(Alkenylalkylidene)(indenyl)ruthenium(II) Complexes: Synthesis by Protonation of Alkenyl Derivatives

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Keywords: Ruthenium / Hydride ligands / Alkenyl complexes / Alkylidene complexes / P ligands

The alkenyl complexes [Ru{(*E*)-C(CO_2Me)=C(H)R}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] [R = CO_2Me (**3**), H (**4**)], [Ru{(*E*)-CH=C(H)Ph}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (**5**) have been prepared by reaction of the hydride complex [RuH(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (**2**) [(*S*)-peap = (–)-(*S*)-*N,N*-bis(diphenylphosphanyl)(1-phenylethyl)amine] with an equimolar amount of dimethyl acetylenedicarboxylate, or with an excess of the terminal alkynes methyl propiolate or phenylacetylene. Similarly, vinylalkenyl complexes **6a**–**d** have been synthesized by the regio- and stereoselective reaction of the hydride complex **2** with 1-ethynylcycloalkynols. Protonation of the vinylalkenyl moiety of complexes **6a**,**c**,**d** with HBF_4·OEt_2 in diethyl ether afforded the cationic alkenylalkylidene complexes **7a**–**c**. The structures of complexes [RuH(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (**2**) and [Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (**3**) have been determined by X-ray diffraction methods. The catalytic activity of (alkenylalkylidene)(indenyl)ruthenium(II) complexes **7a**–**c**, **8** and **9** in the ring-closing metathesis (RCM) of diethyl diallylmalonate has been examined.

Introduction

The discovery of (alkylidene)ruthenium(II) five-coordinate complexes [Ru{=C(H)R′}Cl_2(PR_3)$_2$] (R = Ph, Cy; R′ = Ph, CH=CPh_2) by Grubbs and co-workers[1] as efficient catalysts of olefin metathesis[2] has been the most important cornerstone in the remarkable development of the chemistry of (carbene)ruthenium complexes. A relevant feature of these catalysts is their tolerance towards most functional groups and protic media. The search for novel species, aiming at reproducing or increasing the performance of the Grubbs catalysts, has been an important goal during the last few years. Besides benzylidene,[3] benzyl or methylcarbene[4] complexes **A** and alkenylalkylidene complexes **B** (Scheme 1) are genuine examples of this type of catalysts. The parent complexes **A** and **B** (R = Ph) were originally obtained from the reaction of [$RuCl_2$(PPh_3)$_3$] with either phenyldiazomethane[1c] or 3,3-diphenylcyclopropene.[1a] A few derivatives of **B**, obtained through triphenylphosphane exchange processes or halide metathesis, are also known. These include [Ru(=CH−CH=CPh_2)X_2(PR_3)$_2$] (X = Cl, Br, I; PR_3 = PCy_3, PCy_2Ph, P*i*Pr_3, P*i*Pr_2Ph)[5] and [Ru(=CH−CH=CPh_2)X_2(PPh_3)$_2$] (X = CF_3CO_2).[6] However, other synthetic approaches, which have been designed as alternative procedures in order to avoid the relatively difficult access of the carbene source, are currently known: i) Reaction of *gem*-dichloride $PhCHCl_2$ with [Ru(cod)(cot)] in the presence of PCy_3 gives the complex **A** [Ru(=CHPh)Cl_2(PCy_3)$_2$].[7] A multi-step procedure starting from [$RuCl_2$(cod)], using phenylacetylene as the carbene source,[3a] and a new general synthetic method involving sulfur ylides[3b] have also been recently reported. ii) Reaction of the (hydrido)dihydrogen complex [Ru(Cl)(H)(H_2)(PCy_3)$_2$] with propargyl or vinyl halides gives vinylcarbene complexes [Ru(=CH−CH=CR_2)Cl_2(PCy_3)$_2$].[8] iii) Treatment of the dinuclear hydrido complex [Ru(H)(μ-Cl)(P−P)]$_2$ (P−P = *t*$Bu_2$$PCH_2$P*t*$Bu_2$) with dimethylpropargyl chloride gives [Ru{=CHCH=CMe_2}Cl_2(P−P)]. The related cationic derivative [Ru(=CHCH=CMe_2)Cl(solvent)(P−P)][OTf], which is formed by the treatment of the parent alkenylalkylidene complex with Me_3SiOTf, is also known.[9] iv) Reaction of [$RuCl_2$(PPh_2)$_3$] with diphenylpropargyl alcohol leads to the phenylindenylidene complex [Ru(3-phenylindenylid-1-ene)Cl_2(PPh_3)$_2$] (**C**, Scheme 1). The PPh_3 ligands can be substituted by better donor ligands such as PCy_3, and to the best of our knowledge only one mixed-phosphane-substituted derivative is known, namely the complex [Ru(3-phenylindenylid-1-ene)-Cl_2(PR_3)L] (R = Ph, Cy; L = 1,3-diarylimidazol-2-ylidene).[10]

We have reported a systematic route for the synthesis of a series of (alkenylalkylidene)ruthenium(II) complexes

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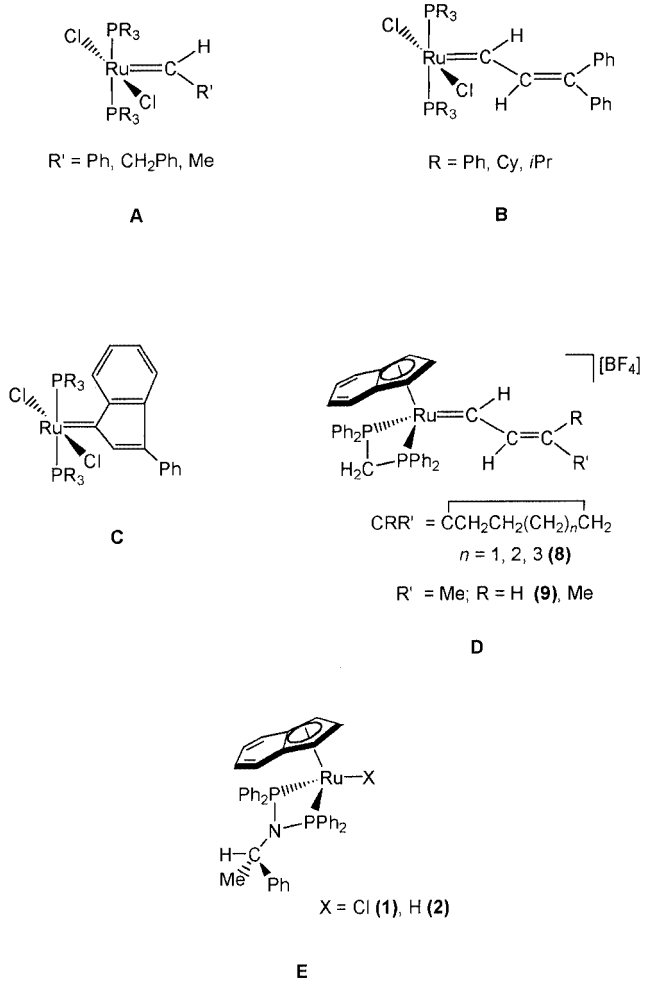


Scheme 1

[Ru(=CH−CH=CR_2)(η^5-C_9H_7)(dppm)][BF_4] [**D**, Scheme 1; dppm = bis(diphenylphosphanyl)methane] in which the unsaturated carbene group is bound to an (indenyl)(phosphane)ruthenium(II) fragment.[11] They have been obtained in high yields by protonation of the vinylalkenyl complexes [Ru{(*E*)-CH=CH−CHR_2)(η^5-C_9H_7)(dppm)]. More recently, this procedure has also been used as an alternative synthetic route for Grubbs catalyst **B** (Scheme 1).[12] Since access to these precursors {by reactions of the hydride complex [RuH(η^5-C_9H_7)(dppm)] with propargyl alcohols} is limited to the presence of the small bite chelate ligand dppm in the hydride precursor, we believed it would be of interest to investigate the applicability of this synthetic methodology using an analogous chelate ligand.

In this paper we report on the synthesis of novel ruthenium(II) precursors **E** (Scheme 1) in which the metal fragment bears the diphosphazane chelate ligand (*S*)-peap [(*S*)-peap = (−)-(*S*)-*N*,*N*-bis(diphenylphosphanyl)(1-phenylethyl)amine], which has a similar small bite angle as dppm. Further, their use as convenient starting materials for the synthesis of alkenylalkylidene complexes is investigated. The synthetic route involves two steps; the synthesis of alkenyl precursors, which are prepared by insertion reactions of the corresponding propargyl alcohol into the Ru−H bond of the hydride complex [RuH(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}], followed by the protonation with HBF_4·OEt_2 to give the desired alkenylalkylidene complexes. Moreover, we have also investigated the ability of the starting hydride complex to undergo insertion at the terminal or internal alkynes, and the catalytic activity of some (alkenylalkylidene)(indenyl)ruthenium(II) in the RCM of olefins (diethyl diallylmalonate). The X-ray crystal structures of the complexes [RuH(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] and [Ru{(*E*)-(CO_2Me)C=CH(CO_2Me)}(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] are also reported.

Results and Discussion

Synthesis of the Precursor Complexes [RuX(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] [X = Cl (1), H (2); (*S*)-peap = (−)-(*S*)-*N*,*N*-bis(diphenylphosphanyl)(1-phenylethyl)amine]

The starting material is the complex [RuCl(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] (**1**), which has been synthesized (83%) by heating a mixture of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] and the diphosphazane (*S*)-peap in toluene under reflux [Equation (1)]. Complex **1** was isolated as an air-stable red solid and characterized by means of spectroscopic methods and elemental analysis (see Exp. Sect. for details). In particular,

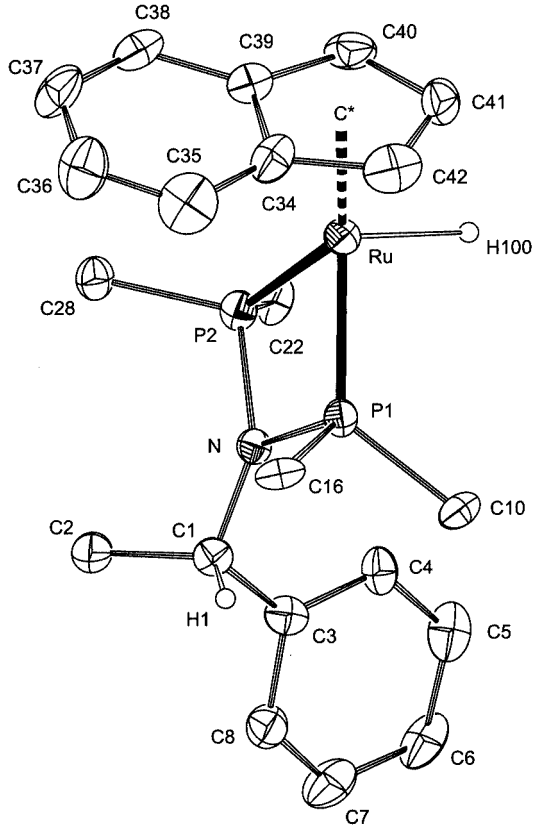


Figure 1. ORTEP-type diagram of [RuH(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] (**2**) with ellipsoids drawn at a 30% probability; phenyl rings of the Ph_2P groups in the diphosphazane have been omitted for clarity

Table 1. Selected bond lengths and slip parameter Δ [Å] and bond angles and dihedral angles HA, FA and CA [°] for complex **2**

Distances			
Ru−C*	1.97(2)	Ru−C(40)	2.266(12)
Ru−H	1.86(8)	Ru−C(41)	2.258(12)
Ru−P(1)	2.199(3)	Ru−C(42)	2.269(12)
Ru−P(2)	2.234(3)	P(1)−N	1.705(8)
Ru−C(34)	2.364(11)	P(2)−N	1.734(9)
Ru−C(39)	2.350(11)	N−C(1)	1.484(13)
Δ[a]	0.089(12)		
Angles			
P(1)−Ru−P(2)	70.44(12)	C*−Ru−P(1)	134.7(7)
P(1)−Ru−H	95(3)	C*−Ru−P(2)	139.4(8)
P(2)−Ru−H	93(3)	C*−Ru−H	109(4)
HA[b]	2.5(10)	CA[c]	20.8(24)
FA[d]	6.8(9)		

[a] Δ = *d*[Ru−C(34),C(39)] − *d*[Ru−C(40),C(42)]. [b] HA (hinge angle) = angle between normals to least-squares planes defined by [C(40), C(41), C(42)] and [C(34), C(39), C(40), C(42)]. [c] CA (conformational angle) = angle between normals to least-squares planes defined by [C**, C*, Ru] and [C*, Ru, H]. C* = centroid of C(34), C(39), C(40), C(41), C(42); C** = centroid of C(34), C(35), C(36), C(37), C(38), C(39). [d] FA (fold angle) = angle between normals to least-squares planes defined by [C(40), C(41), C(42)] and [C(34), C(35), C(36), C(37), C(38), C(39)].

its $^{31}P\{^1H\}$ NMR spectrum shows two doublet signals at δ = 83.2 and 91.4 ($^2J_{P,P'}$ = 112.7 Hz) of an AB system, which is in agreement with the presence of two diastereotopic phosphorus nuclei from the chiral chelate ligand. The ^1H and $^{31}C\{^1H\}$ NMR spectra also display resonances revealing the presence of the indenyl group and the diphosphazane ligand (see Exp. Sect.).

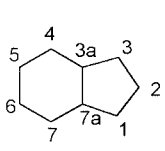
$$[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2] + (S)\text{-peap} \rightarrow [RuCl(\eta^5\text{-}C_9H_7)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}] + 2\ PPh_3 \quad (1)$$

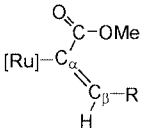
According to the classical route for the synthesis of transition metal hydride derivatives based on the β-hydrogen elimination from a methoxide complex,[13] the hydride complex [RuH(η⁵-C_9H_7){κ²-*P*,*P*-(*S*)-peap}] (**2**) has been prepared (85% yield) by treatment of complex **1** with an excess of NaOMe in refluxing methanol, see Equation (2).

$$[RuCl(\eta^5\text{-}C_9H_7)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}] + NaOMe \rightarrow [RuH(\eta^5\text{-}C_9H_7)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}] + H_2C{=}O + NaCl \quad (2)$$

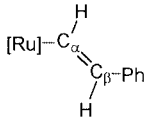
Complex **2** was isolated as an air-stable yellow solid and has been characterized by elemental analysis, IR and NMR (^1H,$^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectroscopy, which support the proposed formulation. The most significant signals arise from the presence of the two nonequivalent phosphorus nuclei: a) the hydride resonance which appears in the ^1H NMR spectrum as a triplet at δ = −14.33 (t, $^2J_{H,P}$ = $^2J_{H,P'}$ = 29.8 Hz) and b) two doublet resonances in the $^{31}P\{^1H\}$ spectrum at δ = 101.22 and 101.73 ($^2J_{P,P'}$ = 87.6 Hz) typical of an AB system. The structure of complex **2** has also been determined by X-ray diffraction. An ORTEP-type view of the molecular structure is shown in Fig-

Table 2. $^{31}P\{^1H\}$ and ^1H NMR spectroscopic data for the alkenyl complexes **3**, **4**, **5** and vinylalkenyl complexes **6a−d**





R = CO_2Me **(3)**
R = H **(4)**



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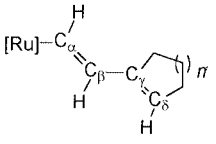


n = 1 **(6a)**, 2 **(6b)**, 3 **(6c)**, 4 **(6d)**

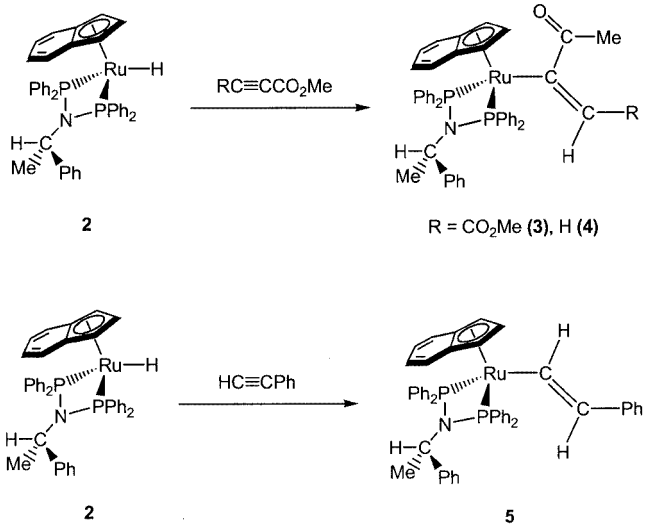
Complex	$^{31}P\{^1H\}$[a][d]	^1H[a][b] (*S*)-peap *CH[e]	Me	η⁵-C_9H_7[c] 1,2,3-H	$C_\alpha H$[c]	$C_\beta H$[c]	$C_\delta H$[c]	Others
3	97.26 d, 104.32 d (106.3)	4.80 m	1.11 d (7.2)	4.97 s, 4.98 s, 5.10 s	–	5.10 s	–	3.29, 3.67 (s, CO_2Me), 6.75−7.64 (m, PPh_2, *CPh, 4,5,6,7-H)
4	93.62 d, 95.57 d (118.0)	4.23 m	0.32 d (7.6)	4.91 s, 4.97 s, 5.30 s	–	4.46 d (2.3), 6.53 bs	–	2.99 (s, CO_2Me), 6.80−7.96 (m, PPh_2, *CPh, 4,5,6,7-H)
5	99.23 d, 107.33 d (106.3)	4.36 m	0.47 d (7.2)	5.27 s, 5.31 s, 5.33 s	[f]	5.65 d (15.9)	–	6.82−8.28 (m, $C_\alpha H$, PPh_2, *CPh, =CPh, 4,5,6,7-H)
6a[g]	98.81 d, 102.33 d (101.7)	4.42 m	0.52 d (7.3)	5.14 s, 5.15 s, 5.18 s	6.30 m	5.66 d (16.4)	4.50 bs	1.52−2.17 (m, CH_2), 6.77−7.80 (m, PPh_2, *CPh, 4,5,6,7-H)
6b	98.86 d, 102.50 d (104.2)	4.50 m	0.68 d (7.0)	5.28 s, 5.29 s, 5.36 s	6.62 m	5.82 d (16.1)	5.14 bs	1.54−2.22 (m, CH_2), 6.84−7.82 (m, PPh_2, *CPh, 4,5,6,7-H)
6c	98.84 d, 102.12 d (103.8)	4.46 m	0.64 d (7.0)	5.27 bs, 5.32 s	6.66 m	5.69 d (15.7)	5.22 t (6.5)	1.39−2.28 (m, CH_2), 6.83−7.88 (m, PPh_2, *CPh, 4,5,6,7-H)
6d[h]	97.53 d, 101.86 d (105.8)	4.54 m	0.72 d (7.4)	5.13 s, 5.15 s, 5.16 s	6.38 m	5.60 d (16.1)	4.73 t (8.7)	0.89−2.18 (m, CH_2), 6.77−7.68 (m, PPh_2, *CPh, 4,5,6,7-H)

[a] Spectra were recorded in C_6D_6. δ in ppm and *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; bs, broad singlet. [b] $J_{H,H}$ in parentheses. [c] Legend for indenyl and alkenyl skeletons. [d] $^2J_{P,P'}$ in parentheses. [e] *C = asymmetric carbon atom of (*S*)-peap ligand. [f] Signal overlapped by aromatic signals. [g] ^1H NMR spectrum recorded in CD_2Cl_2. [h] Spectra recorded in $CDCl_3$.

ure 1 and selected bond lengths and angles are presented in Table 1. The complex shows the typical pseudo-octahedral three-legged piano-stool geometry of indenylruthenium(II) complexes,[14] in which the metal atom is bonded to the η^5-indenyl group, the two phosphorus atoms of the chelate diphosphazane and the hydrogen atom. Significantly, the bite angle P(1)−Ru−P(2) [70.44(12)°] of the chelate (*S*)-peap ligand shows a value that is quite similar to that seen in the complex [$PdCl_2\{\kappa^2$-*P,P*-(*S*)-peap}] [71.5(1)°][15] and by the analogous chelate dppm ligand in the complex [$RuH(\eta^5$-C_9H_7)(dppm)] [dppm = bis(diphenylphosphanyl)methane] [71.28(2)°].[16] The rest of the main structural parameters [i.e. Ru−P(1) = 2.199(3) Å, Ru−P(2) = 2.234(3) Å, Ru−C* = 1.97(2) Å (C* = centroid of the five-membered indenyl ring), hinge angle (HA) = 2.5(10)°, fold angle (FA) = 6.8(9)°, slippage parameter (Δ) = 0.089(12) Å) are rather similar to those found for analogous (indenyl)(phosphane)ruthenium(II) complexes reported by us,[14] and therefore do not merit further comments.

Synthesis of Alkenyl Complexes [Ru{(*E*)-C(CO_2Me)=C(H)R}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] [R = CO_2Me (3), H (4)], [Ru{(*E*)-CH=C(H)Ph}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (5) and Vinylalkenyl Complexes 6a−d

The hydride complex **2** reacted with an equimolar amount of dimethyl acetylenedicarboxylate in refluxing diethyl ether to give the (*E*)-alkenyl complex **3** (71% yield). Similarly, complex **2** reacted with an excess of the terminal alkynes methyl propiolate or phenylacetylene in toluene at 60 and 110 °C, respectively, affording the alkenyl complexes **4** (66% yield) and **5** (73% yield), respectively (Scheme 2). They have been isolated as orange solids and their analyt-



Scheme 2

Table 3. $^{13}C\{^1H\}$ NMR spectroscopic data [spectra recorded in C_6D_6; δ in ppm and $J_{C,P} = J_{C,P'}$ in Hz (in parentheses); abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet] for the alkenyl complexes **3**, **4**, **5** and vinylalkenyl complexes **6a−d**

Complex	(*S*)-peap Me	*C	*CC_{ipso}	η^5-C_9H_7 C-1,3	C-2	C-3a,7a	C_α	C_β[a]	C_γ	C_δ	Others
3	24.94 s	64.80 t (6.9)	144.49 s	73.50 d (5.3), 76.32 d (3.1)	95.95 s	110.59 s, 112.60 d (3.1)	188.68 t (12.8)	[b]	–	–	51.87, 55.60 (s, CO_2*Me*), 126.08, 126.17, 126.72, 127.11 (s, C-4,5,6,7), 128.30−137.16 (m, PPh_2, *C*Ph*, C_β), 141.83−143.35 (m, PC_{ipso}), 163.75, 182.01 (s, *C*O_2Me)
4	21.09 s	62.91 t (7.0)	142.26 s	70.90 d (4.1), 71.99 d (6.4)	94.60 s	110.16 s	154.85 t (12.5)	135.57 s	–	–	50.75 (s, CO_2*Me*), 123.37, 123.68, 123.88, 124.86 (s, C-4,5,6,7), 127.30−133.66 (m, PPh_2, *C*Ph*), 138.61−140.30 (m, PC_{ipso}), 176.33 (s, *C*O_2Me)
5[c]	20.68 s	62.09 t (7.0)	[d]	69.40 d (4.1), 69.82 d (3.8)	92.98 s	107.68 t (2.3), 107.95 t (2.9)	154.21 t (14.3)	138.23 s	–	–	121.93, 122.10, 122.18 (s, 3C, C-4,5,6 or 7), 123.32−134.89 (m, PPh_2, *C*Ph*, =C*Ph*, 1 C, C-4,5,6 or 7), 139.59−140.30 (m, PC_{ipso}), 141.56, 141.64 (s, *CC_{ipso}, C_β*C*$_{ipso}$)
6a	23.82 s	64.19 t (7.2)	144.56 s	72.62 s, 73.12 s	97.71 s	110.43 s, 111.32 s	156.33 t (15.1)	149.27 s	139.59 s	117.58 s	25.92, 33.80, 35.04 (s, CH_2), 124.77, 125.08, 126.01, 126.11 (s, C-4,5,6,7), 127.85−136.48 (m, PPh_2, *C*Ph*), 136.88−142.05 (m, PC_{ipso})
6b[c]	21.56 s	62.07 t (6.1)	142.30 s	70.12 s, 70.72 s	94.62 s	108.35 s, 108.65 s	147.22 t (14.7)	141.81 s	139.01 s	116.45 s	23.63, 23.79, 24.65, 25.82 (s, CH_2), 122.37, 122.50, 123.63 (s, C-4,5,6,7), 126.73−135.77 (m, PPh_2, *C*Ph*, PC_{ipso}), 138.41−139.40 (m, PC_{ipso})
6c	21.60 s	62.12 t (6.1)	142.42 s	70.29 s, 70.71 s	95.06 s	108.47 s, 109.13 s	145.59 t (15.1)	142.97 s	146.64 s	121.39 s	26.97, 27.54, 28.59, 28.87, 33.72 (s, CH_2), 122.54, 122.75, 123.90, 123.96 (s, C-4,5,6,7), 126.73−134.35 (m, PPh_2, *C*Ph*), 138.92−139.85 (m, PC_{ipso})
6d	22.00 s	62.00 t (6.3)	142.82 s	70.71 s, 71.29 s	95.55 s	108.37 s, 109.46 s	146.51 t (14.9)	142.60 s	[b]	119.56 s	24.54, 26.99, 27.68, 27.88, 29.58, 31.94 (s, CH_2), 122.71, 123.05, 124.04, 124.12 (s, C-4,5,6,7), 127.17−134.31 (m, PPh_2, *C*Ph*, C_δ), 134.46−140.55 (m, PC_{ipso})

[a] Assigned by using DEPT 135 data. [b] Signal overlapped by aromatic signals. [c] Spectrum recorded in $CDCl_3$. [d] 141.56, 141.64 (s, *CC_{ipso}, C_β*C*$_{ipso}$). [e] Spectrum recorded in CD_2Cl_2.

ical and spectroscopic data (IR and ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR) are in accordance with these formulations. The IR spectra of complexes **3** and **4** show ν(C=O) absorptions in the range of 1675−1699 cm^{-1}, which are typical of uncoordinated CO_2Me groups. The NMR spectroscopic data are shown in Table 2 (^1H and $^{31}P\{^1H\}$) and in Table 3 ($^{13}C\{^1H\}$), and are in agreement with the proposed structures. The $^{13}C\{^1H\}$ and ^1H NMR spectra show the expected resonances of the alkenyl groups which can be compared with those of the analogous (alkenyl)(dppm)ruthenium(II) complexes.[17] In particular, some resonances of the ^1H NMR spectra show coupling constants arising from a *cis* (geminal) arrangement for complex **4** (the relatively small $J_{H,H}$ = 2.3 Hz of the nonequivalent vinylic protons indicates α-metalation) and an (*E*) configuration for complex **5** (the large proton coupling constant $J_{H,H}$ = 15.9 Hz indicates the mutually *trans* arrangement). In order to confirm the stereochemistry of complex **3**, an X-ray crystal structure determination has been carried out. An ORTEP-type view of the molecular structure is shown in Figure 2; selected bond lengths and angles are presented in Table 4. The pseudo-octahedral geometry around the ruthenium atom is quite similar to that found for complex **2**, where the alkenyl group has occupied the hydride position of **2**. The bond lengths Ru−C* = 1.937(13) Å, Ru−P(1) = 2.248(3) Å, Ru−P(2) = 2.259(13) Å, the chelating bite angle P(1)−Ru−P(2) = 70.53(9)° and all the distortion parameters of the indenyl group (HA, FA and Δ) are similar to those shown by complex **2** (see Table 1). The most remarkable feature of the structure is the (*E*) configuration of the alkenyl group which exhibits an Ru−C(1) bond length of 2.030(12) Å that can be compared with the reported values in other alkenylruthenium(II) complexes with the two CO_2Me groups in a mutually *cis* configuration, e.g. 2.07(1) Å and 2.096(7) Å in the complexes [Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_5H_5)(dppm)][18] and [Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-Ph_4C_4COH)$(CO)_2$],[19] respectively. The C(1)−C(2) bond length of 1.373(17) Å (typical of a carbon−carbon double bond) and all the remaining values involving the ester functionalities of the alkenyl group are as expected.

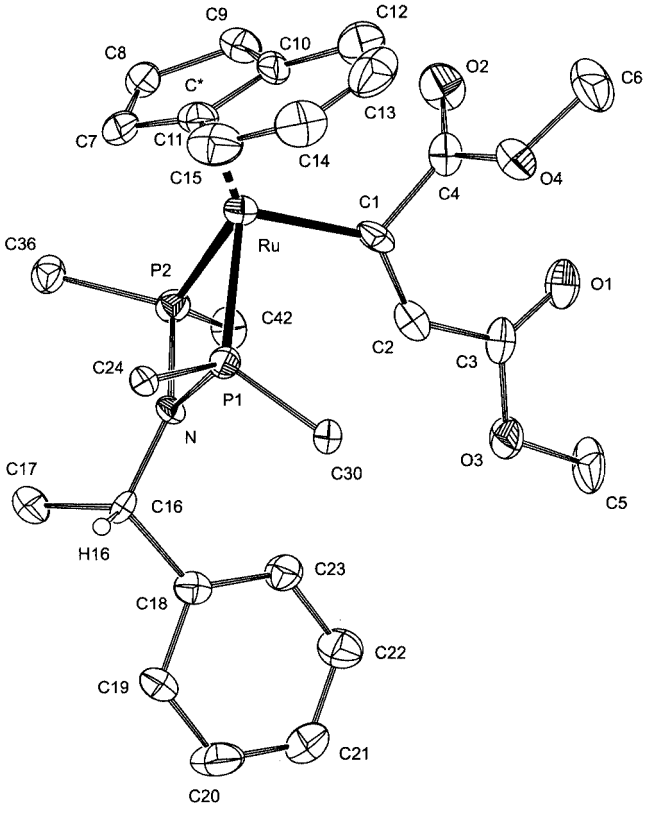


Figure 2. ORTEP-type diagram of [Ru{C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] (**3**) with ellipsoids drawn at a 30% probability; phenyl rings of the Ph_2P groups in the diphosphazane have been omitted for clarity

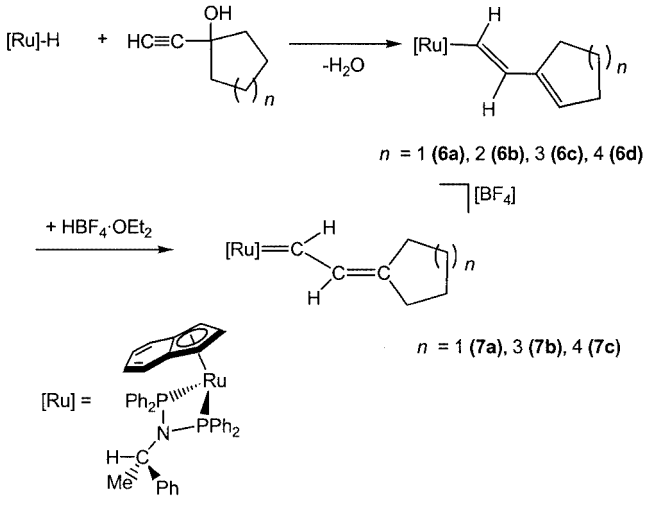
Table 4. Selected bond lengths and slip parameter Δ [Å] and bond angles and dihedral angles HA, FA and CA [°] for complex **3**

Distances			
Ru−C*	1.937(13)	N−C(16)	1.499(12)
Ru−P(1)	2.248(13)	Ru−C(1)	2.030(12)
Ru−P(2)	2.259(13)	C(1)−C(2)	1.373(17)
Ru−C(7)	2.219(12)	C(1)−C(4)	1.488(15)
Ru−C(8)	2.254(12)	C(2)−C(3)	1.422(17)
Ru−C(9)	2.270(11)	C(3)−O(1)	1.191(14)
Ru−C(10)	2.324(14)	C(4)−O(2)	1.221(12)
Ru−C(11)	2.332(16)		
Δ[a]	0.083(14)		
Angles			
P(1)−Ru−P(2)	70.53(9)	C*−Ru−C(1)	126.0(5)
C(1)−Ru−P(1)	92.5(3)	Ru−C(1)−C(2)	129.3(9)
C(1)−Ru−P(2)	91.2(3)	Ru−C(1)−C(4)	118.6(8)
C*−Ru−P(1)	130.2(4)	P(1)−N−P(2)	97.7(4)
C*−Ru−P(2)	129.4(4)	HA[b]	5.4(9)
CA[c]	69.0(5)	FA[d]	6.7(9)

[a] Δ = *d*[Ru−C(10),C(11)] − *d*[Ru−C(7),C(9)]. [b] HA (hinge angle) = angle between normals to least-squares planes defined by [C(7), C(8), C(9)] and [C(7), C(9), C(10), C(11)]. [c] CA (conformational angle) = angle between normals to least-squares planes defined by [C**, C*, Ru] and [C*, Ru, C(1)]. C* = centroid of C(7), C(8), C(9), C(10), C(11); C** = centroid of C(10), C(12), C(13), C(14), C(15), C(11). [d] FA (fold angle) = angle between normals to least-squares planes defined by [C(7), C(8), C(9)] and [C(10), C(12), C(13), C(14), C(15), C(11)].

Complex **2** also reacted with 1-ethynylcycloalkynols in toluene at 100 °C affording the vinylalkenyl complexes **6a**−**d** (Scheme 3). Although no attempts to isolate the intermediate species have been made, the reactions proceed stereo- and regioselectively in a *cis*- (*syn*) and *anti*-Markovnikov fashion through the formation of the corresponding hydroxyalkenyl complexes,[11,20,21] that dehydrate spontaneously to give the desired complexes (69−74% yield). All the alkenyl complexes are isolated as air-stable red-orange solids and have been characterized by elemental analysis, mass spectra (FAB) and NMR spectroscopy (Tables 2 and 3). The $^{31}P\{^1H\}$ NMR spectra show, as for complexes **3**−**5**, doublet signals due to the nonequivalent nature of the two

phosphorus atoms of the chiral diphosphazane. The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are consistent with those reported for similar α,β-unsaturated alkenylruthenium(II) complexes.[11,21,22] Significant features are the $^3J_{H,H}$ coupling constants (15.7−16.4 Hz) which support the *trans* stereochemistry for the RuC*H*=C*H*R double bond. The $^{13}C\{^1H\}$ NMR spectra exhibit all the resonances corresponding to the α,β-unsaturated alkenyl ligands. Significantly, the Ru*C*H=*C*HR carbon resonances appear as triplet ($^2J_{C,P} = {}^2J_{C,P'}$ = 14.3−15.1 Hz) and singlet signals at δ = 145.59−156.33 and 141.81−149.27, respectively. The spectra also exhibit resonances of the indenyl and (*S*)-peap ligand, along with the rest of the expected resonances for the alkenyl groups (see Tables 2 and 3).



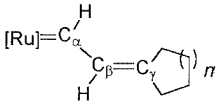
Scheme 3

Synthesis of Alkenylalkylidene Complexes 7a−c

In accordance with the well-established reactivity of alkenyl complexes towards electrophiles[11] which leads to the formation of carbene complexes (theoretical studies support the nucleophilic nature of the C_β atom of the alkenyl group),[23] the treatment of solutions of complexes **6a**, **c** and **d** in diethyl ether with $HBF_4{\cdot}Et_2O$ at −40 °C gave, by precipitation, the alkylidene complexes **7a−c**, respectively (Scheme 3). They were isolated as air-sensitive orange tetrafluoroborate salts (87−92%). They are soluble in chlorinated solvents and acetone. The conductivity data in acetone show values that are expected for 1:1 electrolytes and the IR spectra exhibit the typical ν(B−F) strong absorptions (see Exp. Sect.). All the complexes are characterized by mass spectra (FAB) which support the formulations, and by NMR spectroscopy (Tables 5 and 6). The ^1H and $^{13}C\{^1H\}$ NMR spectra reveal the presence of the alkenylalkylidene groups, which are formally generated from the protonation at the C_δ atoms of the alkenyl chain. The most relevant data arise from the $^{13}C\{^1H\}$ NMR spectra which show the typical low-field carbene resonance at δ = 290.99−294.60 ($^2J_{C,P} = {}^2J_{C,P'}$ = 10.1−12.6 Hz). Resonances that appear more upfield are assigned to the remaining carbon atoms of the hydrocarbon chain [e.g. 142.67−146.27 (C_β); 159.41−165.93 (C_γ)]. The ^1H NMR spectra also show downfield resonances at δ = 13.84−14.09, which are characteristic of the Ru=C*H* proton. The $^{31}P\{^1H\}$ NMR spectra display, as expected, two doublet resonances more upfield than those of the precursor complexes (δ = 91.26−92.20; 94.25−95.20). Similar spectroscopic data have been reported for analogous (alkenylalkylidene)(dppm)(indenyl)ruthenium(II) complexes.[11]

The catalytic activity of **7a−c** and the analogous dppm complexes **8** and **9**[11] (see Scheme 1, **D**) in the RCM of diethyl diallylmalonate was investigated (Scheme 4). The reactions were performed in a sealed tube containing a solution of 5 mol % of the catalyst precursor in CD_2Cl_2 and monitored by ^1H NMR spectroscopy. No transformation of the substrate was observed over 24 h at room or higher temperatures (limited by the thermal stability of the catalyst ca.

Table 5. $^{31}P\{^1H\}$ and ^1H NMR spectroscopic data [spectra recorded in CD_2Cl_2 (**7a**) or in $CDCl_3$ (**7b**, **c**); δ in ppm and *J* in Hz; abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet] for the alkenylalkylidene complexes **7a−c**



n = 1 (**7a**), 3 (**7b**), 4 (**7c**)

Complex	$^{31}P\{^1H\}$[a]	^1H[b] (*S*)-peap *CH	Me	η^5-C_9H_7 1,3-H	2-H	$C_\alpha H$	$C_\beta H$	Others
7a	91.26 d, 94.25 d (83.4)	5.17 m	1.32 d (6.4)	5.69 s, 5.94 s	5.54 t (2.7)	13.84 m	6.72 d (8.6)	1.44-2.12 (m, CH_2), 6.91-8.07 (m, PPh_2, *CPh, 4,5,6,7-H)
7b	91.71 d, 95.00 d (83.4)	5.19 m	1.34 d (7.1)	5.68 s, 5.97 s	5.46 s	14.09 m	6.79 d (8.2)	1.35-1.99 (m, CH_2), 6.87-7.73 (m, PPh_2, *CPh, 4,5,6,7-H)
7c	92.20 d, 95.20 d (81.4)	5.21 m	1.34 d (7.4)	5.67 s, 5.98 s	5.44 t (2.6)	14.08 m	6.80 d (8.1)	1.40-1.87 (m, CH_2), 6.85-7.90 (m, PPh_2, *CPh, 4,5,6,7-H)

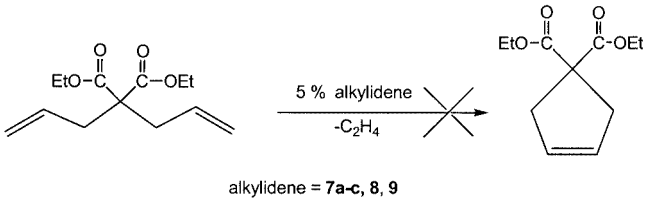
[a] $^2J_{P,P'}$ in parentheses. [b] $J_{H,H}$ in parentheses.

Table 6. $^{13}C\{^1H\}$ NMR spectroscopic data (spectra recorded in $CDCl_3$; δ in ppm and J in Hz. $J_{C,P} = J_{C,P'}$ in parentheses; abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet) for the alkenylalkylidene complexes **7a−c**

Complex	(*S*)-peap CH_3	*C	*CC_{ipso}	η^5-C_9H_7 C-1,3	C-2	C-3a,7a	C_α	C_β [a]	C_γ	Others
7a	22.71 s	62.22 t (5.9)	139.88 s	80.22 s, 80.44 s	98.53 s	110.42 s, 113.53 s	294.60 t (10.1)	142.67 s	165.93 s	25.09, 25.33, 31.45, 35.68 (s, CH_2), 122.68, 123.67, 126.31 (s, 3C, C-4,5,6 or 7), 127.47−132.91 (m, PPh_2, *C*Ph*, 1C, C-4,5,6 or 7), 133.24−134.67 (m, PC_{ipso})
7b	22.81 t (3.6)	62.21 t (6.3)	140.07 s	81.34 s, 81.42 s	97.85 s	110.57 s, 113.59 s	292.43 t (12.6)	145.92 s	159.41 s	25.56, 26.37, 28.35, 29.10, 31.60, 38.98 (s, CH_2), 122.98, 123.74 (s, C-4,7 or C-5,6), 126.48−135.01 (m, PPh_2, *C*Ph*, C-4,7 or C-5,6)
7c	22.89 s	62.15 t (5.4)	140.17 s	81.59 s	97.67 s	110.56 d (1.8), 113.55 s	290.99 t (10.8)	146.27 s	162.13 s	24.77, 25.19, 26.30, 27.53, 27.65, 30.71, 38.51 (s, CH_2), 123.05, 123.81 (s, C-4,7 or C-5,6), 126.54−133.35 (m, PPh_2, *C*Ph*, C-4,7 or C-5,6), 133.50−135.23 (m, PC_{ipso})

[a] Assigned by using DEPT 135 data.

90−100 °C). The substrate also remained unchanged when the reactions were performed in $[D_8]$THF, as well as in the presence of CuCl (10 equiv. with respect to the catalyst) under similar conditions. The addition of CuCl as a co-catalyst has proven to activate the ring-closing metathesis of the substrate with other ruthenium(II) catalysts.[24]



Scheme 4

Conclusions

A series of novel alkenyl- and (vinylalkenyl)ruthenium(II) complexes [Ru{(*E*)-CR=CHR′)(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] [R = CO_2Me; R′= CO_2Me (**3**); R = CO_2Me; R′= H (**4**); R = H; R = Ph (**5**)], **6a−d** containing the chelate diphosphazane ligand (−)-(*S*)-*N*,*N*-bis(diphenylphosphanyl)(1-phenylethyl)amine [(*S*)-peap], have been prepared in good yields. The latter complexes have proven to be good precursors for the synthesis of cationic alkenylakylidene complexes **7a−c** that are synthesized in good yields by protonation of the alkenyl derivatives. Disappointingly, these complexes (along with the dppm analogues **8** and **9**) are completely unreactive towards diethyl diallylmalonate under reaction conditions similar to those used for other ruthenium(II) complexes active in the ring-closing metathesis of olefins.[2,25] Analogous pseudo-octahedral cationic ruthenium complexes, namely [Ru(=CHPh)Tp(S)(PCy_3)]$^+$ [Tp = hydrotris(pyrazolyl)borate; S = H_2O, Py, Me_3CN],[24] have also shown no catalytic activity. Although substitution reactions have been reported in other indenylruthenium(II) complexes favored by a dissociative *indenyl effect*,[26] the cationic nature of the complexes leads to a substantial decrease of the lability of the ligand which is required to allow the coordination of the diolefin substrate.

Experimental Section

General Remarks: The reactions were carried out under dry nitrogen using standard Schlenk techniques. The solvents were dried by standard methods and distilled under nitrogen before use. The complexes [RuCl(η^5-C_9H_7)(PPh_3)$_2$],[27] **8** and **9**[11] and the diphosphazane ligand $(Ph_2P)_2N$[(*S*)-*CHMePh],[15] were prepared by published methods. Dimethyl acetylenedicarboxylate, methyl propiolate, phenylacetylene, propargylic alcohols, HBF_4·OEt_2 and dimethyl diallylmalonate were used as received. Infrared spectra were recorded with a Perkin−Elmer FT-1720-Y spectrometer. C, H and N analyses were carried out with a Perkin−Elmer 240-B microanalyzer (inconsistent analyses are found for complexes **7a−c** due to incomplete combustion). Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. The conductivities were measured at room temperature, in ca. 10^{-3}·mol·dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. NMR spectra were recorded with a Bruker DPX-300 or AC-300 instrument operating at 300 MHz (^1H), 121.5 MHz (^{31}P) and 75.4 MHz (^{13}C) or a Bruker AC-200 instrument operating at 200 MHz (^1H), 81.01 MHz (^{31}P) and 50.32 MHz (^{13}C), using $SiMe_4$ or 85% H_3PO_4 as the standard. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data for some complexes are presented in Tables 2, 3, 5 and 6.

[RuCl(η^5-C_9H_7){κ^2-*P*,*P*-(*S*)-peap}] (1): A mixture of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (1 g, 1.29 mmol) and a slight excess of the diphosphazane ligand $(Ph_2P)_2N$[(*S*)-*CHMePh] [(*S*)-peap)] (0.79 g, 1.61 mmol) in 20 mL of toluene was heated under reflux for 8 h. The removal of toluene gave a solid residue which was purified by flash chromatography on silica gel. The triphenylphosphane and the excess diphosphazane were eluted with a mixture of hexane and diethyl ether (10:1), and the red product **1** was eluted with a mixture of dichloromethane and methanol (10:1). The solvent was

evaporated and the dark red oil obtained was recrystallized from diethyl ether, yielding 0.793 g of the red solid **1** (83%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 83.20 (d), 91.40 (d, $^2J_{P,P'}$ = 112.7 Hz). ^1H NMR ($CDCl_3$): δ = 0.77 (d, $J_{H,H}$ = 7.1 Hz, 3 H, Me), 4.24, 4.27 and 4.48 (s, 1 H each, 1,2,3-H), 4.59 (m, 1 H, *CH), 6.85−7.93 (m, 29 H, PPh_2, *CPh, 4,5,6,7-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.19 (t, $^3J_{C,P} = {}^3J_{C,P'}$ = 2.2 Hz, Me), 62.21 (t, $^2J_{C,P} = {}^2J_{C,P'}$ = 6.5 Hz, *C), 65.42 (m, C-1 and C-3), 92.56 (s, C-2), 110.07 (m) and 111.51 (d, $^2J_{C,P}$ = 3.6 Hz) (C-3a and C-7a), 123.47, 124.12, 125.29 and 126.11 (s, C-4,5,6,7), 127.00−134.69 (m, PPh_2, *C*Ph*, PC_{ipso}), 137.45−139.41 (m, PC_{ipso}), 141.07 (s, *CC_{ipso}). $C_{41}H_{36}ClNP_2Ru$ (741.22): calcd. C 66.44, H 4.90, N 1.89; found C 66.88, H 5.15, N 1.89.

[RuH(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (2): An excess of NaOMe (ca. 5:1, prepared in situ from NaH and MeOH) was added to a suspension of **1** (0.74 g, 1 mmol) in MeOH (100 mL). The mixture was heated under reflux for 1 h and the color of the solution changed from red to yellow. The solution was cooled at ambient temperature, the liquid decanted and the yellow-orange solid obtained was washed with methanol (3 × 20 mL) and vacuum-dried to yield 0.60 g of **2** (85%). IR (KBr): $\tilde{\nu}$ = 1992 cm^{-1} [w, ν(Ru−H)]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 101.22 (d), 101.73 (d, $^2J_{P,P'}$ = 87.6 Hz). ^1H NMR ($CDCl_3$): δ = −14.33 (t, $^2J_{H,P} = {}^2J_{H,P'}$ = 29.8 Hz, Ru−H), 0.58 (d, $J_{H,H}$ = 6.9 Hz, 3 H, Me), 4.24 (m, 1 H, *CH), 5.01, 5.06 and 5.36 (s, 1 H each, 1,2,3-H), 6.27−8.01 (m, 29 H, PPh_2, *CPh, 4,5,6,7-H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 21.87 (s, Me), 61.05 (t, $^2J_{C,P} = {}^2J_{C,P'}$ = 6.9 Hz, *C), 66.89 (t, $^2J_{C,P} = {}^2J_{C,P'}$ = 4.6 Hz) and 68.56 (t, $^2J_{C,P} = {}^2J_{C,P'}$ = 4.6 Hz) (C-1 and C-3), 88.43 (s, C-2), 106.29 and 107.69 (s, C-3a and C-7a), 121.97, 122.58, 123.26 and 126.33 (s, C-4,5,6,7), 127.39−135.83 (m, PPh_2, *C*Ph*), 139.05−140.87 (m, PC_{ipso}), 143.11 (s, *CC_{ipso}). $C_{41}H_{37}NP_2Ru$ (706.78): calcd. C 69.67, H 5.28, N 1.98; found C 69.47, H 5.47, N 1.96.

[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (3): A mixture of **2** (0.25 g, 0.35 mmol) and an equimolar amount of dimethyl acetylenedicarboxylate (43 μL, 0.35 mmol) in diethyl ether (40 mL) was heated under reflux for 3 h. The solvent was evaporated and the solid obtained was dried under vacuum, yielding 0.21 g (71%) of **3** as an orange solid. IR (KBr): $\tilde{\nu}$ = 1688 s, 1699 cm^{-1} (s, 2 CO_2Me). $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are presented in Tables 2 and 3. $C_{47}H_{43}NO_4P_2Ru$ (848.89): C 66.50, H 5.11, N 1.65; found C 65.50, H 5.03, N 1.53.

[Ru{C(CO_2Me)=CH_2}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (4): A mixture of **2** (0.25 g, 0.35 mmol) and an excess of methyl propiolate (95 μL, 1.05 mmol) in toluene (40 mL) was heated at 60 °C for 6 h. The solvent was removed under vacuum and the solid obtained was washed with pentane (3 × 10 mL) and dried under reduced pressure to yield 0.183 g (66%) of **4** as an orange solid. MS (FAB): *m*/*z* = 791 [M$^+$], 760 [M$^+$ − OMe], 706 [M$^+$ − R], 629 [M$^+$ − R − Ph], 590 [M$^+$ − R − C_9H_7 − 1]; R: CH_2=C(CO_2Me) (correct isotope patterns observed for each fragment). IR (KBr): $\tilde{\nu}$ = 1675 cm^{-1} (s, CO_2Me). $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are presented in Tables 2 and 3.

[Ru{(*E*)-CH=CHPh}(η^5-C_9H_7){κ^2-*P,P*-(*S*)-peap}] (5): A mixture of **2** (0.25 g, 0.35 mmol) and a large excess of phenylacetylene (385 μL, 3.5 mmol) in toluene (40 mL) was heated at 110° C for 4 h. The solvent was removed under vacuum and the solid obtained was washed with pentane (3 × 10 mL) and dried under reduced pressure to yield 0.207 g (73%) of **5** as an orange solid. $C_{49}H_{43}NP_2Ru$ (808.91): calcd. C 72.76, H 5.36, N 1.73; found C 72.52, H 5.44, N 1.46. $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are presented in Tables 2 and 3.

Complexes 6a−d: A solution of **2** (0.25 g, 0.35 mmol) and an excess of the corresponding propargylic alcohol (3.5 mmol) in toluene (40 mL) was heated at 100 °C for 3 h. The solvent was evaporated to dryness and the resulting red-orange solid was washed with pentane (3 × 20 mL) and dried under vacuum to give **6a−d**. NMR spectroscopic data are presented in Tables 2 and 3. Yield, analytical data and mass spectrum (FAB, correct isotope patterns observed for each fragment) are as follows. **6a:** 71%. $C_{48}H_{45}NP_2Ru$ (798.92): calcd. C 72.16, H 5.68, N 1.75; found C 71.72, H 5.66, N 1.65. **6b:** 69%. $C_{49}H_{47}NP_2Ru$ (812.94): calcd. C 72.39, H 5.83, N 1.72; found C 70.66, H 6.10, N 1.33. *m*/*z* = 813 [M$^+$], 706 [M$^+$ − C_8H_{11}], 590 [M$^+$ − C_8H_{11} − C_9H_7 − 1], 401 [M$^+$ − C_8H_{11} − (*S*)-peap]. **6c:** 73%. $C_{50}H_{49}NP_2Ru$ (826.97): calcd. C 72.62, H 5.97, N 1.69; found C 71.29, H 6.33, N 1.31. *m*/*z* = 827 [M$^+$], 706 [M$^+$ − C_9H_{13}], 590 [M$^+$ − C_9H_{13} − C_9H_7 − 1], 401 [M$^+$ − C_9H_{13} − (*S*)-peap]. **6d:** 74%. $C_{51}H_{51}NP_2Ru$ (841.00): calcd. C 72.84, H 6.11, N 1.66; found C 71.81, H 6.08, N 1.46.

Complexes 7a−c: A dilute solution of HBF_4 in diethyl ether (0.13 mmol) was added dropwise to a stirred solution of the corresponding vinylalkenyl complex (**6a**, **c**, **d**; 0.12 mmol) in 20 mL of diethyl ether, cooled at − 40 °C. Immediately, an orange solid precipitated. The liquid was decanted and the solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. NMR spectroscopic data are presented in Tables 5 and 6. Yield, IR (KBr), conductivity (acetone, 20 °C) and mass spectrum (FAB, correct isotope patterns observed for each fragment) are as follows: **7a:** 87%. $\tilde{\nu}$ = 1062 cm^{-1} [b, s, ν(BF_4^-)]. 134 Ω^{-1}cm^2 mol^{-1}. *m*/*z* = 800 [M$^+$], 706 [M$^+$ − C_7H_{10}]. **7b:** 90%. $\tilde{\nu}$ = 1063 cm^{-1} [b, s, ν(BF_4^-)]. 128 Ω^{-1}cm^2 mol^{-1}. *m*/*z* = 828 [M$^+$], 706 [M$^+$ − C_9H_{14}], 401 [M$^+$ −C_9H_{14} − (*S*)-peap]. **7c:** 92%. $\tilde{\nu}$ = 1060 cm^{-1} [b, s, ν(BF_4^-)]. 117 Ω^{-1}cm^2 mol^{-1}. *m*/*z* = 842 [M$^+$], 706 [M$^+$ − $C_{10}H_{16}$].

Procedure for Ring-Closing Metathesis of Diethyl Diallylmalonate: Solutions of the complexes **7a−c**, **8** or **9** (5 μmol) and diethyl diallylmalonate (0.1 mmol, 24 μL) in CD_2Cl_2 (0.4 mL) were combined in a sealed tube. The reaction mixtures were stirred at room temperature and under more drastic conditions (heating the solutions until 100 °C in an oil bath) for 24 h. The development of the reactions was monitored by ^1H NMR spectroscopy. The diene signals appeared intact in the spectra. In addition, CuCl (10 equiv. based on **7c**) was added to a solution of complex **7c** as a co-catalyst under similar reaction conditions, but we have found that the mixture of alkylidene/CuCl is inactive for olefin metathesis.

X-ray Crystallographic Study of 2 and 3: Data were collected with a Nonius CAD4 single-crystal diffractometer. The intensities were measured using the ω-2θ scan technique with a scan angle of 1.5° intensity of the primary and a variable scan rate with a maximum scan time of 60 s per reflection. The beam was checked throughout the collection by monitoring three standard reflections every 60 min. Profile analysis was performed on all reflections.[28] Some double measured reflections were averaged and Lorentz and polarization corrections were applied. The structures were solved by Patterson interpretation and phase expansion using DIRDIF.[29] Isotropic least-squares refinement on F^2 using SHELXL97.[30] During the final stages of the refinements, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located and riding with common isotropic thermal parameters, except the hydride H atom (H100) in complex **2** which was located by Fourier difference synthesis and isotropically refined. The function minimized was $([\Sigma w F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (nP)^2]$ (n = 0.0337 for **2** and n = 0.0467 for **3**) with $\sigma(F_o^2)$ from counting statistics and $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$. Atomic scattering factors were taken

Table 7. Crystallographic data for complexes **2** and **3**

	2	**3**
Empirical formula	$C_{41}H_{37}NP_2Ru$	$C_{47}H_{43}NO_4P_2Ru$
a [Å]	12.595(5)	10.907(4)
b [Å]	13.576(3)	18.091(2)
c [Å]	19.319(5)	20.77(12)
Formula mass	706.73	848.83
Z	4	4
V [Å^3]	3303.5(17)	4098(23)
$D_{calcd.}$ [g cm^{-3}]	1.421	1.376
Wavelength [Å]	0.71073	0.71073
Temperature [K]	293(2)	293(2)
Radiation	Mo-K_α	Mo-K_α
Space group	$P2_12_12_1$	$P2_12_12_1$
Crystal system	orthorhombic	orthorhombic
Crystal size [mm]	0.46 × 0.23 × 0.13	0.36 × 0.26 × 0.1
μ [mm^{-1}]	0.602	0.505
F(000)	1456	1752
Diffraction geometry	ω-2θ	ω-2θ
θ range [°]	1.83−25.98	1.49−25.97
Index ranges for data collection	$0 \le h \le 15$	$0 \le h \le 13$
	$0 \le k \le 16$	$0 \le k \le 22$
	$0 \le l \le 23$	$0 \le l \le 25$
S	1.014	1.006
Reflections collected	3626	4435
Independent reflections	3626	4434 [*R*(int) = 0.0528]
Final *R* factors [$I > 2\sigma(I)$]	$R_1 = 0.0445$, $\omega R_2 = 0.0802$	$R_1 = 0.0461$, $\omega R_2 = 0.0934$
R indices (all data)	$R_1 = 0.1920$, $\omega R_2 = 0.1165$	$R_1 = 0.2048$, $\omega R_2 = 0.1318$

from International Tables for X-ray Crystallography.[31] Plots were made with the EUCLID package.[32] Geometrical calculations were made with PARST.[33] All calculations were made at the Scientific Computer Centre of the University of Oviedo and with the X-ray group computers. Selected crystal and refinement data are presented in Table 7. The unit-cell dimensions were determined from the angular settings of 25 reflections in the range $6° \le \theta \le 10°$ for **2**, and in the range $10° \le \theta \le 15°$ for **3**. CCDC-174083 (**2**) and -174084 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Dirección General de Investigación Científica y Técnica of Spain (DGICYT, Project PB96−0558) and the EU (Human Capital Mobility Program, Project ERBCHRXCT 940501). K. B. and M. P. thank the EU and the "European Tempus Program" for a postdoctoral grant and a fellowship, respectively.

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Received November 23, 2001
[I01482]