

Unusual activation of 1-ethynyl-1-cyclohexanol by $[\text{RuCl}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2]$: synthesis and reactivity of the allenylidene derivative $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$

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The reaction of $[\text{RuCl}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2]$ with an excess of 1-ethynyl-1-cyclohexanol and NaPF_6 in refluxing methanol yielded the allenylidene complex $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **1** via an unprecedented coupling of two molecules of the propargyl (prop-2-ynyl) alcohol derivative. Complex **1** can also be obtained by reaction of the vinylvinylidene derivative $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **2** ($\text{R} = 1\text{-cyclohexenyl}$) with 1-ethynyl-1-cyclohexanol or 1-ethynylcyclohexene in refluxing methanol. The behaviour of **2** towards other 1-alkyn-3-ols has been studied but only the replacement of the vinylidene moiety by the propargyl alcohols, via an $\eta^1\text{-vinylidene}-\eta^2\text{-alkyne}$ tautomerization process, to generate both vinylvinylidene $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ ($\text{R} = 1\text{-cyclopentenyl}$, 1-cycloheptenyl or 1-cyclooctenyl) or allenylidene $[\text{Ru}(\text{C}=\text{C}=\text{CR}_2)(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ ($\text{R} = \text{Ph}$ or $\text{R}_2 = 2,2'\text{-biphenyldiyl}$) complexes along with 1-ethynylcyclohexene was observed. A similar 1,3-enyne elimination also takes place in the reaction of **2** with phenylacetylene or acetonitrile to afford $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ and $[\text{Ru}(\text{N}=\text{CMe})(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$, respectively. On the basis of these observations a mechanism for the formation of **1** is proposed. The allenylidene complex **1** regioselectively reacts with NaR , in THF at -20°C , to yield the neutral $\sigma\text{-alkynyl}$ derivatives $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{C}_{13}\text{H}_{20})\text{R}\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2]$ ($\text{R} = \text{C}\equiv\text{N}$ or OMe). Protonation of the $\text{R} = \text{CN}$ derivative with $\text{HBF}_4\cdot\text{Et}_2\text{O}$, in diethyl ether at -20°C , afforded the cationic vinylidene complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{C}(\text{C}_{13}\text{H}_{20})\text{C}\equiv\text{N}\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$. In contrast, protonation with $\text{R} = \text{OMe}$ gives back the starting allenylidene derivative **1**.

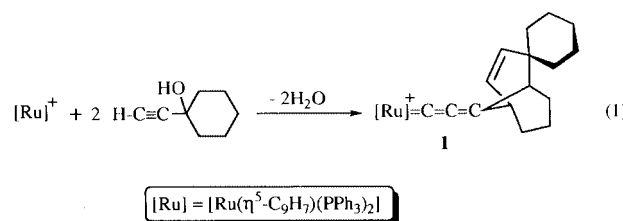
Introduction

The chemistry of ruthenium(II) complexes containing unsaturated carbene ligands $[\text{Ru}=(\text{C}=\text{C})_n\text{CR}_2]$ ("metallacumulenes") has received increasing attention in recent years. In particular, important developments have been achieved by using the ability of vinylidene derivatives (the simplest members of the series, $n = 1$)¹ to promote selective carbon-carbon coupling reactions.² They have also been shown to be active species in several catalytic transformations involving terminal alkynes,³ and useful catalysts for ring opening metathesis polymerization (ROMP) and ring closing-metathesis (RCM) of cyclic or acyclic olefins.³ In contrast, the chemistry of the higher members of this series has been less developed in spite of their potential utility in synthesis due to the presence of a cumulene system and the metal-carbon double bond.¹ In this context, ruthenium(II) allenylidene complexes $[\text{Ru}=\text{C}=\text{C}=\text{CR}_2]$ developed⁴ are excellent substrates for regio- and/or stereo-selective C-C and carbon-heteroatom coupling processes.⁵ More recently, Dixneuf and co-workers⁶ have found that the cationic allenylidene ruthenium(II) derivatives $[\text{Ru}(\text{Cl})(=\text{C}=\text{C}=\text{CR}_2)(\text{PR}_3)(\eta^6\text{-arene})]^+$ are appropriate catalysts for the RCM of olefins.

Following the well established Selegue methodology,⁷ we have recently reported the synthesis of a large variety of indenylruthenium(II) allenylidene complexes using propargyl (prop-2-ynyl) alcohol derivatives as a source of the unsaturated carbene moiety (Chart 1; Path I).⁸ We have also shown that vinylvinylidene complexes can be selectively obtained from 1-ethynyl-1-cycloalkanols, via the initial formation of unstable allenylidene species which rapidly undergo a tautomerization

process through a formal [1,3]-H shift (Chart 1; Path II) to the thermodynamically more stable vinylvinylidene derivatives.^{9,10}

In the course of these studies we have found that the activation of 1-ethynyl-1-cyclohexanol by the metal fragment $[\text{Ru}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2]^+$ proceeds through a different pathway. Thus, we have preliminarily reported the formation of an allenylidene moiety containing a spiro-bicyclic fragment **1** which results from the metal promoted double dehydration of two molecules of the 1-alkyn-3-ol, see eqn. (1).¹¹



In order to ascertain the scope of this unexpected reaction and explore the reactivity of the unprecedented allenylidene complex **1**, we have now studied (a) alternative synthetic approaches to **1** and (b) its utility as a source of functionalized alkynyl (**A**) and vinylidene derivatives (**B**) (Chart 2). A mechanistic account of the formation of complex **1** is proposed and a series of exchange processes of the cyclohexenylvinylidene moiety in the complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_6\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **2** ($\text{R} = 1\text{-cyclohexenyl}$) leading to the formation of other unsaturated carbene complexes is also reported.

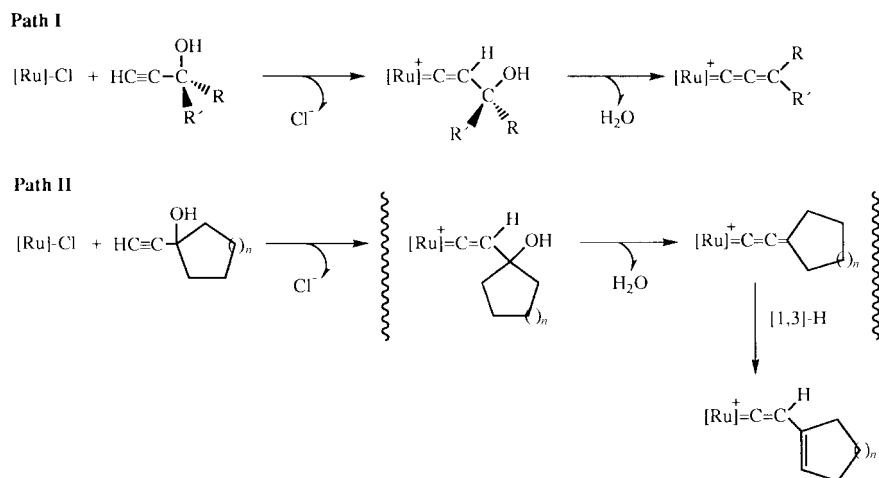


Chart 1

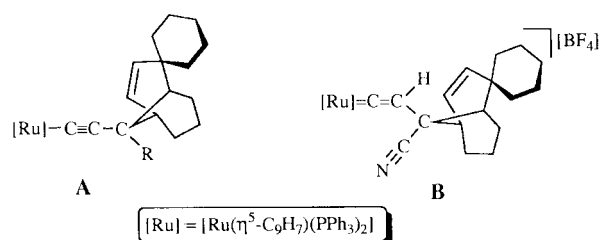


Chart 2

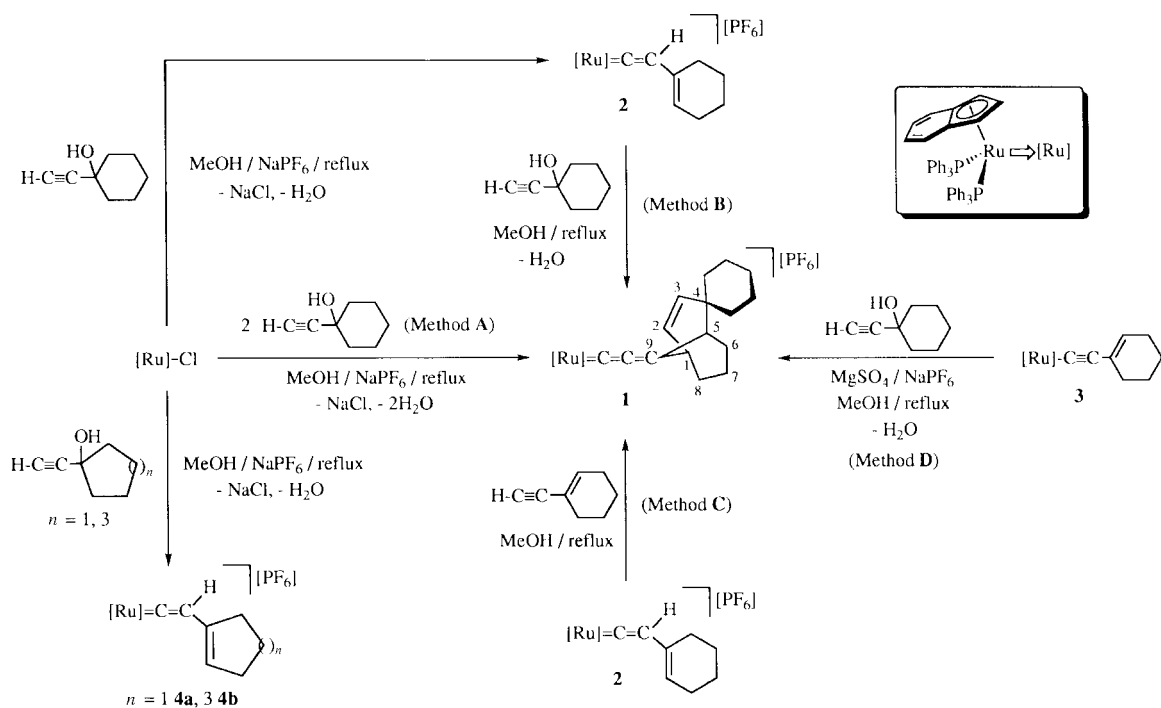
Results

Synthesis and characterization of $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}\text{-(}\eta^5\text{-C}_9\text{H}_7\text{)}(\text{PPh}_3)_2][\text{PF}_6]$ **1**

The reaction of $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ with an excess of 1-ethynyl-1-cyclohexanol, in refluxing methanol (*ca.* 12 h) and in the presence of NaPF_6 , results in the formation of the cationic allenylidene complex $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}\text{-(}\eta^5\text{-C}_9\text{H}_7\text{)}(\text{PPh}_3)_2][\text{PF}_6]$ **1** which has been isolated as an air-stable orange solid (55% yield) (Scheme 1; method A).

Compound **1** is soluble in chlorinated solvents and tetrahydrofuran and has been characterized by microanalysis, conductance measurements, mass spectrometry (FAB), IR and NMR ($^{31}\text{P}\text{-}\{^1\text{H}\}$, ^1H and $^{13}\text{C}\text{-}\{^1\text{H}\}$) spectroscopy (details are given in the Experimental section). The structure has been confirmed unequivocally by X-ray crystallography.¹¹ Complex **1** consists of a cationic indenylruthenium(II) allenylidene containing a spiro(bicyclo[3.3.1]non-2-en-9-ylidene-4-cyclohexane) moiety, with the 9-carbon atom being C_γ of the unsaturated chain (see Scheme 1 for numbering of the bicyclic skeleton). The IR spectrum (KBr) exhibits, in addition to the expected absorption for the hexafluorophosphate anion (839 cm^{-1}), a strong $\nu(\text{C}=\text{C}=\text{C})$ band (asymmetric stretching vibration) at 1940 cm^{-1} . The ^1H and $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectra also support the formation of the spiro-bicyclic allenylidene moiety (see the Experimental section). In particular the following features are noted: (i) the typical carbene $\text{Ru}=\text{C}_\alpha$ low-field resonance in the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum which appears as a virtual triplet at $\delta_{\text{C}} 304.48$ ($^2J(\text{CP}) = ^2J(\text{CP}') = 19.4\text{ Hz}$), and (ii) the expected singlet resonances of the C_β and C_γ carbons at $\delta_{\text{C}} 186.83$ and 191.07 .

Complex **1** is also formed (69% yield) by treatment of the



Scheme 1

vinylvinylidene complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **2** (R = 1-cyclohexenyl) with an excess of 1-ethynyl-1-cyclohexanol (*ca.* 3:1) in refluxing methanol (*ca.* 12 h) (Scheme 1; method B). It is worth mentioning that on monitoring this reaction by $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy no intermediate species was observed. Since complex **2** is generated by the treatment of $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ with 1-ethynyl-1-cyclohexanol in refluxing methanol (*ca.* 30 min),⁹ it is apparent that **2** is a transient species in the formation of **1**, eqn. (1), being able to activate the formal addition and the dehydration of a second molecule of the alkyne. Allenylidene complex **1** can be also obtained (71% yield) by reaction of **2** with the 1,3-enyne 1-ethynyl-1-cyclohexene which actually is acting as the dehydrated species of the parent 1-ethynyl-1-cyclohexanol (Scheme 1; method C). Similarly, the reaction of the neutral σ -enynyl complex $[\text{Ru}(\text{C}\equiv\text{CR})(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ **3** (R = 1-cyclohexenyl)⁹ with 1-ethynyl-1-cyclohexanol, in refluxing methanol and in the presence of MgSO_4 and NaPF_6 , also gives complex **1** (63% yield) (Scheme 1; method D).

Attempts to form similar allenylidene complexes from $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ using an excess of analogous 1-ethynyl-1-cycloalkanol $\text{HC}\equiv\text{C}(\text{OH})\text{CH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2$ ($n = 1$ or 3), under similar reaction conditions, have been unsuccessful (Scheme 1). The reactions lead instead to the formation of the corresponding vinylvinylidene complexes $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ (R = 1-cyclopentenyl **4a** or 1-cycloheptenyl **4b**) in good yields.⁹

Reactions of $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **2** (R = 1-cyclohexenyl) with 1-alkyn-3-ols

Since the direct synthetic approach for allenylidene complexes analogous to **1** from $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ is only suitable for 1-ethynyl-1-cyclohexanol, an alternative procedure was envisaged. Thus, given that the vinylvinylidene complex **2** is an intermediate in the formation of complex **1**, being able to couple one further molecule of 1-ethynyl-1-cyclohexanol, its reaction was tested with other 1-ethynyl-1-cycloalkanol in order to achieve analogous mixed coupling reactions. However, the processes proceed through a different pathway showing that the vinylidene moiety in **2** is remarkably labile being easily replaced by the 1-alkyn-3-ol derivatives (Scheme 2).

Thus, the treatment of complex **2** with an excess of 1-ethynyl-1-cyclopentanol, -1-cycloheptanol or -1-cyclooctanol (*ca.* 10:1) in refluxing methanol (*ca.* 3 h) results in clean formation of the vinylvinylidene derivatives $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ (R = 1-cyclopentenyl **4a**,⁹ 1-cycloheptenyl **4b**⁹ or 1-cyclooctenyl **4c**) (65–85% yield). The concomitant elimination of 1-ethynylcyclohexene was detected by GC of the crude reaction

mixtures (Scheme 2). No products resulting from a formal coupling between **2** and the cyclic alkynols analogous to **1** were observed even when a longer reaction time was used.

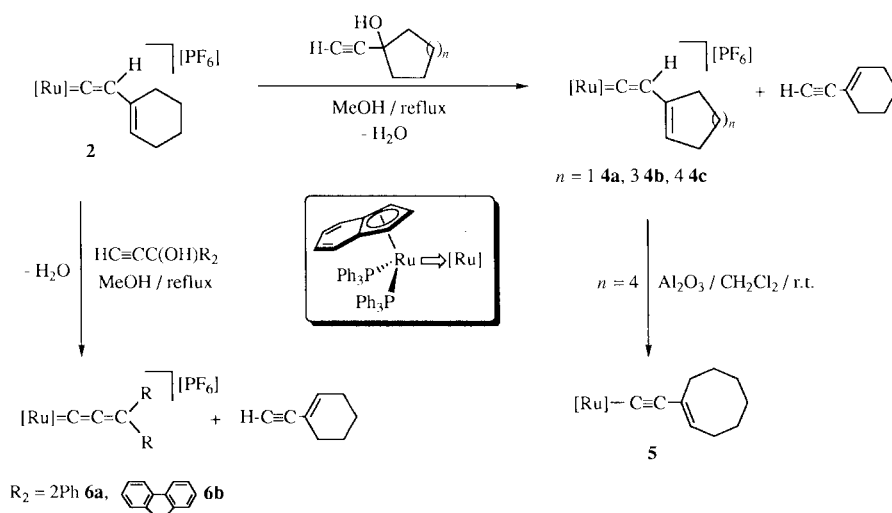
The novel vinylvinylidene complex **4c** (81% yield) has been fully characterized by elemental analysis, IR and NMR ($^{31}\text{P}\{-^1\text{H}\}$, ^1H and $^{13}\text{C}\{-^1\text{H}\}$) spectroscopy, showing similar spectroscopic properties to those reported for **2** and **4a**,**4b**.⁹ In particular, the most remarkable features of the NMR spectra are: (i) (^1H) the singlet and triplet resonances at δ_{H} 4.82 and 5.27 ($J(\text{HH}) = 8.4$ Hz) of the $\text{Ru}=\text{C}=\text{CH}$ and $=\text{CH}$ protons, respectively, and (ii) ($^{13}\text{C}\{-^1\text{H}\}$) the typical low-field triplet resonance of the carbenic atom $\text{Ru}=\text{C}_\alpha$ at δ_{C} 355.29 ($^2J(\text{CP}) = 16.5$ Hz) as well as the expected C_β and olefinic singlet resonances at δ_{C} 120.99 (C_β), 125.81 ($=\text{CH}$) and 126.44 ($=\text{C}$). The proposed structure for **4c** was also assessed by studying its reactivity. Thus, the acidic vinylidene proton can easily be abstracted by treatment of a dichloromethane solution with Al_2O_3 to afford the neutral σ -enynyl derivative $[\text{Ru}(\text{C}\equiv\text{CR})(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ **5** (R = 1-cyclooctenyl) which is isolated (89% yield) as an air-stable orange solid (Scheme 2). The presence of the enynyl group in **5** is clearly confirmed by the appearance of (i) a $\nu(\text{C}\equiv\text{C})$ absorption band at 2067 cm^{-1} in the IR spectrum (KBr), and (ii) typical resonances for the $\text{Ru}-\text{C}_\alpha$, C_β and C_γ carbon atoms in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra at δ_{C} 103.82 ($^2J(\text{CP}) = 25.4$ Hz), 116.99 and 129.68, respectively, the $=\text{CH}$ carbon resonance falling within the aromatic region.

The lability of the cyclohexenylvinylidene moiety in complex **2** is confirmed by reactions with 1,1-diphenyl-2-propyn-1-ol and 9-ethynyl-9-fluorenyl which generate the previously reported allenylidene derivatives $[\text{Ru}(\text{C}=\text{C}=\text{CR}_2)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ (R = Ph **6a** (78% yield), $\text{R}_2 = 2,2'$ -biphenyldiyl **6b** (69% yield))^{8a} (Scheme 2).

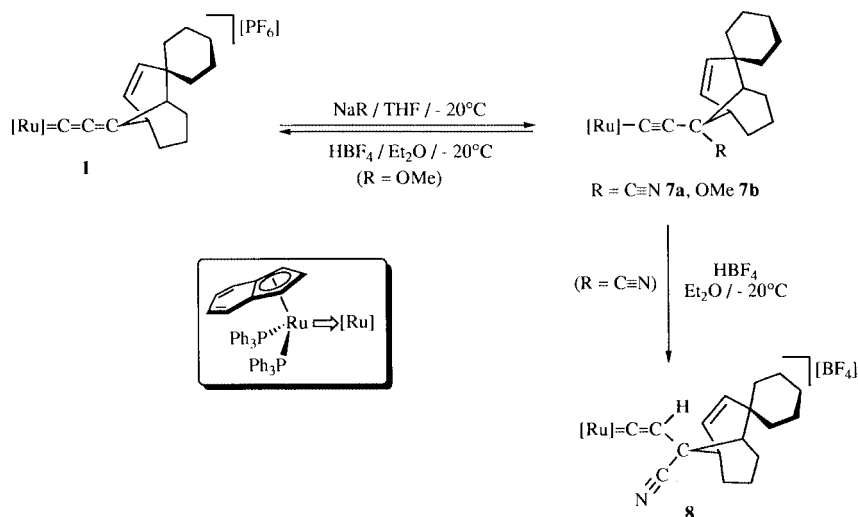
Reactivity of $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **1**: Synthesis of σ -alkynyl complexes $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{C}_{13}\text{H}_{20})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ (R = C \equiv N **7a** or OMe **7b**) and the vinylidene complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{C}(\text{C}_{13}\text{H}_{20})\text{C}\equiv\text{N}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$ **8**

The allenylidene complex $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **1** regioselectively reacts with an equimolar amount of NaR (R = C \equiv N or OMe), in THF at -20°C to afford the neutral σ -alkynyl derivatives $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{C}_{13}\text{H}_{20})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ (R = C \equiv N **7a** or OMe **7b**) isolated in 53 and 68% yield, respectively (Scheme 3).

Complexes **7a**,**7b** have been analytically and spectroscopically characterized. The formation of the alkynyl chain is clearly confirmed by the appearance in the IR spectra (KBr) of a $\nu(\text{C}\equiv\text{C})$ absorption at 2082 cm^{-1} **7a** and 2056 cm^{-1} **7b**. The $^{31}\text{P}\{-^1\text{H}\}$



Scheme 2



Scheme 3

NMR spectra display two doublet signals (AB system) (**7a**: δ 51.11 and 51.52 ($^2J(\text{PP}) = 31.4$ Hz); **7b**: 50.30 and 52.43 ppm ($^2J(\text{PP}) = 31.3$ Hz)). The non-equivalence of the phosphorus nuclei is due to the presence of stereogenic centres on the spiro-bicyclic fragment. The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra are consistent with the proposed formulations (details in the Experimental section). The most remarkable features in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra are: (i) the characteristic virtual triplet resonance (*ca.* $^2J(\text{CP}) = ^2J(\text{CP}') = 24$ Hz) for the Ru- C_α carbon nucleus (δ_{C} 98.34 **7a** and 90.71 **7b**), and (ii) the singlet resonances of C_β (δ_{C} *ca.* 109 **7a** and 114.85 **7b**), C_γ (δ_{C} *ca.* 40.00 **7a** and 74.51 **7b**), as well as $\text{C}\equiv\text{N}$ (**7a**, δ_{C} 123.44) and OMe (**7b**, δ_{C} 47.63) carbon nuclei.

Addition of electrophiles to the C_β of σ -alkynyl complexes has been described as one of the most versatile entries into vinylidene derivatives.¹ Thus, the protonation of **7a** with an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, in diethyl ether at -20°C , yields the monosubstituted cationic vinylidene complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{C}(\text{C}_{13}\text{H}_{20})\text{C}\equiv\text{N}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$ **8** (76% yield) (Scheme 3). Analytical and spectroscopic data are in accord with the proposed formulation (see the Experimental section). In particular, the presence of the vinylidene moiety was identified, as usual, on the basis of: (i) (^1H NMR) the singlet resonance of the Ru=C=CH proton (δ_{H} 4.14), and (ii) ($^{13}\text{C}\{-^1\text{H}\}$ NMR) the low-field resonance of the carbene carbon Ru= C_α (δ_{C} 340.90) which appears as a virtual triplet ($^2J(\text{CP}) = ^2J(\text{CP}') = 15.7$ Hz). In contrast, the treatment of **7b** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ gives back the precursor allenylidene derivative **1** in almost quantitative yield (Scheme 3). It is interesting that the elimination of methanol also occurs in the reactions of the analogous indenylruthenium(II) methoxyalkynyl complexes $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{OMe})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)\text{L}_2]$ with acids.¹²

Discussion

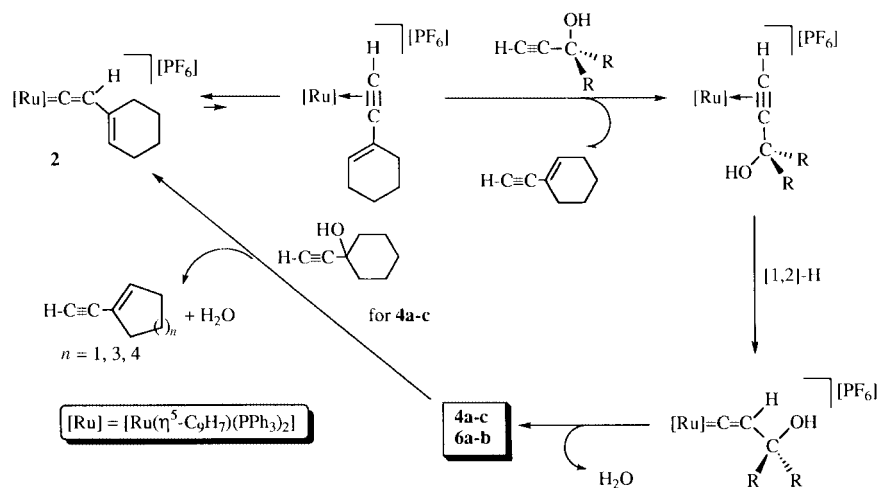
Reactions with 1-ethynyl-1-cycloalkanols

The activation of cyclic or acyclic propargylic alcohols $\text{HC}\equiv\text{CC}(\text{OH})\text{R}^1\text{R}^2$ by ruthenium(II) chloride derivatives is a well known synthetic methodology for either vinylvinylidene or allenylidene complexes which are selectively formed depending on the nature of the alcohol. To date a wide series of derivatives such as *trans*- $[\text{RuCl}_2\text{L}_2]$ ($\text{L}_2 = \text{dppm}$ or dppe),¹³ $[\text{RuCl}(\eta^5\text{-C}_5\text{R}_5)\text{L}_2]$ ^{5f,k,7,10a,c} and $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{L}_2]$ ^{8,9} have been shown to promote such a type of transformation. In particular, we have reported the synthesis of vinylvinylidene complexes $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)\text{L}_2][\text{PF}_6]$ ($\text{L} = \text{PPh}_3$, $\text{L}_2 = \text{dppe}$; $\text{R} = 1\text{-cyclopentenyl}$, 1-cyclohexenyl or $1\text{-cyclo-$

heptenyl) which are rapidly formed in refluxing methanol by the reaction of $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{L}_2]$ with cyclic alkynols $\text{HC}\equiv\text{CC}(\text{OH})\text{CH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2$ ($n = 1, 2$ or 3) in the presence of NaPF_6 .⁹ Although a longer treatment does not affect the process with the cyclic pentanol and heptanol derivatives, nonetheless the reaction of $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ with 1-ethynyl-1-cyclohexanol in refluxing methanol for 12 h gives the novel allenylidene complex **1** containing the spiro-bicyclic fragment [3.3.1]non-2-en-9-ylidene (Scheme 1). The formation of **1** is the result of the formal addition of two dehydrated molecules of 1-ethynyl-1-cyclohexanol to the metal auxiliary $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]^+$ via an unusual metal-promoted double dehydration of the alkynol, eqn. (1).

At present we are unable to give a plausible explanation for this unprecedented and selective transformation of 1-ethynyl-1-cyclohexanol which does not occur for the rest of the cyclic alkynols. Apparently, this coupling reaction is controlled by the thermodynamic stability of the allenylidene complex **1** which in contrast seems to be less favourable with respect to the formation of the corresponding vinylvinylidene complex for the analogous cyclic alkynols. This is confirmed by the selective formation of **1** starting either from the cyclohexenylvinylidene complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **2** ($\text{R} = 1\text{-cyclohexenyl}$) (Scheme 1; methods **B** and **C**) or the σ -enynyl derivative $[\text{Ru}(\text{C}\equiv\text{CR})(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ **3** ($\text{R} = 1\text{-cyclohexenyl}$) (Scheme 1; method **D**). These transformations are rapid and thermodynamically favourable since by monitoring the reactions by $^{31}\text{P}\{-^1\text{H}\}$ NMR no transient species other than the starting and final complexes are observed. They shed light on the first steps of the reaction pathway (see below).

It is apparent that mixed coupling reactions between the cyclohexenylvinylidene complex **2** and cyclic alkynols $\text{HC}\equiv\text{CC}(\text{OH})\text{CH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2$ ($n = 1, 3$ or 4) are also thermodynamically disfavoured (Scheme 2). They proceed through dehydration of the parent alcohol leading to the formation of vinylvinylidene complexes **4a–4c** and 1-ethynylcyclohexene. These processes can be described as a formal exchange of the cyclohexenylvinylidene moiety $=\text{C}=\text{C}(\text{H})(\text{C}_6\text{H}_9)$ by the analogous $=\text{C}=\text{C}(\text{H})\text{R}$ ($\text{R} = 1\text{-cyclopentenyl}$, 1-cycloheptenyl or 1-cyclooctenyl). Similarly, **2** undergoes an analogous exchange process by the allenylidene moiety $=\text{C}=\text{C}=\text{CR}_2$ to give allenylidene complexes **6a,6b** and 1-ethynylcyclohexene by reactions with acyclic alkynols $\text{HC}\equiv\text{CC}(\text{OH})\text{R}_2$ ($\text{R}_2 = 2\text{Ph}$ or $2,2'\text{-biphenyldiyl}$). Although no intermediate products could be detected by $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy, the formation of complexes **4a–4c** and **6a,6b** may be understood (Scheme 4) assuming that, in refluxing methanol, the vinylvinylidene



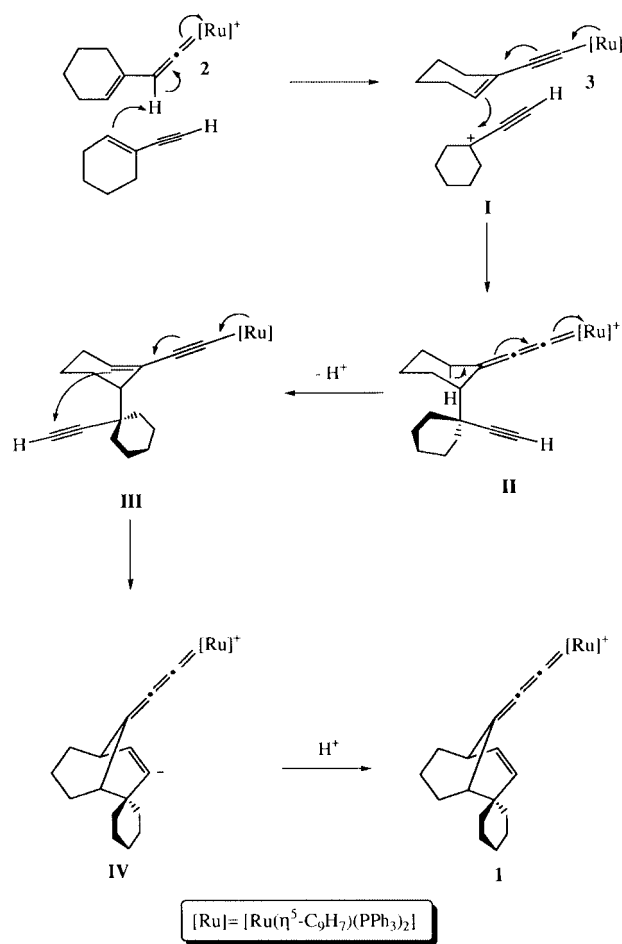
Scheme 4

derivative **2** is in equilibrium with undetectable concentrations of its η^2 -co-ordinated 1,3-enyne tautomer $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CR})(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ ($\text{R} = 1\text{-cyclohexenyl}$)^{2b,8b,14†} which undergoes rapid substitution of the 1-ethynylcyclohexene ligand by the 1-alkyn-3-ol present in the reaction media to afford the corresponding $[\text{Ru}(\eta^2\text{-HC}\equiv\text{C}(\text{OH})\text{R}_2)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ complex. The typical [1,2]-H shift to give the corresponding hydroxyvinylidene complex, followed by a spontaneous dehydration of this intermediate, generates the final vinylvinylidene **4a–4c** or allenylidene **6a,6b** derivatives. Probably, the favourable exchange of the η^2 -co-ordinated 1,3-enyne by the incoming alkynol is the driving force of the overall process.

In accord with the lability of the cyclohexenylvinylidene moiety based on an η^1 -vinylidene to η^2 -alkyne tautomerization, the vinylidene unit in complex **2** can be also replaced by other ligands such as phenylacetylene or acetonitrile to yield the known vinylidene complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **9**¹⁶ and the nitrile derivative $[\text{Ru}(\text{N}=\text{CMe})(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **10**,¹⁵ respectively. It should be noted that these complexes as well as **4a–4c** and **6a,6b** are quantitatively formed. Nevertheless, the addition of an excess (*ca.* 10:1) of 1-ethynyl-1-cyclohexanol or 1-ethynylcyclohexene to refluxing solutions of compounds **4a–4c**, **9** and **10** in methanol leads to quantitative formation of **2** as monitored by ³¹P-¹H and ¹H NMR spectroscopy (see Scheme 4).

Mechanistic proposal for the formation of $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **1**

With all these precedents in mind we can conclude that the allenylidene complex **1** results from the coupling between vinylvinylidene **2** and 1-ethynylcyclohexene. A mechanistic proposal is shown in Scheme 5. We assume that the first step involves transfer of the acidic vinylidene proton from **2** to the carbon-carbon double bond of the 1,3-enyne which generates the neutral σ -enynyl derivative **3**⁹ and the transient carbocation species **I**. A carbon-carbon coupling reaction between both intermediates rapidly takes place to form the allenylidene derivative **II**. The final formation of complex **1** is likely to be



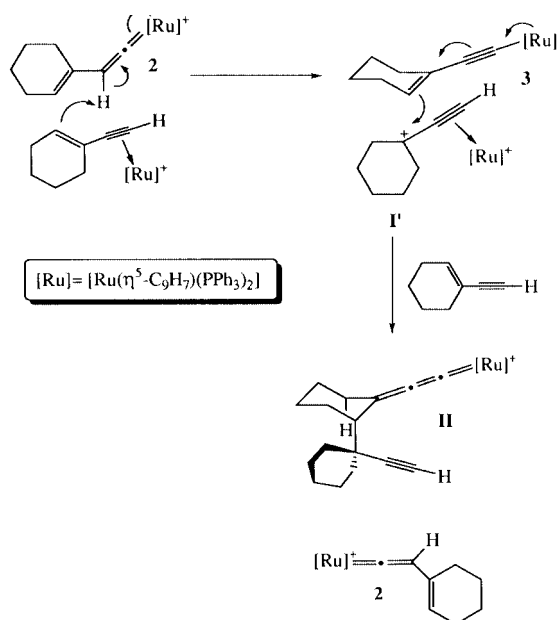
Scheme 5

based on the acidic character of the proton on the C_δ of the allenylidene fragment in **II**. Thus, an initial proton loss generates the neutral σ -enynyl intermediate **III** which undergoes an intramolecular C–C coupling process between the alkenyl and terminal alkyne functionalities to form the zwitterionic allenylidene **IV**. The final protonation of **IV** gives the observed spiro-bicyclic allenylidene complex **1**. It should be noted that related intermolecular coupling reactions between allenylidene complexes containing hydrogen atoms on the C_δ and σ -enynyl derivatives to yield dinuclear cyclic allenylidene species have been reported.^{5a,b,d,f}

† The existence of this equilibrium is confirmed in the reaction of complex **2** with PPh_3 in refluxing methanol which leads to the alkenylphosphonioderivative $(E)\text{-}[\text{Ru}\{\text{C}(\text{H})=\text{C}(\text{PPh}_3)\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ ($\text{R} = 1\text{-cyclohexenyl}$) via nucleophilic addition of PPh_3 on the co-ordinated $\text{C}\equiv\text{C}$ bond of the corresponding η^2 -1,3-enyne tautomer. See ref. 9. *Ab initio* molecular orbital (MO) calculations on the model $[\text{Ru}(\text{C}=\text{CH}_2)(\eta^5\text{-C}_9\text{H}_7)(\text{PH}_3)_2]^+$ show that the energy barrier for tautomerization of vinylidene to π -alkyne is only $22.9 \text{ kcal mol}^{-1}$. This relatively low value can readily be overcome under the reaction conditions.¹⁵

We assume that the key step of this mechanism is the attack of complex **3** on the propargylic cation **I** simultaneously generated from the starting materials under the reaction conditions. This is consistent with the reaction of **3** with 1-ethynyl-1-cyclohexanol using MgSO_4 as a Lewis acid to activate the alcohol which readily leads to the formation of **I** (63%) (Scheme 1; method **D**) while no reaction is observed in the absence of the Lewis acid, showing that the formation of the activated species **I** is required.

Taking into account that the generation of propargylic cations from both 1-alkyn-3-ols or 1,3-enynes is favoured by co-ordination to transition metal complexes,¹⁷ a ruthenium-mediated formation of carbocation **I** cannot be discarded (see Scheme 6). Thus, the initial proton transfer from **2** can



Scheme 6

take place not on the free 1-ethynylcyclohexene molecule, but instead on the transient complex $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CR})(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ ($\text{R} = 1\text{-cyclohexenyl}$) to afford the neutral σ -enynyl derivative **3** and the stabilized propargylic cation **I'**. A carbon-carbon coupling process between both intermediates followed by co-ordination of 1-ethynylcyclohexene present in the reaction media can afford **II** regenerating the starting vinylvinylidene **2**.

Reactivity of the allenylidene complex $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **1**

Although the reactivity of transition-metal allenylidene complexes has only sparsely been investigated, there is ample experimental^{1,5,13} and theoretical^{5e,8a,18} evidence to conclude that the C_α and C_γ atoms of the unsaturated chain are electrophilic centres and that C_β is nucleophilic. During the last few years we have demonstrated that the regioselectivity of the nucleophilic additions on indenylruthenium(II) allenylidene complexes can be controlled by appropriate selection both of the substituents in the allenylidene chain and of the ancillary ligands.^{8,9,12,19} Thus, we have found that allenylidene complexes containing the $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ moiety exhibit an efficient steric protection of the C_α atom due to the preferred *cis* orientation of the indenyl group with respect to the unsaturated chain and to the presence of the bulky ancillary triphenylphosphine ligands. In contrast, the C_γ atom is more accessible and nucleophiles can be added at this position to yield functionalized σ -alkynyl derivatives.^{8a,9,12,19} In accordance, complex **1** undergoes readily nucleophilic additions at the C_γ

atom to give the alkynyl derivatives **7a,7b** (Scheme 3). It is apparent that the electrophilic C_α atom is effectively protected and remains inaccessible with respect to the C_γ atom in spite of this site being relatively sterically crowded. Therefore, these are additional examples which confirm the utility of indenylruthenium(II) allenylidene complexes for the synthesis of functionalized alkynyl derivatives in a regioselective manner.

Conclusion

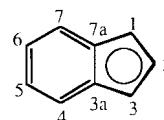
The reaction of the vinylvinylidene complex $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **2** ($\text{R} = 1\text{-cyclohexenyl}$) with 1-ethynyl-1-cyclohexanol to yield the spiro-bicyclic allenylidene derivative $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{C}_{13}\text{H}_{20})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **1** provides a new type of selective carbon-carbon coupling process in the well known chemistry of transition metal vinylidene systems.¹ Furthermore, we have demonstrated that this unprecedented process is based on an initial ruthenium-promoted dehydration of the 1-alkyn-3-ol derivative, involving an η^1 -vinylidene- η^2 -alkyne tautomerism at ruthenium, and subsequent coupling between the resulting 1,3-enyne and the vinylvinylidene moiety of **2**. Unfortunately, the scope of this unusual coupling reaction is limited and small differences in the nature of the propargyl alcohol derivative lead only to replacement of the vinylidene moiety in **2**.

In addition, the allenylidene complex **1** proved to be an excellent precursor for the regioselective synthesis of functionalized σ -alkynyl derivatives $[\text{Ru}\{\text{C}\equiv\text{C}(\text{C}_{13}\text{H}_{20})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ ($\text{R} = \text{C}\equiv\text{N}$ **7a** or OMe **7b**) through its reaction with nucleophiles. The utility of these new derivatives in organic synthesis is assured since we have previously reported a general and useful methodology for liberation of the organic fragment on related indenylruthenium(II) complexes.¹⁵

Experimental

General methods

The reactions were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$,²⁰ $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{R}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ **2** ($\text{R} = 1\text{-cyclohexenyl}$)⁹ and $[\text{Ru}(\text{C}\equiv\text{CR})(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ **3** ($\text{R} = 1\text{-cyclohexenyl}$)⁹ were prepared by the literature methods. 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 microanalyser. Mass spectra (FAB) were recorded using a VG Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol was used as the matrix. The GC analyses were carried out on a Perkin-Elmer 8600 gas chromatograph, equipped with a 12 m AQ2 capillary column (0.22 mm) and a flame ionization detector; quantification was achieved with a Perkin-Elmer Nelson 1020 integrator. The NMR spectra were recorded on a Bruker AC300 instrument at 300 (^1H), 121.5 (^{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 complexes. Abbreviations used: s, singlet; br, broad; d, doublet; dd, doublet of doublets; t, triplet; vt, virtual triplet; m, multiplet.



Preparations

[Ru{C=C=C(C₁₃H₂₀)}(η⁵-C₉H₇)(PPh₃)₂][PF₆] **1**. *Method A*. The salt NaPF₆ (0.08 g, 0.5 mmol) and 1-ethynyl-1-cyclohexanol (0.06 g, 0.5 mmol) were added to a solution of [RuCl(η⁵-C₉H₇)(PPh₃)₂] (0.15 g, 0.2 mmol) in MeOH (45 cm³). The reaction mixture was heated under reflux for 12 h. The solvent was then removed under vacuum, the crude product extracted with CH₂Cl₂ (ca. 20 cm³), and the extract filtered. Concentration of the resulting solution (ca. 5 cm³) followed by the addition of diethyl ether (ca. 50 cm³) precipitated an orange solid, which was washed with diethyl ether (2 × 20 cm³) and dried *in vacuo*. Yield: 0.12 g, 55% (Found: C, 66.58; H, 5.32. C₆₁H₅₇F₆P₃Ru requires C, 66.72; H, 5.23%). Conductivity (acetone, 20 °C): 118 Ω⁻¹ cm² mol⁻¹. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (PF₆⁻) 839s, (C=C=C) 1940s (KBr). $\delta_{\text{p}}(\text{CD}_2\text{Cl}_2)$ 49.56 (br); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 1.20–2.17 (m, 16 H, CH₂), 2.60 and 2.86 (s, 1 H each one, CH), 4.91 (m, 1 H, H-2), 5.39 (m, 2 H, H-1 and H-3), 5.43 (m, 1 H, =CHCH), 5.90 (d, 1 H, *J*(HH) = 9.6 Hz, =CH), 6.34 and 6.51 (m, 1 H each, H-4, H-5, H-6 or H-7) and 6.96–7.39 (m, 32 H, Ph and H-4, H-5, H-6 or H-7); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 18.32, 22.08, 22.84, 26.27, 32.83, 34.24, 35.25 and 39.97 (s, CH₂), 46.11 (s, C), 52.27 and 58.42 (s, CH), 86.11 and 86.94 (s, C-1 and C-3), 97.12 (s, C-2), 110.72 and 112.26 (s, C-3a and C-7a), 123.18–140.07 (m, Ph, CH=CH, C-4, C-5, C-6 and C-7), 186.83 and 191.07 (s, C_β and C_γ) and 304.48 (vt, ²*J*(CP) = ²*J*(CP') = 19.4 Hz, Ru=C_α); $\Delta\delta(\text{C-3a,7a}) = -19.16$ (average). *m/z* (FAB) 953 (M⁺) and 691 (M⁺ – PPh₃).

Method B. A solution of the vinylvinylidene complex **2** (0.15 g, 0.2 mmol) and 1-ethynyl-1-cyclohexanol (0.07 g, 0.6 mmol) in methanol (40 cm³) was heated under reflux for 12 h. The solvent was then removed under vacuum and the resulting solid residue washed with diethyl ether (2 × 15 cm³) to afford **1** in 69% yield (0.15 g).

Method C. As described in method **B**, complex **1** was obtained in 71% yield (0.154 g) starting from **2** (0.15 g, 0.2 mmol) and 1-ethynylcyclohexene (0.07 ml, 0.6 mmol).

Method D. A mixture of the σ-enynyl complex **3** (0.169 g, 0.2 mmol), 1-ethynyl-1-cyclohexanol (0.07 g, 0.6 mmol), NaPF₆ (0.05 g, 0.3 mmol) and MgSO₄ (0.12 g, 1 mmol) in methanol (40 cm³) was heated under reflux for 12 h. The solvent was then removed under vacuum, the crude product extracted with CH₂Cl₂ (ca. 20 cm³), and the extract filtered. Concentration of the resulting solution (ca. 5 cm³) followed by the addition of diethyl ether (ca. 50 cm³) precipitated **1**, which was washed with diethyl ether (2 × 20 cm³) and dried *in vacuo*. Yield: 0.14 g, 63%.

Reactions of [Ru{C=C(H)R}(η⁵-C₉H₇)(PPh₃)₂][PF₆] **2** (R = 1-cyclohexenyl) with propargyl alcohol derivatives: [Ru{C=C(H)R'}(η⁵-C₉H₇)(PPh₃)₂][PF₆] (R' = 1-cyclopentenyl **4a**, 1-cycloheptenyl **4b** or 1-cyclooctenyl **4c**) and [Ru(=C=C=CR₂)(η⁵-C₉H₇)(PPh₃)₂][PF₆] (R₂ = 2Ph **6a** or C₁₂H₈ **6b**). *General procedure*. A solution of the vinylvinylidene complex **2** (0.99 g, 1 mmol) and the corresponding propargyl alcohol (10 mmol for complexes **4a–4c** and 3 mmol for complexes **6a,6b**) in MeOH (50 cm³) was heated under reflux for 3 h. The solvent was then removed under vacuum, and the solid residue extracted with CH₂Cl₂ (ca. 30 cm³) and filtered. Concentration of the resulting solution (ca. 5 cm³) followed by addition of diethyl ether (ca. 50 cm³) precipitated a brown (**4a–4c**) or violet (**6a,6b**) solid, which was washed with diethyl ether (2 × 20 cm³) and dried *in vacuo*. The ³¹P-¹H and ¹H NMR data obtained for complexes **4a,4b** (65 and 85% yield, respectively) and **6a,6b** (78 and 69% yield, respectively) were in agreement with those previously reported.^{8a,9} Complex **4c**: 0.82 g, 81% (Found: C, 64.21; H, 5.08. C₅₅H₅₁F₆P₃Ru requires C, 64.76; H, 5.04%); conductivity (acetone, 20 °C) 109 Ω⁻¹ cm² mol⁻¹; $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (PF₆⁻) 837s (KBr); $\delta_{\text{p}}(\text{CDCl}_3)$ 37.22s; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.48 (m, 6 H, CH₂), 1.65, 1.91 and 2.08 (m, 2 H each one, CH₂), 4.82 (s, 1 H, Ru=C=CH),

5.27 (t, *J*(HH) = 8.4, =CH), 5.54 (d, 2 H, *J*(HH) = 2.5, H-1,3), 5.81 (m, 2 H, H-4,7 or H-5,6), 5.87 (t, 1 H, *J*(HH) = 2.5 Hz, H-2) and 6.78–7.48 (m, 32 H, Ph and H-4,7 or H-5,6); $\delta_{\text{C}}(\text{CDCl}_3)$ 25.92, 26.18, 26.27, 28.41, 29.70 and 30.25 (s, CH₂), 81.84 (s, C-1,3), 99.29 (s, C-2), 116.35 (s, C-3a,7a), 120.99 (s, C_β), 123.21 and 130.22 (s, C-4,7 and C-5,6), 125.81 (s, =CH), 126.44 (s, =C), 128.40–133.61 (m, Ph) and 355.29 (t, ²*J*(CP) = 16.5 Hz, Ru=C_α); $\Delta\delta(\text{C-3a,7a}) = -14.35$.

[Ru(C≡CR)(η⁵-C₉H₇)(PPh₃)₂] **5** (R = 1-cyclooctenyl). A mixture of the vinylvinylidene complex **4c** (0.30 g, 0.3 mmol) and neutral Al₂O₃ (excess, 5 cm³) in CH₂Cl₂ (20 cm³) was stirred at room temperature for 2 h. The solvent was then removed under vacuum, and the solid residue extracted with diethyl ether (ca. 50 cm³) and filtered. Evaporation of the solvent gave the σ-enynyl complex **5** as an orange solid. Yield: 0.23 g, 89% (Found: C, 75.39; H, 5.85. C₅₅H₅₀P₂Ru requires C, 75.58; H, 5.76%). $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (C≡C) 2067m (KBr). $\delta_{\text{p}}(\text{C}_6\text{D}_6)$ 52.67s; $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 1.60 (m, 6 H, CH₂), 1.68, 2.32 and 2.55 (m, 2 H each one, CH₂), 4.69 (d, 2 H, *J*(HH) = 2.4, H-1,3), 5.50 (t, *J*(HH) = 2.4, H-2), 5.97 (t, 1 H, *J*(HH) = 8.3 Hz, =CH), 6.35 and 6.68 (m, 2 H each, H-4,7 and H-5,6) and 6.90–7.53 (m, 30 H, Ph); $\delta_{\text{C}}(\text{C}_6\text{D}_6)$ 26.63, 27.30, 27.62, 29.31, 31.63 and 31.99 (s, CH₂), 74.91 (s, C-1,3), 95.56 (s, C-2), 103.82 (t, ²*J*(CP) = 25.4 Hz, Ru=C_α), 109.21 (s, C-3a,7a), 116.99 (s, C_β), 123.10 and 125.87 (s, C-4,7 and C-5,6), 129.68 (s, =C) and 127.00–139.08 (m, Ph and =CH); $\Delta\delta(\text{C-3a,7a}) = -21.49$.

[Ru{C≡C(C₁₃H₂₀)R}(η⁵-C₉H₇)(PPh₃)₂] (R = C≡N **7a** or OMe **7b**). *General procedure*. A solution of the allenylidene complex **1** (1.09 g, 1 mmol) in THF (50 cm³) was treated, at –20 °C, with the corresponding NaR reagent (1 mmol). The mixture was allowed to warm to room temperature, and the solvent then removed under vacuum. The solid residue was extracted with diethyl ether (for **7a**) or hexane (for **7b**) and filtered. Evaporation of the solvent gave the σ-alkynyl complexes **7a,7b** as yellow-orange solids. Complex **7a** was purified by column chromatography (neutral Al₂O₃; activity grade I) collecting the orange band eluted with hexane–diethyl ether (4:1): 0.52 g, 53% (Found: C, 76.29; H, 6.06; N, 1.34. C₆₂H₅₇NP₂Ru requires C, 76.05; H, 5.86; N, 1.43%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (C≡C) 2082m, (C≡N) 2221w (KBr); $\delta_{\text{p}}(\text{C}_6\text{D}_6)$ 51.11 (d, ²*J*(PP) = 31.4, PPh₃) and 51.52 (d, ²*J*(PP) = 31.4 Hz, PPh₃); $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 1.26–1.84 (m, 13 H, CH₂), 2.03 (m, 3 H, CH₂), 2.26 and 2.45 (m, 1 H each one, CH), 4.48 and 4.62 (m, 1 H each, H-1 and H-3), 5.37 (m, 1 H, H-2), 5.50 (dd, 1 H, *J*(HH) = 10.0, 6.0, =CHCH), 5.80 (d, 1 H, *J*(HH) = 10.0 Hz, =CH), 6.18 and 6.60 (m, 2 H each, H-4, H-5, H-6 and H-7) and 6.93–7.36 (m, 30 H, Ph); $\delta_{\text{C}}(\text{C}_6\text{D}_6)$ 17.29, 22.72, 22.87, 25.61, 26.74, 26.82, 36.24 and 37.51 (s, CH₂), 39.13 and 40.38 (s, C and C_γ), 41.57 and 41.66 (s, CH), 73.43 (d, ²*J*(CP) = 6.1, C-1 or C-3), 73.91 (d, ²*J*(CP) = 5.6, C-1 or C-3), 95.22 (s, C-2), 98.34 (vt, ²*J*(CP) = ²*J*(CP') = 23.8 Hz, Ru=C_α), 108.51, 109.42 and 109.73 (s, C-3a, C-7a and C_β), 123.06, 123.67, 124.50, 125.84, 126.06 and 138.48 (s, C-4, C-5, C-6, C-7, =CHCH and =CH), 123.44 (s, C≡N) and 127.37–138.92 (m, Ph). Complex **7b**: 0.67 g, 68% (Found: C, 75.28; H, 6.02. C₆₂H₆₀OP₂Ru requires C, 75.66; H, 6.14%). $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (C≡C) 2056m (KBr); $\delta_{\text{p}}(\text{C}_6\text{D}_6)$ 50.30 (d, ²*J*(PP) = 31.3, PPh₃) and 52.43 (d, ²*J*(PP) = 31.3 Hz, PPh₃); $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 0.93–2.11 (m, 17 H, CH₂ and CH), 2.41 (m, 1 H, CH), 2.80 (s, 3 H, OCH₃), 4.42 and 4.58 (m, 1 H each, H-1 and H-3), 5.43 (m, 1 H, H-2), 5.57 (dd, 1 H, *J*(HH) = 9.9, 6.3, =CHCH), 5.76 (d, 1 H, *J*(HH) = 9.9 Hz, =CH), 5.93 and 6.40 (m, 2 H each, H-4, H-5, H-6 and H-7) and 6.65–7.18 (m, 30 H, Ph); $\delta_{\text{C}}(\text{C}_6\text{D}_6)$ 16.30, 21.32, 21.65, 23.35, 25.70, 35.52 and 35.91 (s, CH₂), 39.16 (s, C), 39.37 and 40.89 (s, CH), 47.63 (s, OCH₃), 71.90 (d, ²*J*(CP) = 7.4, C-1 or C-3), 73.40 (d, ²*J*(CP) = 7.0, C-1 or C-3), 74.51 (s, C_γ), 90.71 (vt, ²*J*(CP) = ²*J*(CP') = 23.9 Hz, Ru=C_α), 94.69 (s, C-2), 107.31 and 109.58 (s, C-3a and C-7a), 114.85 (s, C_β) and

121.48–138.69 (m, Ph, C-4, C-5, C-6, C-7, =CHCH and =CH); $\Delta\delta(\text{C-3a}, 7\text{a}) = -22.25$ (average).

[Ru{C=C(H)C(C₁₃H₂₀)C≡N}(η⁵-C₉H₇)(PPh₃)₂][BF₄]⁻ **8**. A solution of the σ-alkynyl complex **7a** (0.98 g, 1 mmol) in diethyl ether (100 cm³), at -20 °C, was treated dropwise stirring vigorously with a dilute solution of HBF₄·Et₂O in diethyl ether. Immediately, an insoluble solid precipitated but the addition was continued until no further solid formed. The solution was then decanted and the brown solid washed with diethyl ether (3 × 20 cm³) and vacuum dried. Yield: 0.81 g, 76% (Found: C, 68.89; H, 5.19; N, 1.24. C₆₂H₅₈BF₄NP₂Ru requires C, 69.79; H, 5.48; N, 1.31%). Conductivity (acetone, 20 °C): 110 Ω⁻¹ cm² mol⁻¹. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (BF₄⁻) 1060s, (C≡N) 2232w (KBr). $\delta_{\text{P}}(\text{CDCl}_3)$ 38.42 (d, ²J(PP) = 22.4, PPh₃) and 39.23 (d, ²J(PP) = 22.4 Hz, PPh₃); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.37–2.03 (m, 16 H, CH₂), 2.13 and 2.30 (m, 1 H each, CH), 4.14 (s, 1 H, Ru=C=CH), 5.30–5.81 (m, 5 H, H-1, H-2, H-3, =CHCH and =CH), 5.97 and 6.20 (m, 1 H each, H-4, H-5, H-6 or H-7) and 6.64–7.51 (m, 32 H, Ph and H-4, H-5, H-6 or H-7); $\delta_{\text{C}}(\text{CDCl}_3)$ 16.51, 22.15, 25.57, 25.68, 26.21, 35.60 and 37.36 (s, CH₂), 37.87 and 39.14 (s, C), 39.95 and 41.97 (s, CH), 82.90 (d, ²J(CP) = 5.1, C-1 or C-3), 85.03 (d, ²J(CP) = 3.3, C-1 or C-3), 98.43 (s, C-2), 112.76 and 118.36 (s, C-3a and C-7a), 118.07 (s, C_β), 123.16 (s, C≡N), 122.08–137.59 (m, Ph, C-4, C-5, C-6, C-7, =CHCH and =CH) and 340.90 (vt, ²J(CP) = ²J(CP') = 15.7 Hz, Ru=C_α); $\Delta\delta(\text{C-3a}, 7\text{a}) = -15.14$ (average).

Reaction of complex 2 with phenylacetylene: [Ru{C=C(H)Ph}(η⁵-C₉H₇)(PPh₃)₂][PF₆]⁻ **9**. This complex has been prepared analogously to **4a–4c** and **6a, 6b** starting from **2** (0.15 g, 0.2 mmol) and phenylacetylene (0.2 ml, 2 mmol). Yield: 0.17 g, 86%. The ³¹P-¹H and ¹H NMR spectra were in agreement with the literature.¹⁶

Reaction of complex 2 with acetonitrile: [Ru(N≡CMe)(η⁵-C₉H₇)(PPh₃)₂][PF₆]⁻ **10**. A solution of the vinylvinylidene complex **2** (0.05 g, 0.05 mmol) in acetonitrile (10 cm³) was heated under reflux for 1 h. The solvent was then removed under vacuum, and the yellow solid residue washed with diethyl ether (2 × 5 cm³) and dried *in vacuo*. Yield: 0.04 g, 81%. The ³¹P-¹H and ¹H NMR data obtained for complex **10** were in agreement with those previously reported.¹⁵

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