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Indenyl–ruthenium(II) allenylidene complexes containing terpenic substituents as precursors of optically active terminal alkynes: scope and limitations †

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The optically active allenylidene complex [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C(C_9H_{16}) = (1*R*,4*S*)-1,3,3-trimethyl-bicyclo[2.2.1]hept-2-ylidene) **1** regio- and stereoselectively reacts with unhindered anionic nucleophiles to yield the neutral σ-alkynyl derivatives [Ru{C≡CC(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$] (R = H **2a**, C≡N **2b**, Me **2c**, C≡CPh **2d**). Protonation of **2a**–**d** with HBF_4·Et_2O affords the cationic vinylidene complexes [Ru{=C=C(H)C(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] **3a**–**d**, which can be easily demetalated, by treatment with acetonitrile, yielding the corresponding chiral acetylenic compounds HC≡C(C_9H_{16})R **4a**–**d**. The novel optically active indenyl–ruthenium(II) allenylidene complexes [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C(C_9H_{16}) = (1*R*,4*R*)-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ylidene) **9** and [Ru{=C=C=C(C_9H_{14})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C(C_9H_{14}) = (1*S*,5*S*)-4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-ylidene) **10** have been prepared by activation of propargylic alcohols derived from the natural ketones (+)-camphor and (−)-verbenone, respectively, with [RuCl(η^5-C_9H_7)(PPh_3)$_2$] **6**. Treatment of **9** with anionic nucleophiles generates the neutral σ-enynyl complex [Ru{C≡CC(C_9H_{15})}(η^5-C_9H_7)(PPh_3)$_2$] **11** (C(C_9H_{15}) = (1*R*,4*R*)-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-en-2-yl).

Introduction

Since the discovery of the first allenylidene complex in 1976,[1] the chemistry of these unsaturated species has been the topic in several research groups due to their great potential in stoichiometric[2] and catalytic processes.[3–6] In fact, cationic transition-metal allenylidene derivatives [M]$^+$=C=C=CR^1R^2, readily available by dehydration of propargylic alcohols upon coordination to an unsaturated metal center,[7] can be regarded as stabilized propargyl cations because of the extensive contribution of the metal–alkynyl resonance form [M]–C≡C–$C^+R^1R^2$.[8] Although the reactivity of cationic allenylidenes is governed by the electron-deficiency of both the C_α and C_γ atoms of the unsaturated chain,[9] it is now well-established that nucleophilic additions at C_γ regioselectively occur when electron-rich and/or bulky metallic fragments are used, leading to a large variety of σ-alkynyl complexes [M]–C≡C–C(Nu)R^1R^2.[2] In the context of our studies in the chemistry of indenyl–ruthenium(II) complexes,[10] and based on these regioselective nucleophilic attacks, we have developed an efficient synthetic procedure for the propargylic substitution of 2-propyn-1-ols mediated by the metallic fragment [Ru(η^5-C_9H_7)(PPh_3)$_2$]$^+$ (Chart 1).[11] Thus, in a first step allenylidene complexes **A** are formed and subsequently transformed into the corresponding σ-alkynyl derivatives **B** which undergo a selective C_β protonation to afford the vinylidene complexes **C**.[12] Finally, demetalation of **C** with acetonitrile leads to the functionalized terminal alkynes **D** in excellent yields.

This synthetic methodology constitutes an alternative to the well-known Nicholas reaction in which propargylic alcohols are easily functionalized *via* [$Co_2(CO)_6$]-stabilized propargyl cations.[13] Although both synthetic procedures require the same number of steps, the quantitative recovery of the metal fragment as the solvato complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$]$^+$ represents a major advantage compared to the classical

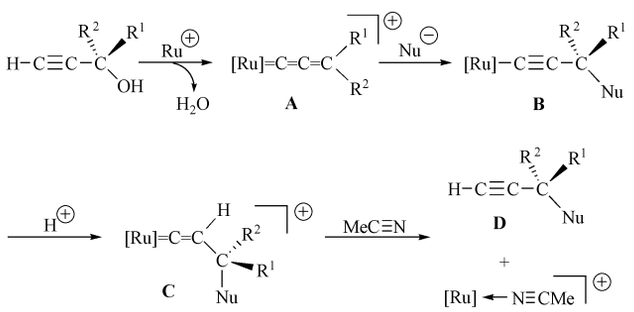

Chart 1 [Ru(η^5-C_9H_7)(PPh_3)$_2$]$^+$-mediated propargylic substitutions.

Nicholas reaction in which the metal auxiliary can not be recovered after the oxidative decomplexation step.

The efficient access to acetylenes **D**, prompted us to study the asymmetric version of our synthetic protocol in order to obtain novel optically active terminal alkynes. To achieve this, two different strategies have been developed: (*i*) the use of chiral nucleophiles,[11d,f] and (*ii*) the use of allenylidene derivatives bearing chiral auxiliaries.[11c,d,e,14] In particular, concerning the latter strategy, we have recently synthesized the indenyl–ruthenium(II) allenylidene complex [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C(C_9H_{16}) = (1*R*,4*S*)-1,3,3-trimethyl-bicyclo[2.2.1]hept-2-ylidene) **1**, which incorporates a chiral bicyclic substituent derived from the natural source (−)-fenchone (Chart 2).[11c]

This system has demonstrated to be a useful chiral inductor, since the nucleophilic addition of lithium enolates and allylmagnesium bromide was found to take place diastereoselectively on the less sterically congested *exo* face of the allenylidene chain, giving rise to the high-yield synthesis of optically active γ-keto acetylenes **E** and the 1,5-enyne **F**, respectively (see Chart 2).[11c,d,e]

In order to evaluate the scope of this stereoselective synthetic approach to the preparation of novel optically pure terminal alkynes, in this paper we report on the reactivity of [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] **1** towards a series of

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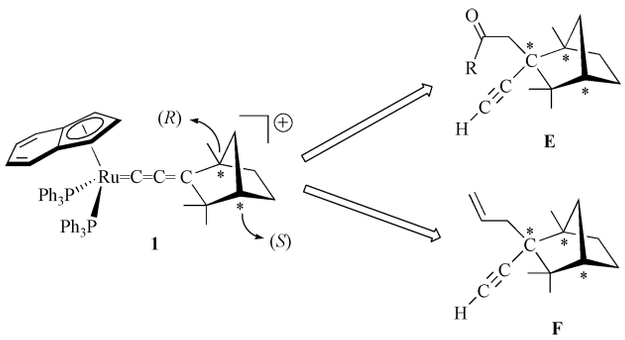


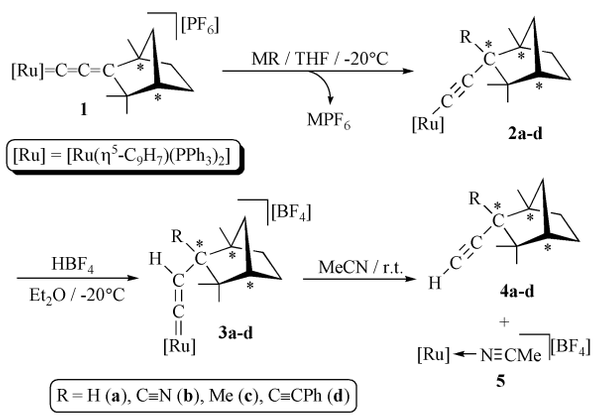
Chart 2 Structure of the optically active compounds **1**, **E** and **F**.

unhindered anionic nucleophiles. In addition, the synthesis and reactivity of two new chiral indenyl–ruthenium(II) allenylidene complexes derived from the commercially available ketones (+)-camphor and (−)-verbenone is also reported.

Results and discussion

Synthesis and characterization of the optically active terminal alkynes HC≡CC(C_9H_{16})R (R = H 4a, C≡N 4b, Me 4c, C≡CPh 4d)

As expected from our previous studies,[11c,d,e] the allenylidene complex [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] **1** reacts with a slight excess (*ca.* 1.1 equiv.) of LiHBEt$_3$, NaC≡N, LiMe or LiC≡CPh, in tetrahydrofuran at −20 °C, to afford the neutral σ-alkynyl derivatives [Ru{C≡CC(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$] (R = H **2a**, C≡N **2b**, Me **2c**, C≡CPh **2d**), resulting from the regioselective addition of the nucleophile at the C_γ atom of the cumulenic chain (75–91% yield; Scheme 1).



Scheme 1 Synthetic procedure used in the preparation of the optically active terminal alkynes **4a**–**d**.

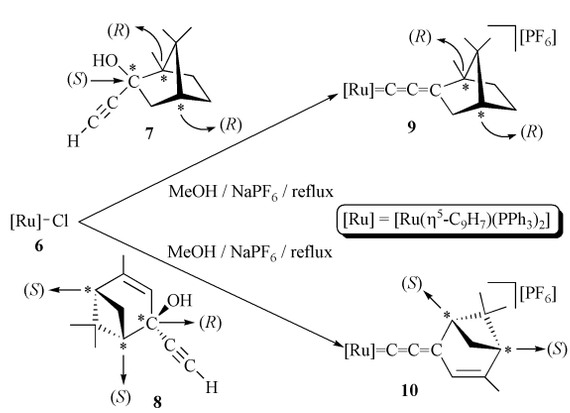
Complexes **2a**–**d** have been analytically and spectroscopically characterized (IR and ^{31}P-{^{1}H}, ^{1}H and ^{13}C-{^{1}H} NMR; see the Experimental section for details). In particular, the formation of an alkynyl chain was identified on the basis of: (*i*) (IR) the presence of a typical *ν*(C≡C) absorption band at 2069–2089 cm^{-1}, and (*ii*) (^{13}C-{^{1}H} NMR) characteristic resonances for the Ru–C_α≡C_β–C_γ carbon nuclei (δ_C 90.64–102.45 (dd, *ca.* ^2J(CP) = 23 Hz, C_α), 107.14–116.40 (s, C_β) and 53.46–56.09 (s, C_γ)). Remarkably, these nucleophilic attacks proceed also in a diastereoselective manner since only one diastereoisomer was detected by NMR spectroscopy. By analogy with our previous reports,[11c,d,e] an *exo* addition of the incoming nucleophiles to the allenylidene chain in **1** is proposed. These results confirm that the bicyclic (1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene unit is an excellent chiral inductor, even when small nucleophiles are employed.

Transformation of σ-alkynyl complexes **2a**–**d** into the corresponding terminal alkynes HC≡CC(C_9H_{16})R (R = H **4a**, C≡N **4b**, Me **4c**, C≡CPh **4d**) using our two-step method proceeds cleanly and efficiently (see Scheme 1). Thus, the cationic vinylidene derivatives [Ru{=C=C(H)C(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (R = H **3a**, C≡N **3b**, Me **3c**, C≡CPh **3d**) were initially prepared (78–92% yield) by selective protonation of **2a**–**d** with HBF_4 in diethyl ether at −20 °C.[12] Analytical and spectroscopic data are in agreement with the proposed formulations (see the Experimental section for details). Relevant spectroscopic features are: (*i*) (^{1}H NMR) the doublet (**3a**; ^3J(HH) = 10.5 Hz) or singlet (**3b**–**d**) signal for the acidic Ru=C=CH proton (δ_H 3.88–4.08), and (*ii*) (^{13}C-{^{1}H} NMR) the typical low-field resonance of the carbenic Ru=C_α carbon, which appears as a doublet of doublets (^2J(CP) = 15.3–17.7 Hz) at δ_C 342.03–347.75, as well as the C_β singlet signal (δ_C 108.34–116.84). In a second step vinylidenes **3a**–**d** were treated with acetonitrile at room temperature, affording the novel optically active terminal alkynes **4a**–**d** and the cationic nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] **5** (see Scheme 1). Alkynes **4b**–**d** have been easily isolated from the reaction mixture by filtering off the unsoluble solvate **5** (77–89% yield). In contrast, due to its low boiling point, alkyne **4a** could not be isolated being instead characterized *in situ* by NMR spectroscopy. Characteristic spectroscopic data for **4a**–**d** are: (*i*) (^{1}H NMR) the doublet (**4a**; ^4J(HH) = 2.4 Hz) or singlet (**4b**–**d**) resonance for the acetylenic ≡CH proton at δ_H 1.91–2.35, (*ii*) (^{13}C-{^{1}H} NMR) the typical signals for the HC≡C carbons which appear in the ranges 71.95–75.47 and 78.55–89.35 ppm, respectively, and (*iii*) (IR) the stretching *ν*(≡C–H) and *ν*(C≡C) absorption bands at 3251–3324 and 2070–2111 cm^{-1}, respectively.

Synthesis and reactivity of novel optically active indenyl–ruthenium(II) allenylidene complexes

The high diastereoselectivity observed in the nucleophilic additions on complex **1** prompted us to prepare novel indenyl–ruthenium(II) allenylidene derivatives containing optically active substituents. To this regard the chemical behaviour of the chloride complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$] **6**[15] towards propargylic alcohols derived from the commercially available and optically pure ketones (+)-camphor and (−)-verbenone, *i.e.* (1*R*,2*S*,4*R*)-2-ethynyl-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol **7** and (1*S*,2*R*,5*S*)-2-ethynyl-4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-ol **8** (see Scheme 2),[16,17] has been explored. Thus, following the standard Selegue synthetic procedure,[7] the chiral allenylidene derivatives [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C(C_9H_{16}) = (1*R*,4*R*)-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ylidene) **9** and [Ru{=C=C=C(C_9H_{14})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C(C_9H_{14}) = (1*S*,5*S*)-4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-ylidene) **10** have been prepared by reaction of **6** with propargylic alcohols **7** and **8**, respectively, in refluxing methanol and in the presence of $NaPF_6$ (Scheme 2).

Allenylidene complexes **9** and **10** have been isolated as air-stable red solids in 80 and 75% yields, respectively. Their



Scheme 2 Synthesis of the optically active indenyl–ruthenium(II) allenylidene complexes **9** and **10**.

spectroscopic data are in agreement with the presence of an allenylidene chain and can be compared to those previously reported for other indenyl–ruthenium(II) allenylidene complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$.[9c,18] Thus, the IR spectra (KBr) exhibit a broad and strong ν(C=C=C) absorption band (asymmetric stretching vibration) at *ca.* 1960 cm^{-1} and the $^{13}C\text{-}\{^1H\}$ NMR spectra display the characteristic low-field resonance for the carbenic Ru=C_α atom (δ_C 305.06 (**9**) and 280.16 (**10**); dd signal, $^2J(CP)$ = 18.9–20.2 Hz). The spectra also show two singlet signals in the range 174.75–202.21 ppm corresponding to the β- and γ-carbon nuclei of the cumulenic chain.

The selective synthesis of allenylidenes **9** and **10** from propargylic alcohols **7** and **8** is noteworthy since the competitive formation of their vinylvinylidene tautomers is not observed. As it is well-known,[2] dehydration of coordinated 2-propyn-1-ol derivatives containing hydrogen atoms adjacent to the hydroxy group can also occur giving rise to vinylvinylidene derivatives **G** (see Chart 3). Indeed, this is the main drawback of the Selegue protocol for the synthesis of transition-metal allenylidenes. Thus, we have reported that activation of such type of propargylic alcohols by $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **6** leads preferentially to the corresponding vinylvinylidene isomers.[19] *Ab initio* theoretical calculations are consistent with this behaviour, disclosing that the vinylvinylidene model $[Ru\{=C=C(H)CH=CH_2\}(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$ is *ca.* 2.1 kcal mol^{-1} more stable than its allenylidene tautomer $[Ru\{=C=C=C(H)CH_3\}(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$.[19b] The experimental formation of the allenylidenes **9** and **10** *vs.* the expected vinylvinylidene isomers (according the calculations) stems from the higher strain energy shown by the endocyclic cycloalkene units of the latter. The relief of this energy by the adoption of the less strained exocyclic counterparts is likely the driving force which leads to the selective formation of the allenylidenes.

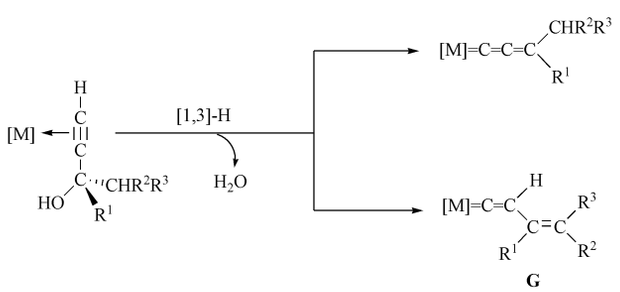
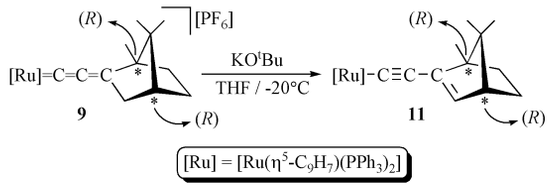


Chart 3 Competitive allenylidene *vs.* vinylvinylidene formation.

In order to asses the capacity of the chiral bicyclic units in complexes **9** and **10** to induce stereoselective nucleophilic additions at C_γ, their reactivity towards anionic nucleophiles has been studied. Thus, we have found that the treatment of allenylidene **9** with *ca.* 1.1 equiv. of $LiHBEt_3$, NaC≡N, LiMe or LiC≡CPh, in THF at −20 °C, generates the σ-enynyl derivative $[Ru\{C\equiv CC(C_9H_{15})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **11** ($C(C_9H_{15})$ = (1*R*,4*R*)-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-en-2-yl), resulting from the formal deprotonation of the methylenic C_δ atom of the (1*R*,4*R*)-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ylidene unit. NMR spectra of the crude reaction mixtures show no resonances of the expected σ-alkynyl species $[Ru\{C\equiv CC(C_9H_{16})R\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$. Complex **11** can be also prepared (87% yield) by reaction of **9** with typical bases such as KO^{t}Bu (Scheme 3).

Although addition products have been observed after the treatment of allenylidene **10** with anionic nucleophiles, the reactions lead to unseparable mixtures of complexes. Two competitive processes, *i.e.* nucleophilic addition at C_γ *vs.* nucleophilic addition at the endocyclic carbon–carbon double bond,[20] may be operative.

Analytical and spectroscopic data (IR and $^{31}P\text{-}\{^1H\}$, ^1H and $^{13}C\text{-}\{^1H\}$ NMR) of **11** support the proposed formulation (see



Scheme 3 Synthesis of the optically active σ–enynyl complex **11**.

the Experimental section). In particular, the presence of a σ-enynyl moiety was identified on the basis of: (*i*) (IR) the expected ν(C≡C) absorption band at 2060 cm^{-1}, (*ii*) (^1H NMR) the appearance of a doublet signal ($^3J(HH)$ = 3.3 Hz) at δ_H 5.94 assignable to the endocyclic olefinic proton, and (*iii*) ($^{13}C\text{-}\{^1H\}$ NMR) typical resonances for the Ru–C_α and C_β carbon atoms, which appear at δ_C 113.14 (dd, $^2J(CP)$ = 25.1 Hz) and 110.21 (s), respectively.

The formation of σ-enynyl complex **11** most probably involves an initial isomerization of **9** into its vinylvinylidene tautomer **H** (Fig. 1), followed by the classical deprotonation of the acidic [Ru]=C=CH proton in the presence of base.[12,19b] However, the direct deprotonation of one of the methylenic protons in the δ position of allenylidene **9** cannot be totally discarded.[2] Remarkably, treatment of **11** with HBF_4 regenerates quantitatively the allenylidene derivative **9**, confirming the higher thermodynamic stability of **9** *vs.* **H**. Assuming that vinylidene **H** is the first product formed in this protonation process,[21] the final isolation of **9** clearly confirms that vinylvinylidene–allenylidene tautomerizations can easily occur in solution.[19b]

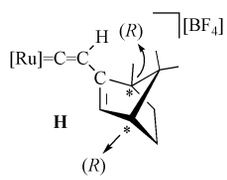


Fig. 1 Structure of the vinylvinylidene complex **H**.

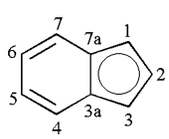
Conclusions

In this work we report further applications of the synthetic protocol developed in our group (Chart 1),[11] which allows the preparation of the novel functionalized terminal alkynes **4a**–**d** in optically pure form. They have been obtained *via* regio- and diastereoselective nucleophilic additions at C_γ of the chiral allenylidene complex $[Ru\{=C=C=C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($C(C_9H_{16})$ = (1*R*,4*S*)-1,3,3-trimethyl-bicyclo[2.2.1]hept-2-ylidene) **1** (Scheme 1). These results show the excellent chiral induction of the bicyclic $C(C_9H_{16})$ moiety even when small nucleophiles are used. In contrast, the treatment of the analogous allenylidene complex $[Ru\{=C=C=C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$($C(C_9H_{16})$=(1*R*,4*R*)-1,7,7-trimethyl-bicyclo[2.2.1]-hept-2-ylidene) **9**, bearing methylenic hydrogen atoms at C_δ, with anionic nucleophiles leads to a deprotonation process affording the σ-enynyl derivative $[Ru\{C\equiv CC(C_9H_{15})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **11** (Scheme 3). This behaviour is in accord with the competitive tautomerization of allenylidene–vinylvinylidene that enables the deprotonation of the [Ru]=C=CH moiety in the latter tautomer due to the basic properties of the nucleophiles. Moreover, we have found that the presence of an endocyclic C=C bond on the chiral unit of the allenylidene chain, *i.e.* complex $[Ru\{=C=C=C(C_9H_{14})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($C(C_9H_{14})$ = (1*S*,5*S*)-4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-ylidene) **10**, leads to competitive nucleophilic addition at C_γ *vs.* endocyclic olefin. These facts limit the scope of our synthetic methodology of optically active terminal alkynes. In summary, the results reported here provide an extension of our previous studies directed to the application of ruthenium(II)–allenylidene complexes in stereoselective organic synthesis.

Experimental

General comments

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. Compounds [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] **1**,[11c] [RuCl(η^5-C_9H_7)(PPh_3)$_2$] **6**,[15] (1*R*,2*S*,4*R*)-2-ethynyl-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol **7** [16] and (1*S*,2*R*,5*S*)-2-ethynyl-4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-ol **8** [17] were prepared following the methods reported in literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. 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 2400 microanalyzer. High-resolution mass spectra were recorded using a MAT-95 spectrometer. FAB mass spectra were recorded using a VG-Autospec spectrometer operating in positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker DPX300 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 compounds reported in this paper. Abbreviations used: s, singlet; br, broad singlet; d, doublet; dd, doublet of doublets; m, multiplet. The numbering for the indenyl skeleton is as follows:



Preparations

[Ru{C≡CC(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$] (R = H 2a, C≡N 2b, Me 2c, C≡CPh 2d). *General procedure.* A solution of the allenylidene complex [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (1.05 g, 1 mmol) in 50 cm^3 of THF was treated at −20 °C with a slight excess (1.1 mmol) of $LiHBEt_3$ (1 M solution in THF), NaC≡N, LiMe (1.6 M solution in diethyl ether) or LiC≡CPh (prepared *in situ* by addition of Li^{n}Bu 1.6 M to a solution of PhC≡CH in THF at −20 °C). The reaction mixture was slowly warmed to room temperature and then evaporated to dryness. The resulting solid residue was dissolved in diethyl ether (*ca.* 20 cm^3) and filtered through Al_2O_3 (neutral; activity grade I). Removal of the solvent gave the σ-alkynyl complexes **2a**–**d** as orange solids. **2a:** Yield: 0.80 g, 89% (Found: C, 75.43; H, 6.08. $RuC_{57}H_{54}P_2$ requires C, 75.89; H, 6.03%.); ν_{max}/cm^{-1} (C≡C) 2089m (KBr); δ_P (C_6D_6) 53.40 and 53.69 (d, ^2J(PP) = 31.5 Hz); δ_H (C_6D_6) 1.25, 1.27 and 1.41 (s, 3H each, CH_3), 1.31 (m, 2H, CH_2), 1.55 (br, 1H, CH), 1.64, 1.90, 2.08 and 2.42 (m, 1H each, CH_2), 2.67 (m, 1H, CH), 4.64 and 4.69 (d, 1H each, ^3J(HH) = 2.7 Hz, H-1 and H-3), 5.51 (dd, 1H, ^3J(HH) = 2.7 and 2.7 Hz, H-2), 6.42 and 6.68 (m, 2H each, H-4, H-5, H-6 and H-7), 6.92–7.49 (m, 30H, Ph); δ_C (C_6D_6) 21.72, 25.73 and 32.49 (s, CH_3), 27.14, 29.32 and 43.99 (s, CH_2), 40.11 and 50.72 (s, C), 49.17 (s, CH), 56.09 (s, C_γH), 74.33 (d, ^2J(CP) = 4.9 Hz, C-1 or C-3), 74.54 (d, ^2J(CP) = 3.7 Hz, C-1 or C-3), 90.64 (dd, ^2J(CP) = 23.8 and 23.8 Hz, Ru–C_α), 94.78 (s, C-2), 108.82, 109.54 and 110.24 (s, C-3a, C-7a and C_β), 122.95, 123.37, 125.60 and 125.99 (s, C-4, C-5, C-6 and C-7), 127.21–139.02 (m, Ph). **2b:** Yield: 0.84 g, 91%; ν_{max}/cm^{-1} (C≡C) 2070m, (C≡N) 2218w (KBr); δ_P ($CDCl_3$) 54.04 and 54.58 (d, ^2J(PP) = 32.5 Hz); δ_H ($CDCl_3$) 1.13, 1.23 and 1.30 (s, 3H each, CH_3), 0.86, 1.38, 1.57, 1.67, 1.77 and 1.86 (m, 1H each, CH_2), 2.18 (m, 1H, CH), 4.42 and 4.48 (d, 1H each, ^3J(HH) = 2.4 Hz, H-1 and H-3), 5.09 (dd, 1H, ^3J(HH) = 2.4 and 2.4 Hz, H-2), 6.45 and 6.74 (m, 2H each, H-4, H-5, H-6 and H-7), 7.03–7.30 (m, 30H, Ph); δ_C ($CDCl_3$) 19.35, 26.01 and 30.28 (s, CH_3), 26.18, 29.47 and 42.00 (s, CH_2), 43.63 (s, C), 48.70 (s, CH), 55.04 (s, C and C_γ), 73.88 (s, C-1 and C-3), 93.90 (s, C-2), 102.45 (br, Ru–C_α), 108.92 and 109.38 (s, C-3a, C-7a and C_β), 121.61 (s, C≡N), 122.26, 122.95, 125.26 and 126.02 (s, C-4, C-5, C-6 and C-7), 127.01–138.12 (m, Ph); MS (FAB) *m*/*z* 927 [M + 1], 741 [M − $C_{13}H_{16}N$ + 1], 478 [M − $C_{13}H_{16}N$ − PPh_3 + 1], 363 [M − $C_{13}H_{16}N$ − PPh_3 − C_9H_7 + 1]. This complex was too sensitive to moisture and oxygen to give satisfactory elemental analyses. **2c:** Yield: 0.77 g, 84% (Found: C, 76.04; H, 6.16. $RuC_{58}H_{56}P_2$ requires C, 75.88; H, 6.04%.); ν_{max}/cm^{-1} (C≡C) 2072m (KBr); δ_P (C_6D_6) 54.12 and 54.95 (d, ^2J(PP) = 34.0 Hz); δ_H (C_6D_6) 1.21 (s, 6H, CH_3), 1.30 and 1.85 (m, 2H each, CH_2), 1.40 and 1.58 (s, 3H each, CH_3), 1.66 and 2.14 (m, 1H each, CH_2), 2.91 (m, 1H, CH), 4.67 and 4.70 (d, 1H each, ^3J(HH) = 2.6 Hz, H-1 and H-3), 5.47 (dd, 1H, ^3J(HH) = 2.6 and 2.6 Hz, H-2), 6.48–7.77 (m, 34H, Ph, H-4, H-5, H-6 and H-7); δ_C (C_6D_6) 18.98, 24.90, 27.81 and 28.85 (s, CH_3), 27.13, 34.36 and 41.30 (s, CH_2), 43.55 and 51.10 (s, C), 50.72 (s, CH), 53.46 (s, C_γ), 74.61 (br, C-1 and C-3), 86.30 (dd, ^2J(CP) = 23.2 and 23.2 Hz, Ru–C_α), 95.06 (s, C-2), 109.77, 110.19 and 116.40 (s, C-3a, C-7a and C_β), 123.34, 123.74, 125.72 and 126.02 (s, C-4, C-5, C-6 and C-7), 127.16–139.32 (m, Ph). **2d:** Yield: 0.75 g, 75% (Found: C, 77.84; H, 5.95. $RuC_{58}H_{56}P_2$ requires C, 77.90; H, 5.83%.); ν_{max}/cm^{-1} (C≡C) 2069m, (C≡C) 2210w (KBr); δ_P (C_6D_6) 53.76 and 55.11 (d, ^2J(PP) = 32.1 Hz); δ_H (C_6D_6) 1.32, 1.61 and 1.73 (s, 3H each, CH_3), 1.36 and 1.93 (m, 2H each, CH_2), 1.57 and 2.36 (m, 1H each, CH_2), 2.63 (m, 1 H, CH), 4.61 (br, 2H, H-1 and H-3), 5.54 (br, 1H, H-2), 6.49–7.59 (m, 39H, Ph, H-4, H-5, H-6 and H-7); δ_C (C_6D_6) 20.47, 27.38 and 31.00 (s, CH_3), 27.21, 31.21 and 42.54 (s, CH_2), 45.05 and 54.70 (s, C), 49.86 (s, CH), 56.06 (s, C_γ), 74.22 (d, ^2J(CP) = 2.8 Hz, C-1 or C-3), 74.49 (d, ^2J(CP) = 4.6 Hz, C-1 or C-3), 83.43 (s, *C*≡CPh), 94.00 (dd, ^2J(CP) = 23.6 and 23.6 Hz, Ru–C_α), 95.07 (s, C-2), 95.89 (s, C≡*C*Ph), 107.14, 109.80 and 110.05 (s, C-3a, C-7a and C_β), 123.21, 123.78, 126.06 and 126.22 (s, C-4, C-5, C-6 and C-7), 127.10–139.00 (m, Ph).

[Ru{=C=C(H)C(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (R = H 3a, C≡N 3b, Me 3c, C≡CPh 3d). *General procedure.* A diluted solution of HBF_4·Et_2O in diethyl ether was added dropwise at −20 °C to a stirred solution of the corresponding σ-alkynyl complex [Ru{C≡CC(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$] **2a**–**d** (1 mmol) in 100 cm^3 of diethyl ether. Immediately, an insoluble brown solid precipitated but the addition was continued until no further solid was formed. The solution was then decanted, and the solid residue washed with diethyl ether (3 × 20 cm^3) and vacuum-dried. **3a:** Yield: 0.77 g, 78% (Found: C, 69.16; H, 5.60. $RuC_{57}H_{55}F_4P_2B$ requires C, 68.83; H, 5.53%.); conductivity (acetone, 20 °C) 118 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (BF_4^-) 1057s (KBr); δ_P (CD_2Cl_2) 40.52 and 40.65 (d, ^2J(PP) = 22.3 Hz); δ_H (CD_2Cl_2) 0.62, 0.65 and 1.08 (s, 3H each, CH_3), 1.17, 1.31 and 1.45 (m, 2H each, CH_2), 1.63 (m, 1H, CH), 2.27 (d, 1H, ^3J(HH) = 10.5 Hz, C_γH), 4.08 (d, 1H, ^3J(HH) = 10.5 Hz, Ru=C=CH), 5.38 (br, 2H, H-1 and H-3), 5.76 (m, 2H, H-4, H-5, H-6 or H-7), 5.91 (br, 1H, H-2), 6.78–7.48 (m, 32H, Ph and H-4, H-5, H-6 or H-7); δ_C (CD_2Cl_2) 21.62, 23.45 and 31.66 (s, CH_3), 26.26, 27.95 and 44.37 (s, CH_2), 41.06 and 50.19 (s, C), 48.69 (s, CH), 51.76 (s, C_γH), 81.54 and 82.57 (br, C-1 and C-3), 99.12 (s, C-2), 110.80 (s, C_β), 116.64 and 117.03 (s, C-3a and C-7a), 123.49, 123.66, 130.78 and 130.65 (s, C-4, C-5, C-6 and C-7), 128.66–134.45 (m, Ph), 342.03 (dd, ^2J(CP) = 16.3 and 16.3 Hz, Ru=C_α). **3b:** Yield: 0.77 g, 78%; conductivity (acetone, 20 °C) 115 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (BF_4^-) 1057s, (C≡N) 2230w (KBr); δ_P ($CDCl_3$) 36.22 and 38.16 (d, ^2J(PP) = 21.5 Hz); δ_H ($CDCl_3$) 0.61, 1.08 and 1.17 (s, 3H each, CH_3), 1.12 (m, 2H, CH_2), 1.20–1.41 (m, 3H, CH_2), 1.76 (m, 1H, CH), 1.95 (m, 1H, CH_2), 3.88 (s, 1H, Ru=C=CH), 5.57 (br, 2H, H-1 and H-3), 5.62 (d, 1H, ^3J(HH) = 7.8 Hz, H-4, H-5, H-6 or H-7), 5.79 (d, 1H, ^3J(HH) = 8.3 Hz, H-4, H-5, H-6 or H-7), 6.05 (br, 1H, H-2), 6.70–7.60 (m, 32H, Ph and H-4, H-5, H-6 or H-7); δ_C ($CDCl_3$) 18.72, 23.92

and 30.00 (s, CH_3), 25.25, 28.54 and 42.18 (s, CH_2), 44.86 and 51.13 (s, C), 48.21 (s, CH), 54.87 (s, C_γ), 79.82 (d, ^2J(CP) = 7.5 Hz, C-1 or C-3), 81.39 (d, ^2J(CP) = 6.5 Hz, C-1 or C-3), 99.47 (s, C-2), 108.34 (s, C_β), 116.48 and 117.87 (s, C-3a and C-7a), 121.90 (s, C≡N), 123.37 and 123.76 (s, C-4, C-5, C-6 or C-7), 128.28–133.89 (m, Ph and C-4, C-5, C-6 or C-7), 345.26 (dd, ^2J(CP) = 17.4 and 17.4 Hz, Ru=C_α); MS (FAB) *m*/*z* 927 [M^+], 741 [$M^+ - C_{13}H_{16}N$], 478 [$M^+ - C_{13}H_{16}N - PPh_3$], 363 [$M^+ - C_{13}H_{16}N - PPh_3 - C_9H_7$]. This complex was too sensitive to moisture and oxygen to give satisfactory elemental analyses. **3c:** Yield: 0.77 g, 87% (Found: C, 69.67; H, 5.42. $RuC_{58}H_{57}F_4P_2B$ requires C, 69.39; H, 5.72%.); conductivity (acetone, 20 °C) 112 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (BF_4^-) 1057s (KBr); δ_P ($CDCl_3$) 34.18 and 39.07 (d, ^2J(PP) = 22.5 Hz); δ_H ($CDCl_3$) 0.62, 0.71, 0.86 and 1.05 (s, 3H each, CH_3), 1.15, 1.22 and 1.44 (m, 2H each, CH_2), 1.59 (m, 1H, CH), 4.04 (s, 1H, Ru=C=CH), 5.39 and 5.57 (br, 1 H each, H-1 and H-3), 5.45 and 5.60 (d, 1H each, ^3J(HH) = 8.3 Hz, H-4, H-5, H-6 or H-7), 5.99 (br, 1H, H-2), 6.53–7.50 (m, 32H, Ph and H-4, H-5, H-6 or H-7); δ_C ($CDCl_3$) 18.04, 22.48, 25.42 and 26.53 (s, CH_3), 25.08, 32.99 and 39.97 (s, CH_2), 44.24 and 51.23 (s, C), 49.29 (s, CH), 53.51 (s, C_γ), 78.85 and 81.00 (d, ^2J(CP) = 8.5 Hz, C-1 and C-3), 99.04 (s, C-2), 113.71 (d, ^2J(CP) = 2.4 Hz, C-3a or C-7a), 116.84 (s, C_β), 120.24 (s, C-3a or C-7a), 122.03 and 124.58 (s, C-4, C-5, C-6 or C-7), 128.24–134.23 (m, Ph and C-4, C-5, C-6 or C-7), 342.06 (dd, ^2J(CP) = 17.7 and 15.3 Hz, Ru=C_α). **3d:** Yield: 1.00 g, 92% (Found: C, 71.57; H 5.36. $RuC_{65}H_{59}F_4P_2B$ requires C, 71.62; H, 5.45%.); conductivity (acetone, 20 °C) 115 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (BF_4^-) 1057s, (C≡C) 2205w (KBr); δ_P (CD_2Cl_2) 36.68 and 39.10 (d, ^2J(PP) = 21.7 Hz); δ_H (CD_2Cl_2) 0.77 (s, 3H, CH_3), 1.35 (s, 6H, CH_3), 1.18–1.25 (m, 3H, CH_2), 1.42 (m, 2H, CH_2), 1.77 (m, 1H, CH_2), 2.17 (m, 1H, CH), 4.05 (s, 1H, Ru=C=CH), 5.36 and 5.44 (br, 1H each, H-1 and H-3), 5.69 and 5.79 (d, 1H each, ^3J(HH) = 7.9 Hz, H-4, H-5, H-6 or H-7), 6.20 (br, 1H, H-2), 6.84–7.50 (m, 37H, Ph and H-4, H-5, H-6 or H-7); δ_C (CD_2Cl_2) 19.72, 25.29 and 30.51 (s, CH_3), 25.86, 30.51 and 42.12 (s, CH_2), 46.50 and 52.26 (s, C), 49.23 (s, CH), 56.40 (s, C_γ), 79.31 and 80.40 (d, ^2J(CP) = 8.0 Hz, C-1 and C-3), 86.44 (s, *C*≡CPh), 94.52 (s, C≡*C*Ph), 99.50 (s, C-2), 112.23 (s, C_β), 116.68 and 118.76 (s, C-3a and C-7a), 123.46–134.29 (m, Ph, C-4, C-5, C-6 and C-7), 347.75 (dd, ^2J(CP) = 17.1 and 17.1 Hz, Ru=C_α).

Spectroscopic characterization of HC≡CC(C_9H_{16})H 4a. In an NMR-tube, the vinylidene complex **3a** (0.099 g, 0.1 mmol) was dissolved in acetonitrile-d_3 (*ca.* 0.7 cm^3). After 5 h at room temperature, the terminal alkyne **4a** and [Ru(N≡CCD_3)(η^5-C_9H_7)-(PPh_3)$_2$][BF_4] were formed in almost quantitative yield. δ_H (CD_3CN) 0.99, 1.00 and 1.11 (s, 3H each, CH_3), 1.21, 1.40, 1.54 and 1.74 (m, 1H each, CH_2), 1.65 (m, 2H, CH_2), 2.12 (dd, 1H, ^4J(HH) = 2.4 and 2.4 Hz, CH), 2.25 (m, 1H, CH), 2.35 (d, 1H, ^4J(HH) = 2.4 Hz, ≡CH); δ_C (CD_3CN) 20.58, 24.46 and 31.78 (s, CH_3), 26.61, 29.28 and 44.15 (s, CH_2), 39.71 and 50.07 (s, C), 49.26 and 51.33 (s, CH), 73.57 (s, C≡*C*H), 84.60 (s, *C*≡CH).

HC≡CC(C_9H_{16})R (R = C≡N 4b, Me 4c, C≡CPh 4d). *General procedure.* A solution of the corresponding vinylidene complex [Ru{=C=C(H)C(C_9H_{16})R}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] **3b**–**d** (1 mmol) in 40 cm^3 of acetonitrile was stirred at room temperature for 5 h. The solvent was then removed under vacuum and the solid residue extracted with diethyl ether (*ca.* 60 cm^3) and filtered through silica-gel. A yellow solid containing mainly the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] **5** remained insoluble. The extract was evaporated to dryness yielding terminal alkynes **4b**–**d**. **4b:** Yield: 0.14 g (yellow solid), 77% (Found: C, 83.47; H, 9.08; N, 7.34. $C_{13}H_{17}N$ requires C, 83.37; H, 9.15; N, 7.48%.); ν_{max}/cm^{-1} (C≡C) 2070w, (C≡N) 2236w, H–C≡) 3251s (KBr); δ_H (C_6D_6) 0.91, 1.14 and 1.30 (s, 3H each, CH_3), 0.99, 1.05, 1.61 (m, 1H each, CH_2), 1.36 (m, 2H, CH_2), 1.75 (m, 2H, CH_2 and CH), 1.91 (s, 1H, ≡CH); δ_C (C_6D_6) 18.75, 24.89 and 29.73 (s, CH_3), 25.60, 29.78 and 42.08 (s, CH_2), 43.74 and 52.15 (s, C), 48.83 (s, CH), 54.82 (s, *C*C≡CH), 75.47 (s, C≡*C*H), 78.55 (s, *C*≡CH), 118.69 (s, C≡N). **4c:** Yield: 0.14 g (colourless oil), 82 %; ν_{max}/cm^{-1} (C≡C) 2104w, (H–C≡) 3314s (Nujol); δ_H (C_6D_6) 0.83, 1.05, 1.11 and 1.20 (s, 3H each, CH_3), 0.94, 1.15, 1.32 and 1.74 (m, 1H each, CH_2), 1.52 (m, 2H, CH_2), 1.98 (s, 1H, ≡CH), 2.25 (m, 1H, CH); δ_C (C_6D_6) 17.82, 22.88, 26.55 and 26.79 (s, CH_3), 25.96, 33.85 and 40.63 (s, CH_2), 42.57 and 47.63 (s, C), 50.09 (s, CH), 52.11 (s, *C*C≡CH), 71.95 (s, C≡*C*H), 89.35 (s, *C*≡CH); HRMS *m*/*z* calcd. for $C_{13}H_{20}$ (found) 176.156545 (176.157256). **4d:** Yield: 0.23 g (colourless oil), 89%; ν_{max}/cm^{-1} (C≡C) 2111w, (C≡C) 2164w, (H–C≡) 3324s (Nujol); δ_H (C_6D_6) 1.22 (m, 1H, CH_2), 1.36, 1.44, 1.62 (s, 3H each, CH_3), 1.24–1.42 and 1.75–1.83 (m, 2H each, CH_2), 2.16 (m, 1H, CH_2), 2.17 (s, 1H, ≡CH), 2.26 (m, 1H, CH), 7.05–7.41 (m, 5H, Ph); δ_C (C_6D_6) 19.45, 26.12 and 30.04 (s, CH_3), 26.38, 31.17 and 42.35 (s, CH_2), 44.50 and 51.45 (s, C), 49.64 (s, CH), 55.31 (s, *C*C≡CH), 73.03 (s, C≡*C*H), 83.82 and 85.33 (s, *C*≡CH and *C*≡CPh), 91.15 (s, C≡*C*Ph), 128.05, 128.50 and 132.02 (s, CH of Ph), 138.81 (C of Ph); HRMS *m*/*z* calcd. for $C_{20}H_{22}$ (found) 262.172241 (262.172151).

[Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] 9. To a solution of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] **6** (0.776 g, 1 mmol) in 50 cm^3 of MeOH were added $NaPF_6$ (0.336 g, 2 mmol) and (1*R*,2*S*,4*R*)-2-ethynyl-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol **7** (0.356 g, 2 mmol). The reaction mixture was heated under reflux for 30 min. The solvent was then removed under vacuum, the crude product extracted with CH_2Cl_2, and the extract filtered. Concentration of the resulting solution to *ca.* 5 cm^3 followed by the addition of 50 cm^3 of diethyl ether precipitated a red solid, which was washed with diethyl ether (2 × 20 cm^3) and dried *in vacuo*. Yield: 0.84 g, 80% (Found: C, 64.93; H 5.09. $RuC_{57}H_{53}F_6P_3$ requires C, 64.45; H, 5.09%.); conductivity (acetone, 20 °C) 138 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (=C=C=C) 1963s, (PF_6^-) 838s (KBr); δ_P ($CDCl_3$) 47.09 and 47.21 (d, ^2J(PP) = 23.2 Hz); δ_H ($CDCl_3$) 1.04, 1.05 and 1.14 (s, 3H each, CH_3), 1.30, 1.53, 1.62 and 1.86 (m, 1H each, CH_2), 1.77 (m, 2H, CH_2), 2.27 (m, 1H, CH), 5.19 (br, 2H, H-1 and H-3), 5.35 (br, 1H, H-2), 6.28 and 6.36 (d, 1H each, ^3J(HH) = 7.7 Hz, H-4, H-5, H-6 or H-7), 6.91–7.67 (m, 32H, Ph and H-4, H-5, H-6 or H-7); δ_C ($CDCl_3$) 18.87, 25.19 and 26.51 (s, CH_3), 25.24, 34.38 and 44.95 (s, CH_2), 47.72 (s, CH), 57.57 and 64.34 (s, C), 83.52 and 84.60 (br, C-1 and C-3), 98.10 (s, C-2), 112.55 and 114.07 (s, C-3a and C-7a), 123.21, 124.09, 129.17 and 131.39 (s, C-4, C-5, C-6 and C-7), 123.31–135.27 (m, Ph), 183.24 (s, C_β), 202.21 (s, C_γ), 305.06 (dd, ^2J(CP) = 18.9 and 18.9 Hz, Ru=C_α).

[Ru{=C=C=C(C_9H_{14})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] 10. This complex, isolated as a red solid, was prepared as described for **9** starting from [RuCl(η^5-C_9H_7)(PPh_3)$_2$] **6** (0.776 g, 1 mmol), $NaPF_6$ (0.336 g, 2 mmol) and (1*S*,2*R*,5*S*)-2-ethynyl-4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-ol **8** (0.352 g, 2 mmol). Yield: 0.783 g, 75% (Found: C, 62.33; H 4.56. $RuC_{57}H_{51}F_6P_3 \cdot 3/4CH_2Cl_2$ requires C, 62.61; H, 4.77%.); conductivity (acetone, 20 °C) 123 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (=C=C=C) 1959s, (PF_6^-) 840s (KBr); δ_P ($CDCl_3$) 47.99 (br); δ_H ($CDCl_3$) 0.79, 1.27 and 1.85 (s, 3H each, CH_3), 2.14 and 2.86 (br, 1H each, CH), 2.58 and 2.65 (br, 1H each, CH_2), 5.13 (br, 2H, H-1 and H-3), 5.45 (br, 1H, H-2), 5.83 (br, =CH), 6.14 (m, 2H, H-4, H-5, H-6 or H-7), 6.92–7.35 (m, 32H, Ph and H-4, H-5, H-6 or H-7); δ_C ($CDCl_3$) 21.69, 25.33 and 27.21 (s, CH_3), 42.34 (s, CH_2), 51.78 and 60.19 (s, CH), 57.59 (s, C), 82.89 and 83.15 (s, C-1 and C-3), 96.72 (s, C-2), 111.02 and 111.68 (s, C-3a and C-7a), 122.70, 123.06, 128.87 and 129.77 (s, C-4, C-5, C-6 and C-7), 128.03–135.16 (m, Ph), 128.45 (s, =CH), 169.05 (s, =C), 174.75 (s, C_β), 184.47 (s, C_γ), 280.16 (dd, ^2J(CP) = 20.2 and 20.2 Hz, Ru=C_α).

[Ru{C≡CC(C_9H_{15})}(η^5-C_9H_7)(PPh_3)$_2$] 11. KO^{t}Bu (0.146 g, 1.3 mmol) was added, at −20 °C, to a solution of [Ru{=C=C=

$C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ **9** in 60 cm^3 of THF. The mixture was slowly warmed to room temperature, and the solvent was then removed *in vacuo*. The resulting solid residue was dissolved in diethyl ether (*ca.* 20 cm^3) and filtered through Al_2O_3 (neutral; activity grade I). Removal of the solvent gave the σ-enynyl complex **11** as an orange solid. Yield: 0.87 g, 87% (Found: C, 75.81; H 5.82. $RuC_{55}H_{45}P_2$ requires C, 76.07; H, 5.82%.); ν_{max}/cm^{-1} (C≡C) 2060w (KBr); δ_P (C_6D_6) 51.47 and 52.26 (d, ^2J(PP) = 29.5 Hz); δ_H (C_6D_6) 0.92 and 1.39 (s, 3H each, CH_3), 1.20 (br, 4H, CH_3 and CH_2), 1.36, 1.66 and 2.05 (m, 1H, each, CH_2), 2.42 (dd, 1 H, ^3J(HH) = 3.3 and 3.3 Hz, CH), 4.65 and 4.70 (d, 1H each, ^3J(HH) = 2.6 Hz, H-1 and H-3), 5.57 (dd, 1H, ^3J(HH) = 2.6 and 2.6 Hz, H-2), 5.94 (d, 1H, ^3J(HH) = 3.3 Hz, =CH), 6.33 and 6.66 (m, 2H each, H-4, H-5, H-6 and H-7), 6.87–7.70 (m, 30H, Ph); δ_C (C_6D_6) 13.51, 20.52 and 20.62 (s, CH_3), 27.12 and 32.10 (s, CH_2), 51.87 (s, CH), 55.71 and 56.15 (s, C), 74.82 (d, ^2J(CP) = 6.5 Hz, C-1 or C-3), 75.02 (d, ^2J(CP) = 7.6 Hz, C-1 or C-3), 95.55 (s, C-2), 109.04 and 109.72 (s, C-3a and C-7a), 110.21 (s, C_β), 113.14 (dd, ^2J(CP) = 25.1 and 25.1 Hz, Ru–C_α), 122.86, 123.29, 125.73 and 126.12 (s, C-4, C-5, C-6 and C-7), 127.30–139.01 (m, Ph and C=CH).

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