C) = 117 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$ ($CDCl_3$, 121.5 MHz) δ = 39.86 (s); ^1H ($CDCl_3$, 300 MHz) δ = 3.78 (s, 3H, OCH_3), 5.37 (d, 1H, J_{HH} = 9.1 Hz, Ru=C=CH), 5.50 (d, 2H, J_{HH} = 2.6 Hz, H-1,3), 5.82 (t, 1H, J_{HH} = 2.6 Hz, H-2), 5.93−6.06 (m, 4H, =CH and H-4,7 or H-5,6), 6.75−7.49 (m, 36H, Ph, 4-OMe-C_6H_4 and H-4,7 or H-5,6); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 55.30 (s, OCH_3), 84.18 (s, C-1,3), 98.88 (s, C-2), 108.50 and 125.01 (s, =CH), 113.86, 123.00, 127.28 and 130.27 (s, C-4,7, C-5,6 and CH of 4-OMe-C_6H_4), 115.23 (s, C-3a,7a), 118.13 (s, C_β), 128.60−133.53 (m, Ph), 129.61 and 158.96 (s, C of 4-OMe-C_6H_4), 360.22 (t, $^2J_{CP}$ = 16.4 Hz, Ru=C_α). $RuC_{56}H_{47}F_4P_2BO$ (1074.5): calcd C 68.23, H 4.80; found C 68.35, H 4.72. **7c:** yield 0.730 g (73%) as a 2:1 (*E*/*Z*) mixture; IR (KBr) ν = 1062 cm^{-1} (BF_4^-); Λ (acetone, 20 °C) = 116 Ω^{-1} cm^2 mol^{-1}. $RuC_{55}H_{44}F_4O_2P_2BN$ (1000.7): calcd C 66.00, H 4.43, N 1.40; found C 65.41, H 4.22, N 1.52. (*E* isomer): $^{31}P\{^1H\}$ ($CDCl_3$, 121.5 MHz) δ = 38.47 (s); ^1H ($CDCl_3$, 300 MHz) δ = 5.58 (m, 3H, H-1,3 and H-2), 5.91 (m, 2H, H-4,7 or H-5,6), 6.25 (d, 1H, J_{HH} = 10.2 Hz, Ru=C=CH), 6.81−7.50 (m, 34H, Ph, =CH and H-4,7 or H-5,6), 7.05 and 8.03 (d, 2H each one, J_{HH} = 8.8 Hz, 4-NO_2-C_6H_4); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 83.85 (s, C-1,3), 99.33 (s, C-2), 115.89 (s, C-3a,7a), 117.71 and 117.84 (s, =CH and C_β), 122.60−133.54 (m, Ph, C-4,7, C-5,6, =CH and CH of 4-NO_2-C_6H_4), 143.70 and 145.81 (s, C of 4-NO_2-C_6H_4), 356.50 (t, $^2J_{CP}$ = 16.5 Hz, Ru=C_α). (*Z* isomer): $^{31}P\{^1H\}$ ($CDCl_3$, 121.5 MHz) δ = 38.77 (s); ^1H ($CDCl_3$, 300 MHz) δ = 5.58 (m, 3H, H-1,3 and H-2), 5.72 (d, 1H, J_{HH} = 11.2 Hz, =CH), 6.10 (m, 3H, =CH and H-4,7 or H-5,6), 6.30 (d, 1H, J_{HH} = 10.2 Hz, Ru=C=CH), 6.81−7.50 (m, 34H, Ph, 4-NO_2-$C_6H_2H_2$ and H-4,7 or H-5,6), 8.15 (d, 2H, J_{HH} = 8.7 Hz, 4-NO_2-$C_6H_2H_2$); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 83.85 (s, C-1,3), 99.49 (s, C-2), 113.13 and 116.69 (s, =CH and C_β), 115.89 (s, C-3a,-7a), 122.60−133.54 (m, Ph, C-4,7, C-5,6, =CH and CH of 4-NO_2-C_6H_4), 143.58 and 145.81 (s, C of 4-NO_2-C_6H_4), 355.70 (t, $^2J_{CP}$ = 16.2 Hz, Ru=C_α).

Synthesis of HC≡CCH=CR^{1}R^2 (R^1 = R^2 = Ph (8a); R^1 = H, R^2 = 4-OMe-C_6H_4 (8b), 4-NO_2-C_6H_4 (8c), Fc (8d)). A solution of the corresponding vinylidene complex **7a**−**d** (1 mmol) in acetonitrile (50 mL) was heated under reflux for 90 min. The solution was then evaporated to dryness, and the resulting solid residue was extracted with diethyl ether (ca. 150 mL) (a yellow solid containing mainly the complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] remains insoluble). The extract was evaporated to dryness and the crude product was purified by column chromatography on silica gel with hexane as eluent. Enynes **8b**−**d** were obtained as the *E* stereoisomer only. Quantities used: **7a**, 1.031 g (1 mmol); **7b**, 1.074 g (1 mmol); **7c**, 1.000 g (1 mmol); **7d**, 1.063 g (1 mmol). **8a:** yield 0.157 g (77%) as a colorless oil; IR (Nujol) ν = 2092 cm^{-1} (C≡C); ^1H ($CDCl_3$, 300 MHz) δ = 3.02 (d, 1H, J_{HH} = 2.5 Hz, ≡CH), 6.03 (d, 1H, J_{HH} = 2.5 Hz, =CH), 7.27−7.48 (m, 10H, Ph); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 81.43 (s, ≡CH), 82.39 (s, ≡C), 105.93 (s, =CH), 127.92, 127.94, 128.27, 128.50 and 129.88 (s, CH of Ph), 138.78 and 141.04 (s, C of Ph), 154.44 (s, =C); HRMS *m*/*z* calcd for $C_{16}H_{12}$ (found) M$^+$= 204.094289 (204.093900). **8b:** yield 0.094 g (60%) as a colorless oil; IR (Nujol) ν = 2101 cm^{-1} (C≡C); ^1H ($CDCl_3$, 300 MHz) δ = 3.03 (d, 1H, J_{HH} = 2.1 Hz, ≡CH), 3.83 (s, 3H, OCH_3), 6.00 (dd, 1H, J_{HH} = 16.3 Hz, J_{HH} = 2.1 Hz, =CH), 7.00 (d, 1H, J_{HH} = 16.3 Hz, =CH), 6.87 and 7.34 (d, 2H each one, J_{HH} = 8.7 Hz, 4-OMe-C_6H_4); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 55.24 (s, OCH_3), 78.42 (s, ≡CH), 83.25 (s, ≡C), 104.46 and 142.67 (s, =CH), 114.07 and 127.67 (s, CH of 4-OMe-C_6H_4), 128.64 and 160.21 (s, C of 4-OMe−C_6H_4); HRMS *m*/*z* calcd for $C_{11}H_{10}O$ (found) M$^+$= 158.073165 (158.073804). **8c:** yield 0.119 g (69%) as a yellow oil; IR (Nujol) ν = 2106 cm^{-1} (C≡C); ^1H ($CDCl_3$, 300 MHz) δ = 3.22 (d, 1H, J_{HH} = 2.4 Hz, ≡CH), 6.31 (dd, 1H, J_{HH} = 16.3 Hz, J_{HH} = 2.4 Hz, =CH), 7.09 (d, 1H, J_{HH} = 16.3 Hz, =CH), 7.54 and 8.22 (d, 2H each one, J_{HH} = 7.8 Hz, 4-NO_2-C_6H_4); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 81.86 (s, ≡CH), 89.92 (s, ≡C), 111.82 and 140.46 (s, =CH), 124.04 and 168.47 (s, C of 4-NO_2-C_6H_4), 124.10 and 126.82 (s, CH of 4-NO_2-C_6H_4); HRMS *m*/*z* calcd for $C_{10}H_7O_2N$ (found) M$^+$= 173.047678 (173.048423). **8d:** yield 0.170 g (72%) as a red oil; IR (Nujol) ν = 2100 cm^{-1} (C≡C); ^1H ($CDCl_3$, 300 MHz) δ = 2.80 (d, 1H, J_{HH} = 2.1 Hz, ≡CH), 3.86 (s, 5H, C_5H_5), 3.97 and 4.03 (m, 2H each one, C_5H_4), 5.70 (dd, 1H, J_{HH} = 16.1 Hz, J_{HH} = 2.1 Hz, =CH), 6.78 (d, 1H, J_{HH} = 16.1 Hz, =CH); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 67.31 and 69.93 (s, CH of C_5H_4), 69.67 (s, C_5H_5), 78.35 (s, C of C_5H_4), 81.49 (s, ≡C), 83.94 (s, ≡CH), 104.25 and 142.75 (s, =CH); HRMS *m*/*z* calcd for $FeC_{14}H_{12}$ (found) M$^+$= 236.028839 (236.028878).

Synthesis of [Ru{C≡CC(C≡CH)$C_{13}H_{20}$}(η^5-C_9H_7)(PPh_3)$_2$] (10). A large excess (ca. 1:10) of NaC≡CH (suspension in xylene) was added at −20 °C to a solution of the allenylidene complex **9** (1.098 g, 1 mmol) in THF (50 mL). Upon warming to room temperature, the solvent was removed in vacuo, and the resulting orange solid residue dissolved in dichloromethane (ca. 5 mL) and transferred to an Al_2O_3 (neutral; activity grade I) chromatography column. Elution with a mixture of hexane/diethyl ether (4:1) gave an orange band, which was collected and evaporated to give complex **10**: yield 0.597 g (61%); IR (KBr) ν = 2082 and 2275 cm^{-1} (C≡C); $^{31}P\{^1H\}$ (C_6D_6, 121.5 MHz) δ = 50.52 (d, $^2J_{PP}$ = 31.0 Hz, PPh_3), 52.98 (d, $^2J_{PP}$ = 31.0 Hz, PPh_3); ^1H (C_6D_6, 300 MHz) δ = 1.46−1.80 (m, 14H, CH_2), 2.02 (s, 1H, ≡CH), 2.26−2.52 (m, 3H, CH_2 and CH), 2.68 (m, 1H, CH), 4.73 and 4.77 (m, 1H each one, H-1 and H-3), 5.68 (m, 1H, H-2), 5.82(dd, 1H, J_{HH} = 10 Hz, J_{HH} = 6.0 Hz, =C*H*CH), 6.02 (d, 1H, J_{HH} = 10 Hz, =CH), 6.32 and 6.66 (m, 2H each one, H-4, H-5, H-6 and H-7), 6.29−7.53 (m, 30 H, Ph); $^{13}C\{^1H\}$ (C_6D_6, 75.4 MHz) δ = 17.86, 22.83, 23.02, 24.92, 26.40, 26.97, 36.86 and 37.54 (s, CH_2), 38.49 and 39.49 (s, C), 42.68 and 42.91 (s, CH), 71.20 (s, ≡CH), 73.75 (d, $^2J_{CP}$ = 7.6 Hz, C-1

or C-3), 74.56 (d, $^2J_{CP}$ = 7.4 Hz, C-1 or C-3), 89.41 (vt, $^2J_{CP}$ = $^2J_{CP'}$ = 24.9 Hz, Ru−C_α), 90.48 (s, ≡C), 91.15 (s, C-2), 109.25 and 109.98 (s, C-3a and C-7a), 113.65 (s, C_β), 123.15, 123.45, 125.46, 125.87 and 126.42 (s, C-4, C-5, C-6, C-7 and =*C*HCH or =CH), 127.18−139.64 (m, Ph), 138.54 (s, =*C*HCH or =CH). $RuC_{63}H_{58}P_2$ (978.7): calcd C 77.36, H 5.98; found C 77.32, H 6.33.

Synthesis of [Ru{=C=C(H)C(C≡CH)$C_{13}H_{20}$}(η^5-C_9H_7)(PPh_3)$_2$] [BF_4] (11). A solution of the σ-alkynyl complex **10** (0.979 g, 1 mmol) in diethyl ether (100 mL), at −20 °C, was treated dropwise by strong stirring with a diluted solution of HBF_4·Et_2O in diethyl ether. Immediately, an insoluble solid precipitated, but the addition was continued until no further solid was formed. The solution was then decanted and the brown solid washed with diethyl ether (3 × 20 mL) and vacuum-dried: yield 0.842 g (79%); IR (KBr) ν = 1057 cm^{-1} (BF_4^-), 2197 cm^{-1} (C≡C); Λ (acetone, 20 °C) = 108 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$ (CD_2Cl_2, 121.5 MHz) δ = 39.25 (d, $^2J_{PP}$ = 23.5 Hz, PPh_3), 40.62 (d, $^2J_{PP}$ = 23.5 Hz, PPh_3); ^1H (CD_2Cl_2, 300 MHz) δ = 1.38−2.35 (m, 18H, CH_2 and CH), 2.54 (s, 1H, ≡CH), 4.29 (vt, 1H, $^4J_{HP}$ = $^4J_{HP'}$ = 2.3 Hz, Ru=C=CH), 5.32−5.70 (m, 5H, H-1, H-2, H-3, =C*H*CH and =CH), 6.01 and 6.25 (m, 2H each one, H-4, H-5, H-6 and H-7), 6.64−7.50 (m, 30 H, Ph); $^{13}C\{^1H\}$ (CD_2Cl_2, 75.4 MHz) δ = 17.35, 22.79, 24.98, 25.92, 26.39, 36.57 and 37.85 (s, CH_2), 38.69 and 39.39 (s, C), 42.00 and 43.93 (s, CH), 75.24 (s, ≡CH), 82.71 (d, $^2J_{CP}$ = 5.9 Hz, C-1 or C-3), 84.60 (d, $^2J_{CP}$ = 5.7 Hz, C-1 or C-3), 89.78 (s, ≡C), 98.45 (s, C-2), 113.04 (s, C-3a and C-7a), 119.07 (s, C_β), 122.26, 122.54, 125.14 and 125.25 (s, C-4, C-5, C-6 and C-7), 128.81−138.23 (m, Ph, =*C*HCH and =CH), 344.26 (vt, $^2J_{CP}$ = $^2J_{CP'}$ = 15.7 Hz, Ru=C_α). $RuC_{63}H_{59}F_4P_2B$ (1065.9): calcd C 70.98, H 5.58; found C 70.21, H 5.69.

Synthesis of (HC≡C)$_2$C$C_{13}H_{20}$ (12). A solution of complex **11** (1.066 g, 1 mmol) in acetonitrile (25 mL) was heated at 60 °C for 2 h. The solution was then evaporated to dryness, and the resulting yellow residue was extracted with diethyl ether (ca. 150 mL) (a yellow solid containing mainly the complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] remains insoluble). The extract was evaporated to dryness, and the crude product was purified by column chromatography on silica gel with hexane as eluent. Evaporation of the solvent gave **12** as a colorless oil: yield 0.166 g (70%); IR (Nujol) ν = 2113 cm^{-1} (C≡C); ^1H ($CDCl_3$, 300 MHz) δ = 1.23−1.71 (m, 13H, CH_2), 2.02−2.21 (m, 3H, CH_2), 2.22 and 2.50 (s, 1H each one, ≡CH), 2.36 and 2.61 (m, 1H each one CH), 5.56 (dd, 1H, J_{HH} = 10.2 Hz, J_{HH} = 6.2 Hz, =C*H*CH), 5.74 (d, 1H, J_{HH} = 10.2 Hz, =CH); $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz) δ = 16.77, 21.83, 22.35, 23.80, 25.04, 26.05, 35.89 and 36.88 (s, CH_2), 35.36 and 38.76 (s, C), 40.57 and 41.43 (s, CH), 69.88 and 72.55 (s, ≡CH), 87.00 and 89.29 (s, ≡C), 124.24 and 138.68 (s, =*C*HCH and =CH); HRMS *m*/*z* calcd for $C_{18}H_{22}$ (found) M^+= 238.172151 (238.172233).

Computational Details. Ab initio calculations were carried out with the Gaussian 94 set of programs[26] within the framework of DFT at the B3LYP level.[27] 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.[28] The associated double-ζ basis set of P atoms was augmented by a d function.[29] The other atoms were represented by a 6-31G(d,p) basis set.[30] PH_3 and indenyl hydrogen atoms were represented at the STO-3G level.[31] In our calculations we replace the PPh_3 ligand and the monosubtituted acetylene by PH_3 and HC≡CH, respectively.

Full geometry optimization and frequency calculations were performed with C_s symmetry without any further symmetry constraints. A vibrational analysis was performed for the three transition states **B**, **C,** and **D** to confirm that they have only one imaginary frequency, while for **A** and **E** no imaginary frequency was found. The transition-state structures were relaxed after introducing small perturbations to ensure that they are actually connected to the corresponding reactants and the products.

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