From alkenylphosphane aminoallenylidene ruthenium(II) complexes to highly unsaturated ruthenaphosphabicycloheptene complexes

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Abstract

The alkenylaminoallenylidene complex $[Ru(\eta^5-C_9H_7)\{=C=C=C(NEt_2)[C(Me)=CPh_2]\}\{\kappa(P)-Ph_2PCH_2CH=CH_2\}(PPh_3)][PF_6]$ (**2**) has been prepared by the reaction of the allenylidene $[Ru(\eta^5-C_9H_7)(=C=C=CPh_2)\{\kappa(P)-Ph_2PCH_2CH=CH_2\}(PPh_3)][PF_6]$ (**1**) with the ynamine $MeC\equiv CNEt_2$. The reaction proceeds regio- and stereoselectively, and the insertion of the ynamine takes place exclusively at the $C_\beta=C_\gamma$ bond of the unsaturated chain. The secondary allenylidene $[Ru(\eta^5-C_9H_7)\{=C=C=C(H)[C(Me)=CPh_2]\}\{\kappa(P)-Ph_2PCH_2CH=CH_2\}(PPh_3)][PF_6]$ (**3**) is obtained, in a one-pot synthesis, from the reaction of aminoallenylidene **2** with $LiBHEt_3$ and subsequent treatment with silica. Moreover, the addition of an excess of $NaBH_4$ to a solution of the complex **2** in THF at room temperature gives exclusively the alkynyl complex $[Ru(\eta^5-C_9H_7)\{C\equiv CCH_2[C(Me)=CPh_2]\}\{\kappa(P)-Ph_2PCH_2CH=CH_2\}(PPh_3)]$ (**5**). The heating of a solution of allenylidene derivative **3** in THF at reflux gives regio- and diastereoselectively the cyclobutylidene complex $[Ru(\eta^5-C_9H_7)\{\kappa^2(P,C)-\{=\overline{CCH(CH_2PPh_2)CH_2}C=C(H)[C(Me)=CPh_2]\}\}(PPh_3)][PF_6]$ (**4**) through an intramolecular cycloaddition of the C=C allyl and the $C_\alpha=C_\beta$ bonds in the allenylidene complex **3**. The structure of complex **4** has been determined by single crystal X-ray diffraction analysis.

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1. Introduction

During the last decade, the chemistry of transition metal allenylidene complexes has provided important developments in a number of stoichiometric and catalytic processes [1]. These derivatives have a great potential to promote novel carbon–carbon and carbon–heteroatom coupling reactions because of the electrophilic (C_α and C_γ) and nucleophilic (C_β) character of the carbon nuclei of the allenylidene chain. Furthermore, the stoichiometric cycloadditions of allenylidene transition metal complexes are also well-known processes, though they have been much less explored [2–4]. In particular, allenylidene ruthenium complexes are able to promote selective cycloaddition pro-

cesses between the cumulene function and C=N, and C=C substrates [5,6]. Recently, we have reported for the first time the ability of allenylidene derivatives to undergo C—C coupling through the [2+2] intramolecular cycloaddition with tethered C=C double bonds [7]. This method allowed us to implement the regio- and diastereoselective synthesis of ruthenaphosphabicycloheptene systems from complexes $[Ru(\eta^5-C_nH_m)\{\kappa^3(P,C,C)-Ph_2PCH_2CH=CH_2\}-(PPh_3)][PF_6]$ ($C_nH_m = C_9H_7, C_5H_5$) and propargyl alcohols (Chart 1). The formation of these complexes proceeds through an intramolecular [2+2] cycloaddition between the allyl C=C and $C_\alpha=C_\beta$ bonds of the allenylidene complex intermediate. Unfortunately, the scope of this reaction is restricted to the availability of the appropriate propargyl alcohol system.

We have also reported an efficient access to novel unsaturated allenylidenes based on the regio and stereoselective insertion of ynamines $R'C\equiv CNEt_2$ into the $C_\beta=C_\gamma$ bond

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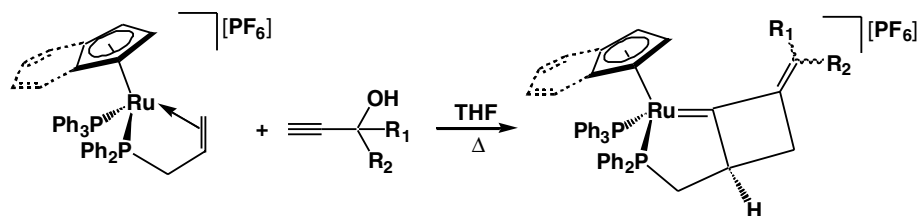 *E-mail addresses:* pgb@uniovi.es (M.P. Gamasa), elb@uniovi.es (E. Lastra).

Chart 1.

of the allenylidene chain of the precursor. This method allows easily to synthesize alkenyl aminoallenylidene complexes, like $[Ru(\eta^5-C_9H_7)\{=C=C=C(NEt_2)[C(R')=C(R)Ph]\}(PPh_3)_2][PF_6]$ and other highly unsaturated allenylidene complexes [8].

Pursuing our studies on this area we describe in this paper the synthesis of novel unsaturated allenylidene and aminoallenylidene alkenylphosphane ruthenium(II) complexes. Also, an highly unsaturated ruthenaphosphabicycloheptene system is synthesized by the diastereoselective intramolecular [2+2] cycloaddition between the allyl C=C and C_α=C_β bonds of the allenylidene precursor.

2. Results and discussion

2.1. Synthesis of the alkenylaminoallenylidene complex $[Ru(\eta^5-C_9H_7)\{=C=C=C(NEt_2)[C(Me)=CPh_2]\}-\{\kappa(P)-Ph_2PCH_2CH=CH_2\}(PPh_3)][PF_6]$ (2)
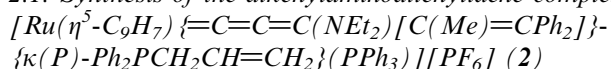
The reaction of the complex $[Ru(\eta^5-C_9H_7)(=C=C=CPh_2)\{\kappa(P)-Ph_2PCH_2CH=CH_2\}(PPh_3)][PF_6]$ (1) with two equivalents of the ynamine $MeC\equiv CNEt_2$ in THF at $-20\ ^\circ C$ leads to the alkenylaminoallenylidene complex 2 in a regio- and stereoselective way (Scheme 1). The resulting complex 2 is isolated as an orange solid in good yield (75%). Complex 2 is soluble in THF, dichloromethane and insoluble in diethyl ether and hexane.

Its analytic and spectroscopic data (IR, ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) support the proposed formulation. In particular: (i) the characteristic $\nu(C=C=C)$ absorption band at $1987\ cm^{-1}$ in the IR spectrum, (ii) two doublet resonances at 52.2 and 46.4 ppm ($^2J_{PP}=29.7$ Hz) in the ^{31}P{^{1}H} NMR spectrum, (iii) the downfield signals for the allenylidene carbon nuclei in the ^{13}C{^{1}H} NMR spectrum at 206.5 ppm (br s, C_α), and 156.4 (s, C_γ) ppm, while the C_β signal is overlapped by the aromatic carbons. The IR $\nu(C=C=C)$ absorption band as well as the ^{13}C{^{1}H} NMR signal of the allenylidene C_α are shifted with respect to those of the allenylidene precursor 1 [$\nu(C=C=C)$

$1922\ cm^{-1}$, and 291.7 (C_α) ppm]. These shifts, along with the non-equivalence of the ethyl substituents of the NEt_2 group in the ^{1}H and ^{13}C{^{1}H} NMR spectra, point to a relevant contribution of the alkynyl ruthenium resonance form in the aminoallenylidene complex 2 (Chart 2), as it was found for other aminoallenylidene complexes [8,9].

The formation of the complex 2 probably proceeds through the initial nucleophilic addition of the ynamine at the C_γ atom of the cumulene moiety, leading to the formation of the cationic complex intermediate (A). The regioselective ring closure involving the C_β atom would provide the [2+2] cycloadduct intermediate (B). Finally, the latter would yield the aminoallenylidene complex 2 through a subsequent cycloreversion reaction (Scheme 2) [8,10].

2.2. Synthesis of complexes $[Ru(\eta^5-C_9H_7)\{=C=C=C(H)-[C(Me)=CPh_2]\}\{\kappa(P)-Ph_2PCH_2CH=CH_2\}(PPh_3)]-[PF_6]$ (3) and $[Ru(\eta^5-C_9H_7)\{\kappa^2(P,C)-\{=\overline{C}CH(CH_2PPh_2)CH_2\overline{C}=C(H)[C(Me)=CPh_2]\}\}(PPh_3)][PF_6]$ (4)

We have recently reported the synthesis of novel ruthenaphosphabicyclic systems by reaction of $\kappa^3(P,C,C)$-alkenylphosphane ruthenium(II) complexes with propargyl alcohols. An allenylidene complex is initially generated which then undergoes formal cycloaddition of the allylic C=C bond to the C_α=C_β bond of the allenylidene group to give a cyclobutylidene ring [7] (Chart 1). These results prompted us to investigate complex 2 as suitable precursor of novel bicyclic systems through [2+2] cycloaddition reactions. However, all the attempts to achieve the intramolecular cycloaddition reaction in the complex 2 have been unsuccessful, the complex 2 being recovered unchanged even under reflux conditions. This lack of reactivity probably arises from the alkynyl resonance form $[Ru]–C\equiv C–C(=N^+Et_2)[C(Me)=CPh_2]$ (see Chart 2) which decreases the reactivity of aminoallenylidene complexes towards the [2+2] cycloaddition reaction.
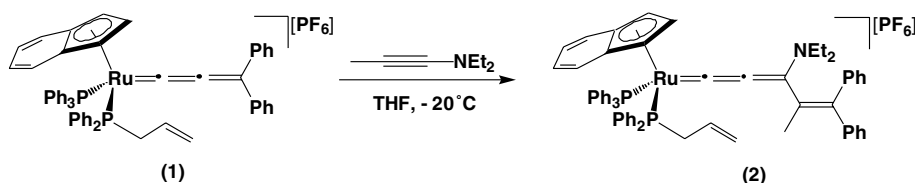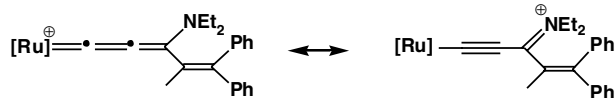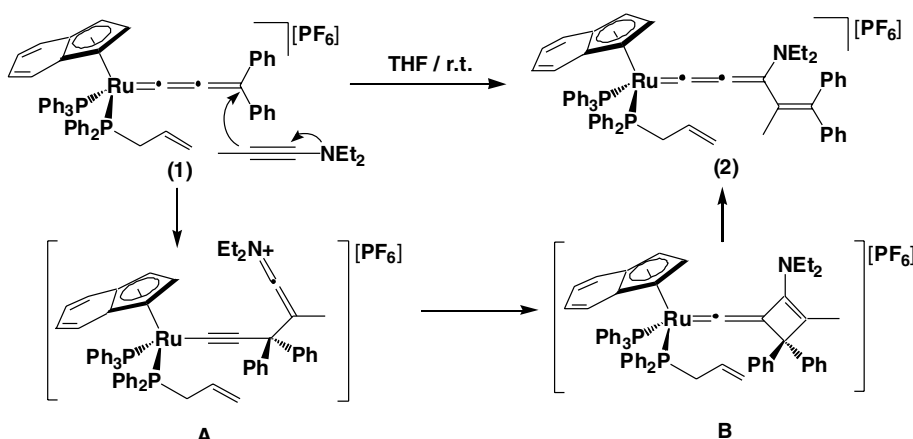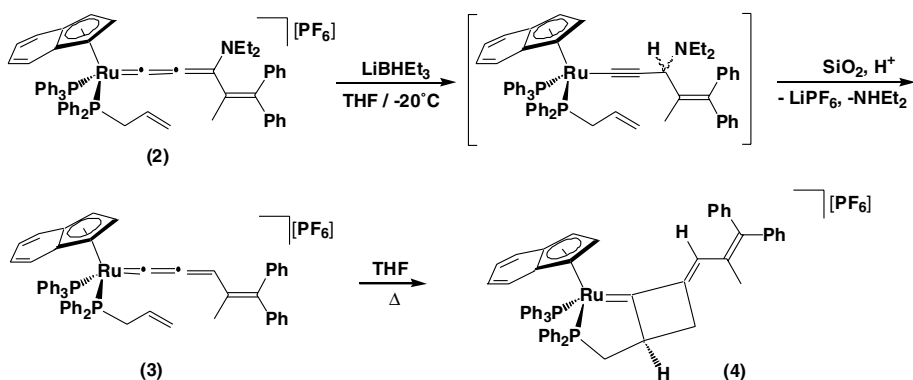

Scheme 1.

Chart 2.

In order to facilitate the intramolecular cycloaddition reaction we decided to remove the amino functionality by transformation of the complex **2** into the corresponding secondary allenylidene [8]. Thus, the slow addition of a slight excess of LiBHEt$_3$ to a solution of the complex **2** in THF at −25 °C, followed by the treatment of the concentrated solution on a silica column, afforded the complex [Ru(η^5-C$_9$H$_7$){=C=C=C(H)[C(Me)=CPh$_2$]}{κ(P)-Ph$_2$P-CH$_2$CH=CH$_2$}(PPh$_3$)][PF$_6$] (**3**), which was isolated as a violet powder (85% yield) (Scheme 3). Further heating of a solution of allenylidene **3** in THF at reflux for 1.5 h resulted in the formation of the complex **4**, isolated as an air stable brown solid in 87% yield after workup. Complexes **3** and **4** are soluble in dichloromethane and THF and insoluble in diethyl ether and hexane. They have been characterized by spectroscopic techniques (IR and ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR), mass spectrometry (FAB) and elemental analyses in the case of complex **4**.

The most representative spectroscopic data are as follows. Complex **3**: (i) the IR spectrum exhibits the expected v(C=C=C) absorption band at 1935 cm^{-1}, (ii) two doublet resonances at 49.7 and 39.0 ppm ($^2J_{PP}$ = 25.2 Hz) are found in the ^{31}P{^{1}H} NMR spectrum, (iii) the downfield allenylidene signals appear in the ^{13}C{^{1}H} NMR spectrum at 290.9 (br s, C$_\alpha$), 206.2 (s, C$_\beta$), and 123.4 (s, C$_\gamma$) ppm, (iii) the C$_\gamma$–H hydrogen of the allenylidene group is observed at δ = 8.42 ppm in the ^{1}H NMR spectrum. Complex **4**: (i) the ^{31}P{^{1}H} NMR spectrum displays two resonance doublets at 79.0 (ADPP) and 44.3 (PPh$_3$) ppm ($^2J_{PP}$ = 32.7 Hz), (ii) the ^{13}C{^{1}H} NMR spectrum shows a doublet at 328.3 ppm (J_{PC} = 15.6 Hz), a singlet at 121.4 ppm and a doublet at 66.5 ppm (J_{PC} = 19.7 Hz), which are assigned to the carbene carbon, the exocyclic CH, and the bridging CH group (sp^3 carbon), respectively. The stereochemistry of the exocyclic double bond has been determined by NOESY experiments. The cross-peak between the exocyclic methyl and the methylene protons indicates the spatial proximity of both groups, thus corroborating their *cis* disposition.
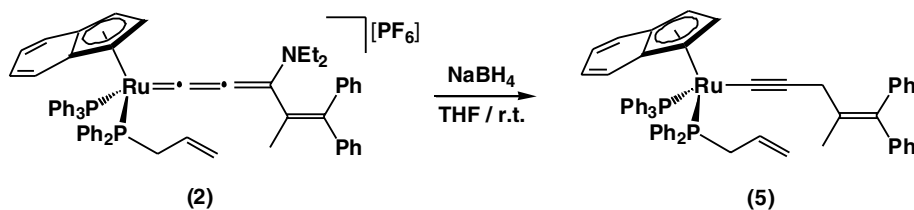
The formation of complex **3** proceeds through an initial nucleophilic addition of hydride to the C$_\gamma$ atom of the cumulene moiety to generate an intermediate alkynyl derivative, subsequent protonation of the NEt$_2$ moiety on a

Scheme 2.

Scheme 3.

Scheme 4.

short silica column and subsequent NHEt$_2$ elimination affords complex **3**. A subsequent intramolecular regio- and diastereoselective [2+2] cycloaddition of the C≡C double bond of the allylphosphane and the C$_\alpha$=C$_\beta$ double bond of the allenylidene chain in complex **3** generates the complex **4** (Scheme 3).

2.3. Synthesis of the complex [Ru(η^5-C$_9$H$_7$){C≡CCH$_2$[C-(Me)=CPh$_2$]}{κ(P)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)] (5)

Whereas the reaction of complex **2** with LiBHEt$_3$ gives complex **3**, the reaction of **2** with NaBH$_4$ proceeds through a different way. Thus, when the reaction of complex **2** and NaBH$_4$ was carried out in THF in a 1:1 molar ratio, a mixture of the complex **5** and the starting complex was obtained, even at low temperature. However, the addition of an excess of NaBH$_4$ to a solution of the complex **2** (1:3 molar ratio) in THF at room temperature yielded exclusively the alkynyl complex [Ru(η^5-C$_9$H$_7$){C≡C-CH$_2$[C(Me)=CPh$_2$]}{κ(P)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)] (**5**), which was isolated as an air stable orange powder in 80% yield (Scheme 4).

Its analytic and spectroscopic data (IR, ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) support the proposed formulation. In particular: (i) complex **5** displays a v(C≡C) absorption band at 2091 cm^{-1} in the IR spectrum, (ii) the ^{31}P{^{1}H} NMR spectrum shows two resonance doublets at 54.3 and 45.9 ppm ($^2J_{PP}$ = 33.1 Hz) for the two phosphanes.

2.4. X-ray crystal structure of the complex [Ru(η^5-C$_9$H$_7$)-{κ^2(P,C)-{=$\overline{CCH(CH_2PPh_2)CH_2}$C=C(H)[C(Me)=CPh$_2$]}}-(PPh$_3$)][PF$_6$] (4)

Suitable crystals for the X-ray study were obtained by slow diffusion of hexane into a solution of **4** in dichloromethane. An ORTEP type view of the cation complex **4** is shown in Fig. 1, and selected bond parameters are listed in Table 1.

Fig. 1 illustrates the R_{Ru},R_C configuration of the cation of complex **4.** Both enantiomers are present in equal proportions in the crystal which belongs to the centrosymmetric space group C2/c.

The molecular structure shows the typical pseudooctahedral three-legged piano-stool coordination around the ruthenium atom, which is η^5 bonded to the indenyl group, the phosphorus atom of PPh$_3$, and the P(2) and C(44) atoms of the ruthenaphosphabicycle. The benzo ring of the indenyl ligand is oriented *trans* to the metallacycle, deviated over the triphenylphosphane ligand as shown by the dihedral angle between the planes C*–C**–Ru(1) and C*–Ru–P(1) of 55.98(2)°. The most remarkable feature is the presence of a ruthenaphosphabicycloheptene. The bicycle contains a five-membered ruthenaphosphacycle fused to a four-membered ring with a dihedral angle of 28.94(37)°.

The bond length Ru(1)–C(44) (1.896(5) Å) of the complex **4** is in the range found for other alkylidene complexes like
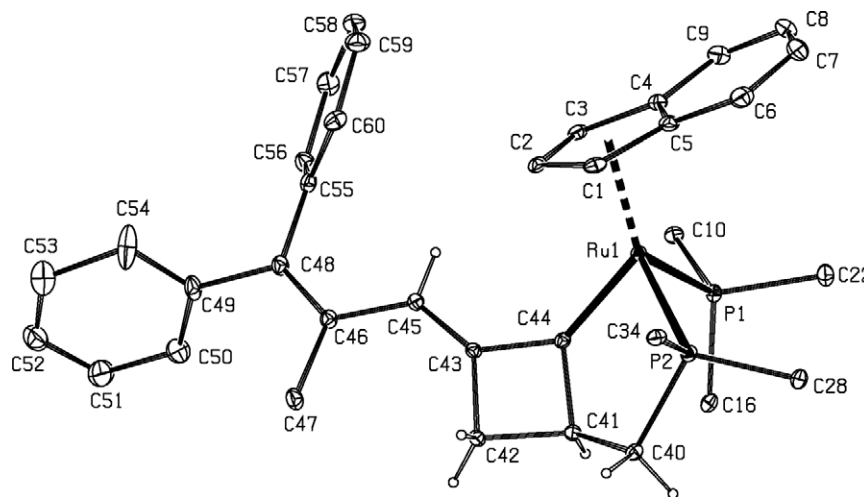
Fig. 1. ORTEP type view of the molecular structure of the cation of complex [Ru(η^5-C$_9$H$_7$){κ^2(P,C)-{=$\overline{CCH(CH_2PPh_2)CH_2}$C=C(H)[C(Me)=CPh$_2$]}}-(PPh$_3$)][PF$_6$] (**4**) drawn at 10% probability level. Dichloromethane molecules and phenyl groups of the phosphane ligands have been omitted for clarity. Only the C *ipso* of the aryl groups are depicted.

Table 1
Selected bond lengths (Å) and angles (°) for complex **4 · 2CH$_2$Cl$_2$**[a]

Bond lengths

Ru(1)–C(44)	1.896(5)	C(41)–C(44)	1.516(6)
Ru(1)–C*	1.9741(3)	C(43)–C(44)	1.457(6)
Ru(1)–P(1)	2.3466(13)	C(43)–C(45)	1.350(6)
Ru(1)–P(2)	2.3177(12)	C(45)–C(46)	1.443(7)
C(40)–P(2)	1.862(5)	C(46)–C(48)	1.359(7)
C(40)–C(41)	1.522(7)	C(48)–C(49)	1.496(7)
C(41)–C(42)	1.549(6)	C(48)–C(55)	1.482(7)
C(42)–C(43)	1.532(6)		

Angles

C(44)–Ru(1)–P(2)	80.58(14)	C(41)–C(44)–Ru(1)	128.0(3)
C(44)–Ru(1)–P(1)	88.31(14)	C(42)–C(41)–C(40)	125.0(4)
P(2)–Ru(1)–P(1)	97.89(4)	C(43)–C(44)–Ru(1)	138.1(3)
P(1)–Ru(1)–C*	124.44(3)	C(44)–C(41)–C(42)	87.9(3)
P(2)–Ru(1)–C*	127.50(3)	C(43)–C(42)–C(41)	87.2(3)
C(44)–Ru(1)–C*	125.07(13)	C(43)–C(44)–C(41)	91.2(4)
C(41)–C(40)–P(2)	107.7(3)	C(45)–C(43)–C(44)	132.2(4)
C(40)–P(2)–Ru(1)	106.15(15)	C(45)–C(43)–C(42)	136.9(4)
C(44)–C(41)–C(40)	114.0(4)	C(44)–C(43)–C(42)	90.7(4)

[a] C* = centroid of C(1), C(2), C(3), C(4), C(5); C*,* = centroid of C(4), C(5), C(6), C(7), C(8), C(9).

[Ru(η^5-C$_9$H$_7$){κ^2(*P,C*)-{=$\overline{\text{CCH(Ph)CH}_2\text{CHCH}_2\text{PPh}_2}$}}-(PPh$_3$)][BF$_4$] (1.864(5) Å) [11], and [Ru(η^5-C$_9$H$_7$)-{κ^2(*P,C*)-{=$\overline{\text{CCH(CH}_2\text{PPh}_2)\text{CH}_2\text{C}=\text{CC}_{12}\text{H}_8}$}}(PPh$_3$)][{3,5-(CF$_3$)$_2C_6H_3$}B] (1.914(3) Å) [7]. Moreover, the lengths of the C(sp^2)–C(sp^2) single-bonds [C(44)–C(43) (1.457(6) Å), C(45)–C(46) (1.443(7) Å), C(48)–C(55) (1.482(7) Å), C(48)–C(49) (1.496(7) Å)] are shorter than expected for a carbon–carbon single-bond. Conversely, the lengths of the C=C [C(sp^2)–C(sp^2)] double-bonds [C(43)–C(45) (1.350(6) Å) and C(46)–C(48) (1.359(7) Å)] are rather longer than expected for a carbon–carbon double-bond. These facts indicate that extensive electronic delocalization along the 1-metala-1,3,5-hexatriene framework occurs and therefore the complex **4** is best represented by the structure shown in Chart 3. The carbon atoms C(44), C(43), C(45), C(46) and C(48) are nearly coplanar, the maximum deviation with respect to the medium plane being 0.0453 Å.

3. Experimental

3.1. General procedures

The manipulations were performed under an atmosphere of dry nitrogen using nitrogen vacuum-line and standard Schlenk techniques. Solvents were dried by stan-
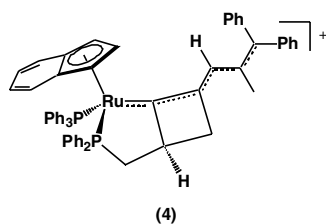

Chart 3.

dard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with exception of compounds MeC≡CNEt$_2$ [12] and [Ru(η^5-C$_9$H$_7$)(=C=C=CPh$_2$){κ(*P*)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)][PF$_6$] [7] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The C, H and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker AC 300 and 300 DPX instruments at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) and on a Bruker AC 400 instrument at 400.1 MHz (^{1}H), 161.9 MHz (^{31}P) or 100.6 MHz (^{13}C) using SiMe$_4$ or 85% H$_3$PO$_4$ as standards. DEPT experiments have been carried out for all the compounds reported. Coupling constants *J* are given in Hertz. *Abbreviations*. Ar, aromatic; s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. The following atom labels have been use for the ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data.
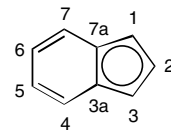
3.1.1. Synthesis of the complex [Ru(η^5-C$_9$H$_7$){=C=C=C-(NEt$_2$)[C(Me)=CPh$_2$]}{κ(*P*)-Ph$_2$PCH$_2$CH=CH$_2$}-(PPh$_3$)][PF$_6$] (2)

A solution of the allenylidene complex [Ru(η^5-C$_9$H$_7$)-(=C=C=CPh$_2$){κ(*P*)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)][PF$_6$]-(107 mg, 0.12 mmol) in tetrahydrofuran (6 mL) was added at −20 °C to a solution of the ynamine MeC≡CNEt$_2$ (23 μl, 0.24 mmol) in tetrahydrofuran (6 mL). The resulting orange solution was stirred for 30 min at the same temperature. The solvent was then removed under vacuum and the orange solid was washed with diethyl ether (2 × 10 mL) and dried in vacuo. Yield (86 mg, 75%). Colour: orange. IR (KBr, *v* cm^{-1}): 1987 (C=C=C), 841 (PF$_6^-$). Conductivity (acetone, 20 °C): 138 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 18 °C): δ = 0.99 (m, 6H, CH$_2$–C*H*$_3$), 1.29 (m, 1H, P–CH$_2$), 2.07 (s, 3H, CH$_3$), 2.92 (m, 1H, P–CH$_2$), 3.15 (m, 1H, C*H*$_2$–CH$_3$), 3.29 (m, 2H, C*H*$_2$–CH$_3$), 3.72 (m, 1H, C*H*$_2$–CH$_3$), 4.19 (m, 1H, =CH$_2$), 4.43 (m, 1H, H-2), 4.59 (d, *J*$_{HH}$ = 9.8 Hz, 1H, =CH$_2$), 4.79 (m, 1H, =CH), 5.11 (m, 2H, H-1, H-3), 6.34 (m, 1H) and 6.80–7.62 (m, 38 H) (Ar, H-4,5,6,7). ^{13}C{^{1}H} NMR (75.4 MHz, CD$_2$Cl$_2$, 18 °C): δ = 12.6 and 13.5 (s, CH$_2$–C*H*$_3$), 21.6 (s, CH$_3$), 32.9 (d, *J*$_{CP}$ = 27.3 Hz, P–CH$_2$), 46.6 and 48.0 (s, C*H*$_2$–CH$_3$), 76.6 and 77.5 (s, C-1,3), 95.9 (s, C-2), 108.9 and 112.1 (s, C-3a,7a), 119.4 (d, ^{3}*J*$_{CP}$ = 9.5 Hz, =CH$_2$), 121.6–142.8 (C$_β$, =CH, *C*Ph$_2$, *C*Me, C-4,5,6,7, Ar), 156.4 (s, C$_γ$), 206.5 (br s, C$_α$). ^{31}P{^{1}H}

NMR (121.5 MHz, CD$_2$Cl$_2$, 18 °C): δ = 46.4 (d, $^2J_{PP}$ = 29.7 Hz), 52.2 (d, $^2J_{PP}$ = 29.7 Hz). Anal. Calc. for C$_{64}$H$_{60}$-P$_3$F$_6$NRu (1151.15): C, 66.78; H, 5.25; N, 1.22. Found: C, 66.42; H, 4.98; N, 0.82%. FAB-MS: m/z = 1007 [M$^+$+1].

3.1.2. Synthesis of the complex [Ru(η^5-C$_9$H$_7$){=C=C= C(H)[C(Me)=CPh$_2$]}{κ(P)-Ph$_2$PCH$_2$CH=CH$_2$}-(PPh$_3$)][PF$_6$] (3)

To a solution of the complex [Ru(η^5-C$_9$H$_7$){=C=C=C-(NEt$_2$)[C(Me)=CPh$_2$]}{κ(P)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)]-[PF$_6$] (2) (115 mg, 0.1 mmol) in tetrahydrofuran (10 mL) cooled at −25 °C was slowly added LiBHEt$_3$ (1 M in THF, 150 μL, 0.15 mmol). The mixture was warmed to room temperature and the solvent was concentrated to ca. 3 mL. The resulting orange solution was transferred to a short silica gel chromatography column. Elution with diethyl ether led to a colour change from orange to violet. After complete colour change the mixture was eluted with tetrahydrofuran allowing to isolate the title compound after solvent removal. Yield (92 mg, 85%). Colour: Violet. IR (KBr, v cm^{-1}): 1935 (C=C=C), 839 (PF$_6^-$). Conductivity (acetone, 20 °C): 122 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 18 °C): δ = 2.01 (m, 1H, P–CH$_2$), 2.35 (s, 3H, CH$_3$), 2.66 (m, 1H, P–CH$_2$), 4.35 (d, J_{HH} = 17.15 Hz, 1H, =CH$_2$), 4.56 (br s, 1H, H-1 or H-3), 4.62 (d, J_{HH} = 10.1 Hz, 1H, =CH$_2$), 4.82 (m, 1H, =CH), 4.95 (t, J_{HH} = 2.6 Hz, 1H, H-2), 5.11 (br s, 1H, H-1 or H-3), 6.51–7.73 (m, 39H, H-4,5,6,7, Ar), 8.42 (s, 1H, CH$_\gamma$). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, −60 °C): δ = 22.0 (s, CH$_3$), 29.8 (d, J_{CP} = 29.5 Hz, P–CH$_2$), 88.1 and 88.6 (s, C-1,3), 98.8 (s, C-2), 107.4 and 119.0 (s, C-3a,7a), 121.4 (br s, =CH$_2$), 123.4 (s, C$_\gamma$), 127.1–158.5 (=CH, =CMe, =CPh$_2$, C-4,5,6,7, Ar), 206.2 (br s, C$_\beta$), 290.9 (br s, C$_\alpha$). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 18 °C): δ = 39.0 (d, $^2J_{PP}$ = 25.2 Hz), 49.7 (d, $^2J_{PP}$ = 25.2 Hz).

3.1.3. Synthesis of the complex [Ru(η^5-C$_9$H$_7$){κ^2(P,C)-{=$\overline{CCH(CH_2PPh_2)CH_2C}$=C(H)[C(Me)=CPh$_2$]}}(PPh$_3$)]-[PF$_6$] (4)

A solution of the complex [Ru(η^5-C$_9$H$_7$){=C=C=C(H)-[C(Me)=CPh$_2$]}(κ(P)-Ph$_2$PCH$_2$CH=CH$_2$)](PPh$_3$)[PF$_6$] (3) (108 mg, 0.1 mmol) in tetrahydrofuran (10 mL) was refluxed during 1.5 h. The solution was then evaporated to dryness and extracted with dichloromethane (2 × 20 mL). The residue was precipitated in a mixture of CH$_2$Cl$_2$/ Et$_2$O (1:5), washed with diethyl ether (2 × 10 mL) and vacuum-dried to afford complex 4. Yield (94 mg, 87%). Colour: brown. IR (KBr, v cm^{-1}): 838 (PF$_6^-$). Conductivity (acetone, 20 °C): 127 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$, 18 °C): δ = 1.49 (m, 1H, CH), 2.01 (m, 1H, P–CH$_2$), 2.28 (s, 3H, CH$_3$), 2.48 (m, 1H, P–CH$_2$), 3.48 (m, 1H, CH$_2$), 3.82 (m, 1H, CH$_2$), 4.09 (s, 1H, H-1 or H-3), 4.41 (s, 1H, H-1 or H-3), 5.77 (br s, 1H, H-2), 6.27 (d, J_{HH} = 8.3 Hz, 1H, =CH), 6.53 (m, 6H), 6.84 (m, 3H) and 7.13–7.58 (m, 30 H) (Ar, H-4,5,6,7). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 18 °C): δ = 17.4 (s, CH$_3$), 33.6 (d, J_{CP} = 31.0 Hz, P–CH$_2$), 35.1

(d, J_{PC} = 6.3, CH$_2$), 66.5 (d, J_{CP} = 19.7 Hz, CH), 80.2 (d, J_{PC} = 7.2 Hz, C-1 or C-3), 81.4 (d, J_{PC} = 9.6 Hz, C-1 or C-3), 103.1 (s, C-2), 111.3 and 118.6 (s, C-3a,7a), 121.4 (s, =CH), 124.8–159.6 (=CMe, =CPh$_2$, C-4,5,6,7, Ar), 328.3 (d, J_{CP} = 15.6 Hz, C$_\alpha$). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 18 °C): δ = 44.3 (d, $^2J_{PP}$ = 32.7 Hz), 79.0 (d, $^2J_{PP}$ = 32.7 Hz). Anal. Calc. for C$_{60}$H$_{51}$P$_3$F$_6$Ru (1080.03): C, 66.72; H, 4.76. Found: C, 66.79; H, 4.71%. FAB-MS: m/z = 935 [M$^+$].

3.1.4. Synthesis of the complex [Ru(η^5-C$_9$H$_7$){C≡CCH$_2$-[C(Me)=CPh$_2$]}{κ(P)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)] (5)

A solution of the complex [Ru(η^5-C$_9$H$_7$){=C=C= C(NEt$_2$)[C(Me)=CPh$_2$]}{κ(P)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)]-[PF$_6$] (2) (115 mg, 0.1 mmol) and NaBH$_4$ (11 mg, 0.3 mmol) in tetrahydrofuran (5 mL) was stirred at room temperature for 4 h. The solvent was then removed under vacuum, and the solid residue was dissolved in a mixture of hexane/ diethyl ether (9:1). The resulting solution was transferred to an Al$_2$O$_3$ (neutral: activity grade I) chromatography column. Elution with hexane/diethyl ether (8:2) and removal of the solvent under vacuum led to the compound 5 as a solid. Yield (75 mg, 80%). Colour: orange. IR (KBr, v cm^{-1}): 2091 (C≡C). ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 18 °C): δ = 2.08 (m, 1H, P–CH$_2$), 2.16 (s, 3H, CH$_3$), 3.54 (d, J_{HH} = 15.7 Hz, 1H, CH$_2$–C≡C), 3.67 (d, J_{HH} = 15.7 Hz, 1H, CH$_2$–C≡C), 4.00 (m, 1H, P–CH$_2$), 4.42 (br s, 1H, H-1 or H-3), 4.58 (br s, 1H, =CH$_2$), 4.61 (br s, 1H, =CH$_2$), 5.01 (br s, 1H, H-1 or H-3), 5.18 (m, 1H, =CH), 5.41 (t, J_{HH} = 2.4 Hz, 1H, H-2), 6.44 (d, J_{HH} = 8.4 Hz, 1H), 6.54 (d, J_{HH} = 8.3 Hz, 1H), 6.69–7.30 (m, 33H), 7.51 (d, J_{HH} = 7.2 Hz, 2H) and 8.07 (t, J_{HH} = 8.7 Hz, 2H) (H-4,5,6,7, Ar). ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 18 °C): δ = 20.8 (s, CH$_3$), 30.7 (s, CH$_2$), 31.3 (d, J_{CP} = 24.1 Hz, P–CH$_2$), 73.1 (m, C-1 and C-3), 94.5 (s, C-2), 106.2, 107.0, 111.5 (s, C-3a, C-7a, C$_\beta$), 117.3 (d, J_{CP} = 8.5 Hz, =CH$_2$), 121.9–144.8 (C$_\alpha$, =CH, =CMe, =CPh$_2$, C-4,5,6,7, Ar). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 18 °C): δ = 45.9 (d, $^2J_{PP}$ = 33.1 Hz), 54.3 (d, $^2J_{PP}$ = 33.1 Hz). Anal. Calc. for C$_{60}$H$_{52}$P$_2$Ru · CH$_2$Cl$_2$ (1033.02): C, 71.76; H, 5.33. Found: C, 72.49; H, 4.58%.

3.2. X-ray crystal structure determination of complex 4 · 2CH$_2$Cl$_2$

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of the complex in dichloromethane. The most relevant crystal and refinement data are collected in Table 2. Diffraction data were recorded at 150(2) K on a Nonius Kappa CCD single crystal diffractometer, using Cu Kα radiation. Crystal-detector distance was fixed at 29 mm, and a total of 1243 frames were collected using the oscillation method, with 2° oscillation and 40 s exposure time per frame. Data collection strategy was calculated with the program COLLECT [13]. Data reduction and cell refinement

Table 2
Crystal data and structure refinement for **4 · 2CH₂Cl₂**

Empirical formula	$C_{62}H_{55}Cl_4F_6P_3Ru$
Formula weight	1249.84
T (K)	150(2)
Wavelength (Å)	1.5418
Cryst system	Monoclinic
Space group	$C2/c$
a (Å)	37.4573(4)
b (Å)	11.1469(2)
c (Å)	27.8104 (4)
β (°)	98.5020(10)
V (Å³)	11484.1(3)
Z	8
D_{calcd} (g cm⁻³)	1.446
Absorption coefficient (mm⁻¹)	5.204
$F(000)$	5104
Crystal size (mm)	$0.15 \times 0.15 \times 0.12$
θ Range (°)	2.39–70.12
Index ranges	$-45 \leqslant h \leqslant 44$
	$0 \leqslant k \leqslant 13,$
	$0 \leqslant l \leqslant 33$
Reflections collected/unique [R_{int}]	21 050/10 673 [0.0469]
Completeness to θ_{max}	97.7%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	10673/0/829
Goodness-of-fit on F^2	1.087
R ($I > 2\sigma^{(1)}$)[a]	$R_1 = 0.0651, wR_2 = 0.1806$
R (all data)	$R_1 = 0.0772, wR_2 = 0.1962$
Largest difference in peak and hole (e Å⁻³)	2.733 and −1.364

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|; wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

were performed using the programs HKL Denzo and Scalepack [14]. Absorption correction was applied by means of SORTAV [15].

The software package WINGX was used for space group determination, structure solution and refinement [16]. The space group determination was based on a check of the Laue symmetry and systematic absences, and ascertained from the structure solution. The structure was solved by Patterson interpretation and phase expansion using DIRDIF [17]. Isotropic least-squares refinement on F^2 using SHELXL-97 was performed [18]. During the final stages of the refinement, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined except for a CH_2Cl_2 molecule (this highly disordered group was found and isotropically refined). The H-atoms were located by difference maps and refined isotropically (with the exception of those of two Ph groups and CH_2Cl_2 molecules which were geometrically located and their coordinates were refined riding on their parent atoms). The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1093P)^2 + 70.9026 P]$ with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$. The maximum residual electron density is located near to the disordered solvent molecules. Atomic scattering factors were taken from International Tables for X-Ray Crystallography [19]. Geometrical calculations were made with PARST [20]. The crystallographic plots were made with PLATON [21].

4. Conclusions

In summary, we describe in this paper the synthesis of a novel unsaturated secondary allenylidene alkenylphosphane ruthenium complex as well as its aminoallenylidene precursor. It is noteworthy the successful intramolecular [2+2] cycloaddition reaction between the allyl C=C and allenylidene C_α=C_β bonds which allowed to access to a highly unsaturated ruthenaphosphabicycloheptene system. The X-ray structure analysis of the complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^2(P,C)\text{-}\{=\overline{CCH(CH_2PPh_2)CH_2C}=C(H)[C(Me)=CPh_2]\}\}(PPh_3)][PF_6]$ **(4)** has been performed.

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 603579 for complex **4**. Copies of this information may be obtained free of charge from: The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.014.

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