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Stereoselective synthesis of chiral terminal (*E*)-1,3-enynes derived from the aldehydes (1*R*)-(−)-myrtenal and (*S*)-(−)-perillaldehyde using the alkynyl–phosphonio complex $[Ru\{C{\equiv}CCH_2(PPh_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ as synthon

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

Treatment of alkynyl–phosphonio complex $[Ru\{C{\equiv}CCH_2(PPh_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**1**) with Li^nBu gives the ylide–alkynyl derivative $[Ru\{C{\equiv}CC(H){=}PPh_3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**2**), which reacts in situ with the optically active aldehydes (1*R*)-(−)-myrtenal and (*S*)-(−)-perillaldehyde via a Wittig process to afford σ-alkynyl complexes $[Ru\{C{\equiv}CC(H){=}C(H)C_9H_{13}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **3** and **7** respectively. Whereas compound **3** has been obtained stereoselectively as the pure *E* stereoisomer, complex **7** has been synthesized as a mixture of the corresponding *E* and *Z* isomers (ca. 4:1 ratio). Protonation of **3** and **7** with $HBF_4{\cdot}Et_2O$ yields the cationic alkenyl–vinylidene derivatives (*E*)-$[Ru\{{=}C{=}C(H)C(H){=}C(H)C_9H_{13}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**4**, **8**), which react with acetonitrile at reflux to afford the nitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**6**), and the corresponding terminal 1,3-enynes (*E*)-$HC{\equiv}CC(H){=}C(H)C_9H_{13}$ **5** and **9** respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkynyl complexes; Allenylidene complexes; 1,3-Enynes; Indenyl; Ruthenium; Vinylidene complexes; Wittig reactions

1. Introduction

One of many expanding areas of interest in organometallic chemistry is the selective formation of carbon–carbon and carbon–heteroatom bonds mediated by transition-metal compounds [1]. In this context, allenylidene complexes $[M]{=}C{=}C{=}CR_2$ have attracted a great deal of attention during the last decade as a new type of organometallic precursor showing a rich and versatile reactivity in stoichiometric processes [2]. In addition, the catalytic activity of allenylidene complexes, i.e. $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}p\text{-cymene})(PR_3)][PF_6]$ ($PR_3{=}PCy_3$, P^iPr_3) or $[RuCl_2({=}C{=}C{=}CPh_2)(PCy_3)(L)]$ ($L = PCy_3$, 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene), in ring-closing metathesis (RCM) of olefins has recently been discovered [3]. The rapid growth of this chemistry stems mainly from the facile synthetic accessibility of these cumulenylidene derivatives based in the conversion of propargylic alcohols $HC{\equiv}CC(OH)R_2$ into $C{=}C{=}CR_2$, which proceeds through elimination of water in the presence of an electron-rich transition-metal center [4]. The chemical behavior of these species is now well established both experimentally [2] and theoretically [5], pointing out that the C_α and C_γ atoms of the unsaturated chain show a marked electron-deficient character while the C_β atom is a nucleophilic site. Significantly, nucleophilic attacks dominate the reactivity of allenylidene complexes as compared to the electrophilic additions giving rise to an useful synthetic route of σ-alkynyl $[M]{-}C{\equiv}C{-}C(Nu)R_2$ or σ-allenyl $[M]{-}C(Nu){=}C{=}CR_2$ species. The regioselectivity of these nucleophilic additions seems to be mainly controlled by the electronic and/or steric properties of the metallic fragment [2].

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As part of our ongoing work dealing with the chemistry of cationic indenyl–ruthenium(II) allenylidene derivatives $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}1,2,3\text{-}R_3C_9H_4)LL']^+$ (L, L′ = phosphine or CO; R = H, Me), we have shown that the regioselectivity of the nucleophilic attacks can be easily controlled by the appropriate selection both of the substituents on the cumulenic chain and of the ancillary ligands [6]. Thus, those complexes containing the $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ moiety add regioselectively a large variety of neutral and anionic nucleophiles at the γ-position to afford functionalized σ-alkynyl species $[Ru\{C{\equiv}CCR^1R^2(Nu)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^{n+}$ $(n = 0, 1)$ [6]. The cationic alkynyl–phosphonio complexes $[Ru\{C{\equiv}CCH(R^1)(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = H, $PR_3 = PPh_3$, R^1 = Ph, $PR_3 = PMe_3$) have proven to be of particular interest in both organometallic and organic synthesis, since they are efficient substrates for Wittig-type reactions and give excellent yields of neutral σ-enynyl complexes of general formula $[Ru\{C{\equiv}CC(R^1){=}CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ [6g,h,7]. Subsequent protonation of these enynyl species proceeds regioselectively at the C_β atom of the alkynyl group, leading to the formation of unprecedented alkenyl–vinylidene derivatives $[Ru\{{=}C{=}C(H)C(R^1){=}CR^2R^3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ [6g,h,7]. More recently, we have found that these derivatives are able to undergo demetalation reactions by heating in acetonitrile, affording quantitatively the corresponding terminal 1,3-enynes $HC{\equiv}CC(R^1){=}CR^2R^3$ and the nitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$. This process, which discloses a new entry for the synthesis of terminal 1,3-enynes, proceeds through the initial tautomerization at the ruthenium center of the η^1-vinylidene group to the η^2-coordinated alkyne and subsequent elimination of the organic fragment from the metal by exchange with acetonitrile [6h].

In order to extend the scope of this synthetic route to new 1,3-enynes, we have examined Wittig-type reactions of the synthon alkynyl–phosphonio complex $[Ru\{C{\equiv}CCH_2(PPh_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ with the optically active aldehydes (1*R*)-(−)-myrtenal (**A**) and (*S*)-(−)-perillaldehyde (**B**). In this paper we report that these reactions proceed stereoselectively and that the demetalation process is very efficient, giving rise to the synthesis of the novel chiral terminal (*E*)-1,3-enynes **C** and **D** (Chart 1).

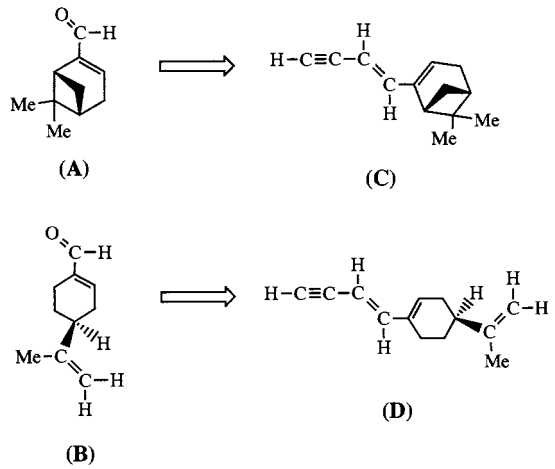
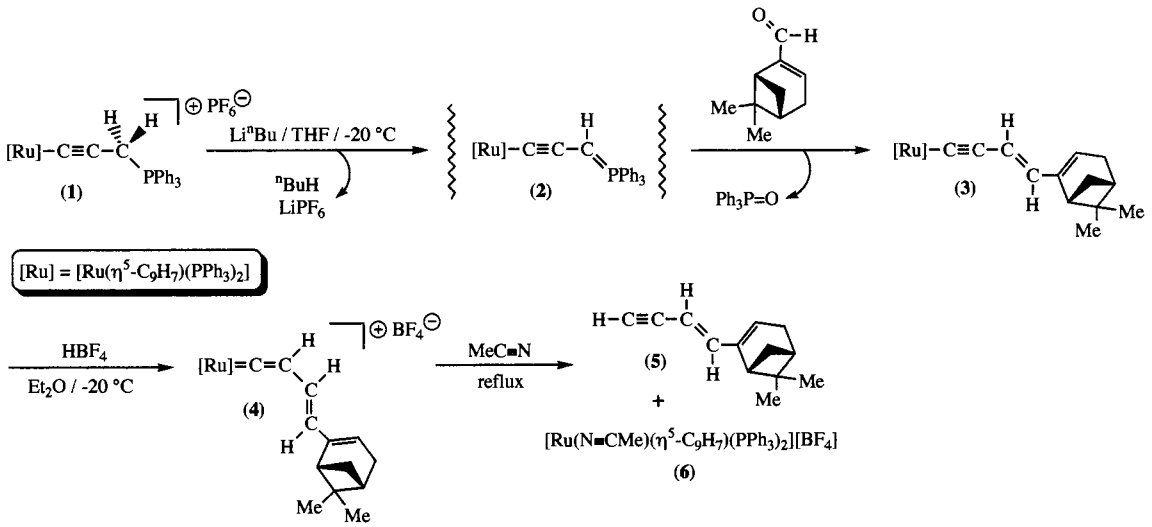


Chart 1.

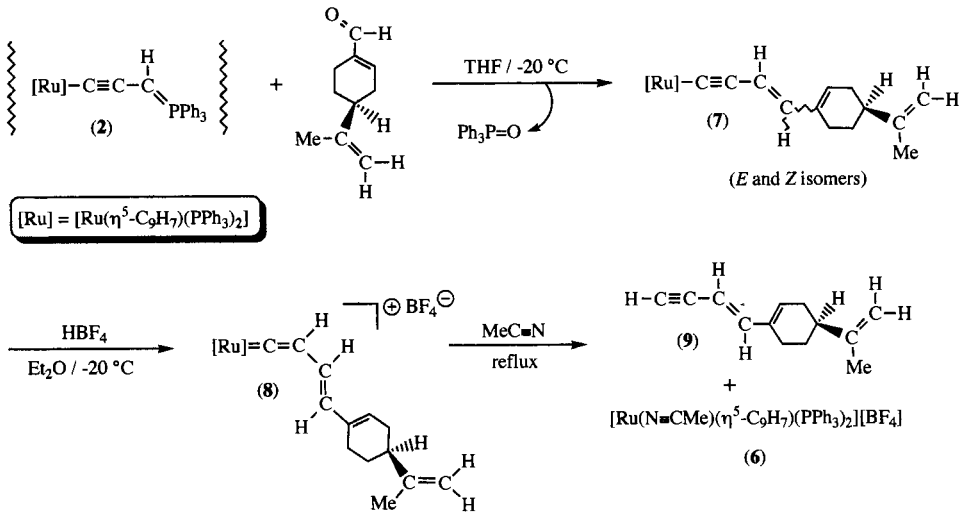
2. Results and discussion

2.1. Transformation of (1R)-(−)-myrtenal into the terminal 1,3-enyne (E)-HC≡CC(H)=C(H)C_9H_{13} (5)

The highly unstable ylide–alkynyl derivative $[Ru\{C{\equiv}CC(H){=}PPh_3\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**2**), obtained in situ by treatment of a THF solution of the alkynyl–



Scheme 1.



Scheme 2.

phosphonio complex [Ru{C≡CCH$_2$(PPh$_3$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**1**) [6g] with one equivalent of Li^{n}Bu at −20°C, reacts stereoselectively with the chiral aldehyde (1*R*)-(−)-myrtenal to afford the optically active σ-enynyl complex (*E*)-[Ru{C≡CC(H)=C(H)C$_9$H$_{13}$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (**3**) (87% yield) (Scheme 1). The unequivocal characterization of **3** was achieved by means of standard spectroscopic techniques (IR and ^{31}P{^{1}H}-, ^{1}H-, and ^{13}C{^{1}H}-NMR), as well as elemental analyses (see Section 4 for details). In particular, the presence of the enynyl moiety was identified on the basis of: (i) (IR) the expected ν(C≡C) absorption band at 2052 cm^{-1}, and (ii) (^{13}C{^{1}H}-NMR) typical resonances for the Ru–C$_\alpha$, C$_\beta$ and olefinic CH=CH carbon atoms, which appear at δ 116.03 ppm (t, $^2J_{CP}$ = 24.9 Hz), 115.95 ppm (s), and 112.98 ppm (s) and 134.89 ppm (s) respectively. It is worth mentioning that the proposed *E* stereochemistry for the novel carbon–carbon double bond has been ascertained from the ^{1}H-NMR spectrum, which shows a mutual coupling constant for the olefinic protons of J_{HH} = 16.1 Hz. The high stereoselectivity observed in this reaction, which contrasts with our previous results using other aldehydes, i.e. MeCHO, 4-R–C$_6$H$_4$CHO, PhC≡CCHO, (*E*)–RCH=CHCHO [6g,h,7], can be rationalized on the basis of the steric demand required by the bulky bicyclic unit.

In agreement with the strong nucleophilic character of the C$_\beta$ of an σ-enynyl ligand [7b], treatment of **3** with HBF$_4$·Et$_2$O in diethyl ether at −20°C gives the cationic alkenyl–vinylidene derivative (*E*)-[Ru{=C=C(H)C(H)=C(H)C$_9$H$_{13}$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**4**), which was isolated as an air-stable brown solid in 93% yield (Scheme 1). The formation of a vinylidene moiety is strongly supported by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy (see Section 4 for details). Thus, the most remarkable feature in the ^{1}H-NMR spectrum is the presence of a doublet signal (J_{HH} = 9.7 Hz) at δ 5.30 ppm attributed to the acidic vinylidene proton Ru=C=CH. No isomerization of the CH=CH double bond takes place in the course of this protonation process, since complex **4** has also been obtained as the pure *E* stereoisomer (J_{HH} = 15.0 Hz). The ^{13}C{^{1}H}-NMR spectrum shows the characteristic low-field triplet resonance ($^2J_{CP}$ = 17.1 Hz) for the carbenic Ru=C$_\alpha$ carbon atom at δ 361.56 ppm, whereas the C$_\beta$ and olefinic CH=CH carbon nuclei resonate as singlets at δ 118.55 ppm, and 107.32 and 130.68 ppm respectively.

As expected, complex **4** reacts rapidly with refluxing acetonitrile, resulting in the quantitative elimination of the 1,3-enyne (*E*)-HC≡CC(H)=C(H)C$_9$H$_{13}$ (**5**) and the formation of the cationic nitrile complex [Ru(N≡CMe)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**6**) [6h] (Scheme 1). Compound **5** has been easily purified from the reaction mixture by column chromatography on silica gel (88% yield) and characterized by mass spectrometry and spectroscopic methods (see Section 4). Thus, the IR spectrum shows the expected ν(C≡C) absorption at 2111 cm^{-1}. The acetylenic proton of the (*E*)-HC≡CCH=CH fragment resonates, in the ^{1}H-NMR spectrum, as a doublet at δ 2.98 ppm (J_{HH} = 1.7 Hz), while the olefinic protons appear at lower fields (δ 5.44 ppm (dd, J_{HH} = 16.3 Hz, J_{HH} = 1.7 Hz) and 6.69 ppm (d, J_{HH} = 16.3 Hz)). The ^{13}C{^{1}H}-NMR spectrum is also in accord with the proposed formulation, showing singlet resonances assigned to the C≡CH carbon nuclei at δ 78.48 (≡CH) and 83.67 ppm (≡C).

2.2. Transformation of (S)-(−)-perillaldehyde into the terminal 1,3-enyne (E)-HC≡CC(H)=C(H)C$_9$H$_{13}$ (9)

The stereoselective access to the chiral 1,3-enyne **5** prompted us to study the reactivity of the ylide–alkynyl complex **2** towards other optically active carbonyl com-

pounds. Thus, under analogous conditions, **2** reacts with (*S*)-(−)-perillaldehyde to give the σ-enynyl derivative [Ru{C≡CC(H)=C(H)C_9H_{13}}(η^5-C_9H_7)-(PPh_3)$_2$] (**7**) (82% yield) (Scheme 2). In contrast to **3**, compound **7** was obtained as a non-separable mixture of the *E* (J_{HH} = 15.7 Hz) and *Z* (J_{HH} = 10.3 Hz) stereoisomers in ca. 4:1 ratio. This result seems to indicate that the steric hindrance between the triphenylphosphine ancillary ligands and the C_δ substituents of the enynyl group decreases when the bicyclic fragment of **3** is replaced by a smaller cyclohexenyl group in **7**, allowing, therefore, the formation of both stereoisomers. Complexes (*E*)-**7** and (*Z*)-**7** have been characterized by microanalysis and IR and NMR ($^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$) spectroscopy, with all data being fully consistent with the proposed formulations (see Section 4). It is worth mentioning that the assignment of the resonances of both isomers has been carried out on the basis of their relative integration values. Surprisingly, the addition of $HBF_4{\cdot}Et_2O$ to a solution of **7**, in diethyl ether at −20°C, affords only the cationic alkenyl–vinylidene derivative (*E*)-[Ru{=C=C(H)C(H)=C(H)C_9H_{13}}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**8**) (89% yield) (Scheme 2). Apparently, the protonation of the 4:1 mixture of the stereoisomers **7** promotes the isomerization of the resulting *Z* vinylidene complex into the thermodynamically stable *E* isomer. This is probably due to a higher steric hindrance between the aryl groups of the phosphine ligands and the C_δ substituents in the vinylidene complex **8** compared with the precursor alkynyl derivative **7**. Spectroscopic data are in agreement with the proposed structure being comparable to those found for the analogous alkenyl–vinylidene derivative **4** (see Section 4). In particular: (i) the [Ru]=C=CH–CH=CH proton resonances appear at δ 5.30 ppm (d, J_{HH} = 9.9 Hz), 5.59 ppm (dd, J_{HH} = 15.4 Hz, J_{HH} = 9.9 Hz) and 5.77 ppm (d, J_{HH} = 15.4 Hz) respectively; (ii) the C_α and C_β carbons of the vinylidene group resonate at δ 360.95 ppm (t, $^2J_{CP}$ = 16.9 Hz) and 118.53 ppm (s) respectively.

The demetalation of complex **8** by reaction with acetonitrile at reflux proceeds cleanly and, besides the nitrile complex **6**, gives the novel optically active enyne (*E*)-HC≡CC(H)=C(H)C_9H_{13} (**9**), which was isolated after column chromatography as a colorless oil in 79% yield (Scheme 2). The most relevant spectroscopic features of **9** are: (i) (^{1}H-NMR) the expected doublet resonance acetylenic proton at δ 2.95 ppm (J_{HH} = 2.2 Hz), as well as the signals for the CH=CH unit (δ 5.44 (dd, J_{HH} = 16.1 Hz, J_{HH} = 2.2 Hz) and 6.69 ppm (d, J_{HH} = 16.1 Hz)), and (ii) ($^{13}C\{^1H\}$-NMR) typical resonances for the HC≡CCH=CH carbon atoms, which appear at δ 77.96 (≡CH), 83.53 (≡C), 103.21 (≡C̲CH=CH) and 146.15 ppm (≡CCH=C̲H).

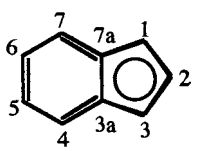
3. Conclusions

Continuing with our interest in studying the synthetic applications of allenylidene indenyl–ruthenium(II) complexes in organic chemistry, in this work we describe the stereoselective synthesis of the unprecedented optically active enynes (*E*)-HC≡CC(H)=C(H)C_9H_{13} **5** and **9**, which have been prepared using our previously reported methodology for the synthesis of terminal 1,3-enynes. These results prove that this synthetic methodology starting from alkynyl–phosphonio derivative [Ru{C≡CCH_2(PPh_3)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**), readily obtained from the allenylidene complex [Ru(=C=C=CH_2)(η^5-C_9H_7)(PPh_3)$_2$][PF_6], can be applied successfully to chiral carbonyl substrates, as has been exemplified by using the commercially available aldehydes (1*R*)-(−)-myrtenal and (*S*)-(−)-perillaldehyde.

4. Experimental

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, with the exception of (S)-(−)-perillaldehyde, which was distilled before use. Solvents were dried by standard methods and distilled under nitrogen before use. Alkynyl–phosphonio complex [Ru{C≡CCH_2-(PPh_3)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**) [6h] was prepared by following the method reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The C and H 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 reported. Abbreviations used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet.

The numbering for the indenyl skeleton is as follows:



4.1. Synthesis of σ-enynyl complex (*E*)-[Ru{C≡CC(H)=C(H)C_9H_{13}}(η^5-C_9H_7)(PPh_3)$_2$] (**3**)

Li^{n}Bu (1.6 M in hexane; 0.526 ml, 0.843 mmol) was added at −20°C to a solution of complex [Ru{C≡CCH_2(PPh_3)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**) (1 g, 0.843 mmol) in THF (40 ml). The reaction mixture was

stirred for 15 min. and (1*R*)-(−)-myrtenal (0.152 ml, 1 mmol) was then added. Upon warming to room temperature (r.t), the solution was stirred for 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 hexane/diethyl ether (3/1) gave a yellow band, which was collected and evaporated to dryness to give complex **3** as a yellow solid. Yield: 87% (0.669 g); Anal. Found: C, 76.09; H, 5.84. Calc. for $C_{58}H_{52}P_2Ru$ (912.066): C, 76.38; H, 5.74%. IR (KBr, cm^{-1}): 2052 ν(C≡C); $^{31}P\{^1H\}$-NMR (C_6D_6) δ 51.85 (br) ppm; ^1H-NMR (C_6D_6) δ 0.95 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.32 (d, 1H, $J_{HH} = 8.7$ Hz, CH_2), 2.05 (m, 1H, CH_2), 2.36–2.73 (m, 4H, CH_2 and CH), 4.71 (br, 2H, H-1 and H-3), 5.47 (br, 1H, H-2), 5.64 (s, 1H, C=CH), 6.34 and 6.68 (m, 2H each one, H-4, H-5, H-6 and H-7), 6.37 and 6.62 (d, 1H each one, $J_{HH} = 16.1$ Hz, CH=CH), 6.90–7.46 (m, 30H, Ph) ppm; $^{13}C\{^1H\}$-NMR (C_6D_6) δ 21.80 and 27.26 (s, CH_3), 32.39 and 32.98 (s, CH_2), 38.61 (s, $\underline{C}(CH_3)_2$), 42.17 and 42.26 (s, CH), 75.63 (s, C-1 and C-3), 96.24 (s, C-2), 110.12 and 110.33 (s, C-3a and C-7a), 112.98 (s, ≡C–$\underline{C}$H=CH), 115.95 (s, C_β), 116.03 (t, $^2J_{CP} = 24.9$ Hz, Ru–C_α), 120.13 (s, C=$\underline{C}$H), 123.78, 123.92, 126.49 and 126.60 (s, C-4, C-5, C-6 and C-7), 134.89 (s, ≡C–CH=$\underline{C}$H), 128.19–140.04 (m, Ph), 148.67 (s, $\underline{C}$=CH) ppm. $\Delta\delta$(C-3a,7a) = −20.47 ppm.

4.2. Synthesis of alkenyl–vinylidene complex (*E*)-[Ru{=C=C(H)C(H)=C(H)C_9H_{13}}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (4)

A solution of the σ-enynyl complex **3** (0.6 g, 0.658 mmol) in diethyl ether (100 ml) was treated dropwise, at −20°C, with a diluted solution of $HBF_4 \cdot Et_2O$ in diethyl ether. An insoluble solid precipitated immediately, 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: 93% (0.611 g); Anal. Found: C, 69.39; H, 5.44. Calc. for $C_{58}H_{53}BF_4P_2Ru$ (999.879): C, 69.67; H, 5.34%. IR (KBr, cm^{-1}): 1062 $\nu(BF_4^-)$; $^{31}P\{^1H\}$-NMR (CD_2Cl_2) δ 39.55 (br) ppm; ^1H-NMR (CD_2Cl_2) δ 0.74 and 1.22 (s, 3H each one, CH_3), 1.04 (d, 1H, $J_{HH} = 8.6$ Hz, CH_2), 1.78–2.44 (m, 5H, CH_2 and CH), 5.30 (d, 1H, $J_{HH} = 9.7$ Hz, Ru=C=CH), 5.38 (br, 1H, C=CH), 5.49 and 5.50 (br, 1H each one, H-1 and H-3), 5.52 (dd, 1H, $J_{HH} = 15.0$ Hz, $J_{HH} = 9.7$ Hz, Ru=C=CH–$\underline{C}$H=CH), 5.77 (d, 1H, $J_{HH} = 15.0$ Hz, Ru=C=CH–CH=$\underline{C}$H), 5.81 (br, 1H, H-2), 6.04 (m, 2H, H-4, H-5, H-6 or H-7), 6.81–7.54 (m, 32H, Ph and H-4, H-5, H-6 or H-7) ppm; $^{13}C\{^1H\}$-NMR (CD_2Cl_2) δ 21.02 and 26.48 (s, CH_3), 31.40 and 32.15 (s, CH_2), 37.85 (s, $\underline{C}(CH_3)_2$), 41.34 (s, 2CH), 84.08 (s, C-1 and C-3), 99.15 (s, C-2), 107.32 (s, Ru=C=CH–$\underline{C}$H=CH), 115.98 and 116.08 (s, C-3a and C-7a), 118.55 (s, C_β), 123.45 (s, C=$\underline{C}$H), 125.08 and 127.70 (s, C-4, C-5, C-6 or C-7), 128.50–134.44 (m, Ph and C-4, C-5, C-6 or C-7), 130.68 (s, Ru=C=CH–CH=$\underline{C}$H), 146.6 (s, $\underline{C}$=CH), 361.56 (t, $^2J_{CP} = 17.1$ Hz, Ru=C_α) ppm. $\Delta\delta$(C-3a,7a) = −14.67 ppm.

4.3. Synthesis of terminal 1,3-enyne (*E*)-HC≡CC(H)=C(H)C_9H_{13} (5)

A solution of the vinylidene complex **4** (0.34 g, 0.34 mmol) in acetonitrile (20 ml) was heated under reflux for 60 min. The solution was then evaporated to dryness and the resulting solid residue extracted with diethyl ether (ca. 50 ml) and filtered. A yellow solid, mainly containing the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**6**), remains insoluble. The extract was evaporated to dryness and the crude product purified by column chromatography on silica gel with hexane as eluent. Evaporation of the solvent gave **5** as a yellow oil. Yield: 88% (0.052 g); IR (Nujol, cm^{-1}): 2111 ν(C≡C), 3312 ν(≡C–H); ^1H-NMR ($CDCl_3$) δ 0.78 and 1.32 (s, 3H each one, CH_3), 1.13 (d, 1H, J_{HH} = 8.2 Hz, CH_2), 2.14 (m, 1H, CH_2), 2.36–2.50 (m, 4H, CH_2 and CH), 2.98 (d, 1H, $J_{HH} = 1.7$ Hz, ≡CH), 5.44 (dd, 1H, $J_{HH} = 16.3$ Hz, $J_{HH} = 1.7$ Hz, ≡C–C$\underline{H}$=CH), 5.70 (s, 1H, C=CH), 6.69 (d, 1H, $J_{HH} = 16.3$ Hz, ≡C–CH=C$\underline{H}$) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ 20.70 and 26.15 (s, CH_3), 31.07 and 32.09 (s, CH_2), 37.69 (s, $\underline{C}(CH_3)_2$), 40.55 and 40.71 (s, CH), 78.48 (s, ≡CH), 83.67 (s, ≡C), 102.65 (s, ≡C–$\underline{C}$H=CH), 128.11 (s, C=$\underline{C}$H), 144.17 (s, ≡C–CH=$\underline{C}$H), 145.91 (s, $\underline{C}$=CH) ppm; HRMS m/z calc. for $C_{13}H_{16}$ (found): M^+ = 172.125 200 (172.125 079).

4.4. Synthesis of σ-enynyl complex (*E,Z*)-[Ru{C≡CC(H)=C(H)C_9H_{13}}(η^5-C_9H_7)(PPh_3)$_2$] (7)

Li^{n}Bu (1.6 M in hexane; 0.526 ml, 0.843 mmol) was added at −20°C to a solution of complex [Ru{C≡CCH_2(PPh_3)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**) (1 g, 0.843 mmol) in THF (40 ml). The reaction mixture was stirred for 15 min and (*S*)-(−)-perillaldehyde (0.155 ml, 1 mmol) was then added. Upon warming to r.t, the solution was stirred for additional 30 min. The solvent was then removed under vacuum and the orange solid residue dissolved in dichloromethane (ca. 5 ml) and transferred to a silica-gel chromatography column. Elution with hexane/diethyl ether (4/1) gave an orange band, which was collected and evaporated to dryness to give complex **7** as an orange solid. This complex was isolated as a mixture of the corresponding *E* and *Z* stereoisomers in ca. 4:1 ratio. Yield: 82%

(0.63 g); Anal. Found: C, 76.63; H, 5.82. Calc. for $C_{58}H_{52}P_2Ru$ (912.066): C, 76.38; H, 5.74%.*E* isomer: IR (KBr, cm^{-1}): 2046 ν(C≡C); $^{31}P\{^1H\}$-NMR (C_6D_6) δ 51.85 (br) ppm; ^1H-NMR (C_6D_6) δ 1.45 and 1.72 (m, 2H each one, CH_2), 1.63 (s, 3H, CH_3), 2.12 (m, 3H, CH_2 and CH), 4.71 and 4.79 (d, 1H each one, J_{HH} = 2.2 Hz, =CH_2), 5.69 (m, 4H, C=C<u>H</u>, H-1, H-2 and H-3), 6.30 and 6.58 (d, 1H each one, J_{HH} = 15.7 Hz, =CH), 6.33 and 6.68 (m, 2H each one, H-4, H-5, H-6 and H-7), 6.90–7.52 (m, 30H, Ph) ppm; $^{13}C\{^1H\}$-NMR (C_6D_6) δ 20.90 (s, CH_3), 25.22, 27.98 and 31.91 (s, CH_2), 41.87 (s, CH), 74.97 (s, C-1 and C-3), 95.51 (s, C-2), 108.94 (s, =CH_2), 109.51 (s, ≡C–<u>C</u>H=CH), 112.58 (s, C-3a and C-7a), 114.06 (t, $^2J_{CP}$ = 25.6 Hz, Ru–C_α), 114.19 (s, C_β), 123.14 and 125.90 (s, C-4, C-5, C-6 or C-7), 124.50 (s, C=<u>C</u>H), 127.38–139.12 (m, Ph and C-4, C-5, C-6 or C-7), 135.87 (s, ≡C–CH=<u>C</u>H), 136.95 (s, <u>C</u>(Me)=CH_2), 149.95 (s, <u>C</u>=CH) ppm. $\Delta\delta$(C-3a,7a) = −18.12 ppm. *Z* isomer: IR (KBr, cm^{-1}): 2017 ν(C≡C); $^{31}P\{^1H\}$-NMR (C_6D_6) δ 51.72 (br) ppm; ^1H-NMR (C_6D_6) δ 1.45 and 1.76 (m, 2H each one, CH_2), 1.63 (s, 3H, CH_3), 2.30 (m, 3H, CH_2 and CH), 4.73 and 4.78 (br, 1H each one, =CH_2), 5.69 (m, 4H, C=C<u>H</u>, H-1, H-2 and H-3), 6.33 and 6.68 (m, 2H each one, H-4, H-5, H-6 and H-7), 6.90–7.52 (m, 30H, Ph), 7.05 and 7.38 (d, 1H each one, J_{HH} = 10.3 Hz, =CH) ppm; $^{13}C\{^1H\}$-NMR (C_6D_6) δ 24.21 (s, CH_3), 25.61, 29.40 and 34.17 (s, CH_2), 41.87 (s, CH), 74.97 (s, C-1 and C-3), 95.51 (s, C-2), 108.94 (s, =CH_2), 111.35 (s, ≡C–<u>C</u>H=CH), 112.58 (s, C-3a and C-7a), 115.20 (t, $^2J_{CP}$ = 25.6 Hz, Ru–C_α), 117.85 (s, C_β), 124.90 (s, C=<u>C</u>H), 125.51 and 126.79 (s, C-4, C-5, C-6 or C-7), 127.38–139.12 (m, Ph and C-4, C-5, C-6 or C-7), 132.25 (s, ≡C–CH=<u>C</u>H), 137.52 (s, <u>C</u>(Me)=CH_2), 146.67 (s, <u>C</u>=CH) ppm. $\Delta\delta$(C-3a,7a) = −18.12 ppm.

*4.5. Synthesis of alkenyl–vinylidene complex (E)-[Ru{=C=C(H)C(H)=C(H)C_9H_{13}}(η^5-C_9H_7)(PPh_3)$_2$]-[BF_4] (**8**)*

A solution of the σ-enynyl complex **7** (0.55 g, 0.603 mmol) in diethyl ether (100 ml) was treated dropwise, at −20°C, with a diluted solution of $HBF_4{\cdot}Et_2O$ in diethyl ether. An insoluble solid precipitated immediately, 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: 89% (0.542 g); Anal. Found: C, 69.48; H, 5.53. Calc. for $C_{58}H_{53}BF_4P_2Ru$ (999.879): C, 69.67; H, 5.34%. IR (KBr, cm^{-1}): 1055 ν(BF_4^-); $^{31}P\{^1H\}$-NMR (CD_2Cl_2) δ 40.35 (br) ppm; ^1H-NMR (CD_2Cl_2) δ 1.46 and 1.79 (m, 2H each one, CH_2), 1.72 (s, 3H, CH_3), 2.20 (m, 3H, CH_2 and CH), 4.69 and 4.71 (s, 1H each one, =CH_2), 5.30 (d, 1H, J_{HH} = 9.9 Hz, Ru=C=CH), 5.48 and 5.50 (br, 1H each one, H-1 and H-3), 5.59 (dd, 1H, J_{HH} = 15.4 Hz, J_{HH} = 9.9 Hz, Ru=C=CH–C<u>H</u>=CH), 5.75 (br, 1H, H-2), 5.77 (d, 1H, J_{HH} = 15.4 Hz, Ru=C=CH–CH=C<u>H</u>), 6.08 (m, 2H, H-4, H-5, H-6 or H-7), 6.84–7.51 (m, 32H, Ph and H-4, H-5, H-6 or H-7) ppm; $^{13}C\{^1H\}$-NMR (CD_2Cl_2) δ 21.03 (s, CH_3), 25.02, 27.64 and 31.60 (s, CH_2), 41.52 (s, CH), 84.45 and 84.50 (s, C-1 and C-3), 99.11 (s, C-2), 107.82 (s, Ru=C=CH–<u>C</u>H=CH), 108.92 (s, =CH_2), 115.74 and 115.82 (s, C-3a and C-7a), 118.53 (s, C_β), 123.45 (s, C=<u>C</u>H), 123.47–134.31 (m, Ph, C-4, C-5, C-6 and C-7), 130.68 (s, Ru=C=CH–CH=<u>C</u>H), 135.34 (s, <u>C</u>(Me)=CH_2), 150.14 (s, <u>C</u>=CH), 360.95 (t, $^2J_{CP}$ = 16.9 Hz, Ru=C_α) ppm. $\Delta\delta$(C-3a,7a) = −14.92 ppm.

*4.6. Synthesis of terminal 1,3-enyne (E)-HC≡CC(H)=C(H)C_9H_{13} (**9**)*

A solution of the vinylidene complex **8** (0.5 g, 0.5 mmol) in acetonitrile (25 ml) was heated under reflux for 60 min. The solution was then evaporated to dryness and the resulting solid residue extracted with diethyl ether (ca. 50 ml) and filtered. A yellow solid, mainly containing the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**6**), remains insoluble. The extract was evaporated to dryness, and the crude product purified by column chromatography on silica gel with hexane as eluent. Evaporation of the solvent gave **9** as a colorless oil. Yield: 79% (0.068 g); IR (Nujol, cm^{-1}): 2103 ν(C≡C), 3247 ν(≡C–H); ^1H-NMR ($CDCl_3$) δ 1.46 (m, 2H, CH_2), 1.75 (s, 3H, CH_3), 1.87–2.33 (m, 5H, CH_2 and CH), 2.95 (d, 1H, J_{HH} = 2.2 Hz, ≡CH), 4.72 and 4.74 (d, 1H each one, J_{HH} = 1.8 Hz, =CH_2), 5.44 (dd, 1H, J_{HH} = 16.1 Hz, J_{HH} = 2.2 Hz, ≡C–C<u>H</u>=CH), 5.89 (s, 1H, C=CH), 6.69 (d, 1H, J_{HH} = 16.1 Hz, ≡C–CH=C<u>H</u>) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ 20.73 (s, CH_3), 24.11, 27.02 and 31.39 (s, CH_2), 40.80 (s, CH), 77.96 (s, ≡CH), 83.53 (s, ≡C), 103.21 (s, ≡C–<u>C</u>H=CH), 108.92 (s, =CH_2), 132.49 (s, C=<u>C</u>H), 134.89 (s, <u>C</u>(CH_3)=CH_2), 146.15 (s, ≡C–CH=<u>C</u>H), 149.20 (s, <u>C</u>=CH) ppm; HRMS *m*/*z* calc. for $C_{13}H_{16}$ (found): M^+ = 172.125 200 (172.124 833).

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