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Synthesis of New Half-Sandwich Ruthenium(II) Complexes Bearing Alkenyl- and Alkynylphosphane Ligands

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Carbonyl substitution of the complex [RuI(η^5-C_9H_7)$(CO)_2$] with the activated phosphanes Ph_2PR (R = $CH_2CH{=}CH_2$, $CH_2CH_2CH{=}CH_2$, and C≡CPh) affords the complexes [RuI(η^5-C_9H_7)(CO)(Ph_2PR-κ*P*)] [R = $CH_2CH{=}CH_2$ (**1a**), $CH_2CH_2CH{=}CH_2$ (**1b**), C≡CPh (**1c**)]. The reaction of the complex [RuCl(η^5-C_9H_7)$(PPh_3)_2$] with the corresponding phosphanes, in refluxing THF, gives the complexes [RuCl(η^5-C_9H_7)(PPh_3)(Ph_2PR-κ*P*)] [R = $CH_2CH_2CH{=}CH_2$ (**2b**), C≡CPh (**2c**)] by substitution of PPh_3. The cationic derivatives [Ru(η^5-C_9H_7)(L)(Ph_2PR-κ^3*P,C,C*)][X] [L = CO, X = SbF_6, R = $CH_2CH{=}CH_2$ (**3a**), $CH_2CH_2CH{=}CH_2$ (**3b**); L = PPh_3, X = PF_6, R = $CH_2CH_2CH{=}CH_2$ (**4b**)] have been prepared by treatment of the complexes **1a**,**b** and **2b** with a halide abstractor such as $AgSbF_6$ or $NaPF_6$, respectively. Deprotonation reactions of the complexes **3b** and **4b** with cesium carbonate have been carried out, giving rise to the neutral complexes [Ru(η^5-C_9H_7)(L)($Ph_2PCH_2CH{=}CHCH_2$-κ^2*P,C*)] [L = CO (**5a**), PPh_3 (**5b**)]. The reaction of complex **3a** with MeCN generates the complex [Ru(η^5-C_9H_7)(MeCN)(CO)($Ph_2PCH_2CH{=}CH_2$-κ*P*)][SbF_6] (**6**). The vinylidene [Ru(η^5-C_9H_7)(PPh_3)($Ph_2PC{\equiv}CPh$-κ*P*)-{C=C(Ph)H}][PF_6] (**7**) and allenylidene [Ru(η^5-C_9H_7)(PPh_3)($Ph_2PC{\equiv}CPh$-κ*P*)(C=C=CPh_2)][PF_6] (**8**) derivatives have been synthesized by reaction of complex **2c** with phenylacetylene or 1,1-diphenylprop-2-yn-1-ol, respectively. The structures of the derivatives **1c**, **3a**, and **4b** have been determined by single-crystal X-ray diffraction analysis.

Introduction

Functionalized phosphanes bearing a multiple carbon–carbon bond display a versatile behavior as ligands in coordination chemistry and have been reasonably well explored to date. Thus, alkenylphosphanes,[1] $R_2P(CH_2)_nCH{=}CH_2$ (*n* = 0–2), and alkynylphosphanes,[2] $R_2PC{\equiv}CR'$, have been used in coordination chemistry with a wide range of transition metals. Moreover, a number of ruthenium(II) complexes bearing different alkenylphosphanes, such as dicyclohexylvinylphosphane (DCVP),[3] vinyldiphenylphosphane (DPVP),[4] and allyldiphenylphosphane (ADPP)[5] have also been described and their ligand hemilabile properties have been repeatedly shown. However, the coordination properties and the hemilabile character of homoallylphosphanes have been much less exploited in the area of ruthenium chemistry. Recently, Kirchner and co-workers have studied the reactions of olefins and acetylenes with the complex [Ru(η^5-C_5H_5)(MeCN)($Ph_2PCH_2CH_2CH{=}CH_2$-κ^3*P,C,C*)][PF_6], which give rise to interesting coupling products.[6] On the other hand, examples of complexes of ruthenium(II) with alkynylphosphanes[7] are also scarce, even though alkynylphosphanes have been extensively used in the synthesis of polynuclear complexes[2f,8] and have been reported to participate in interesting rearrangement processes, some of them involving phosphorus–carbon bond cleavage[9] or carbon–carbon bond formation.[10]

We have previously reported the synthesis and characterization of the ruthenium(II) complexes [Ru(η^5-C_9H_7)(PPh_3)(Ph_2PCH_2C(R)=CH_2-κ^3*P,C,C*)][PF_6] (R = H, Me), which feature a κ^3*P,C,C* coordination mode of the allyldiphenylphosphane as well as a diastereofacial coordination of the olefin at the ruthenium center.[11] Moreover, these complexes have been demonstrated to be useful for further transformations, particularly as substrates in stereoselective nucleophilic addition[11] and intramolecular cycloaddition reactions,[12,13] which lead to interesting ruthenaphosphacyclopentane and ruthenaphosphabicycloheptene complexes, respectively. The progress of the latter reaction confirms the hemilabile character of the allyldiphenylphosphane ligand, a fact that has been corroborated by kinetic studies.[14] Continuing with these studies, we report here the synthesis of new half-sandwich indenyl complexes of ruthenium(II) containing alkenyl and alkynylphosphanes as well as some preliminary results on their reactivity.

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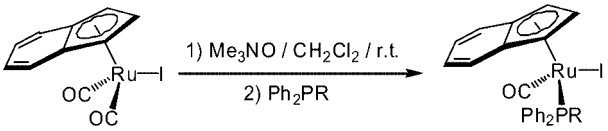
Results and Discussion

Complexes with Alkenyl and Alkynylphosphanes (Ph_2PR) Acting as κ*P* Monodentate Ligands

Synthesis of [RuI(η⁵-C₉H₇)(CO)(Ph₂PR-κP)] [R = CH₂CH=CH₂ (1a), CH₂CH₂CH=CH₂ (1b), C≡CPh (1c)]

The addition of the corresponding phosphane to a dichloromethane solution of the complex [RuI(η⁵-C_9H_7)(CO)(NMe_3)] (prepared in situ by reaction of the complex [RuI(η⁵-C_9H_7)$(CO)_2$] with freshly sublimed trimethylamine oxide) generates the complexes [RuI(η⁵-C_9H_7)(Ph_2PR-κ*P*)(PPh_3)] [R = $CH_2CH=CH_2$ (**1a**), $CH_2CH_2CH=CH_2$ (**1b**), C≡CPh (**1c**)], which were isolated as air-stable red solids (78–97% yield) (Scheme 1).



R = $CH_2CH=CH_2$ (**1a**)
$CH_2CH_2CH=CH_2$ (**1b**)
C≡CPh (**1c**)

Scheme 1.

Complexes **1a**–**c** are soluble in CH_2Cl_2, THF, and diethyl ether and slightly soluble in hexane. Analytical and spectroscopic data (IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy) support the proposed formulation (see Experimental Section for details). In particular, the IR spectra show the strong characteristic ν(CO) absorption at 1940 (**1a** and **1c**) and 1930 cm^{-1} (**1b**) as well as the ν(C≡C) absorption at 2176 cm^{-1} (**1c**), a singlet resonance is observed at δ = 45.0 (**1a**), 44.0 (**1b**) and 22.5 ppm (**1c**) for the phosphanes in the $^{31}P\{^1H\}$ NMR spectra, and a low-field doublet signal is observed in the $^{13}C\{^1H\}$ NMR spectra due to the carbonyl group at δ = 203.0 (**1a**), 203.5 (**1b**) and 202.4 ppm (**1c**) [$^2J_{C,P} \approx$ 20.7–21.3 Hz]. The $^{13}C\{^1H\}$ NMR spectrum of **1c** also shows two doublet signals for the alkynyl carbon nuclei at δ = 84.1 ($J_{C,P}$ = 93.6 Hz) and 108.9 ppm ($^2J_{C,P}$ = 14.4 Hz).

Slow diffusion of hexane into a solution of **1c** in diethyl ether allowed the isolation of crystals suitable for X-ray diffraction studies. An ORTEP-type representation of the molecule is shown in Figure 1. Selected bonding data are collected in the caption.

The molecule exhibits a pseudooctahedral three-legged piano-stool geometry. The η⁵-indenyl ligand displays the usual allylene coordination mode with the benzo ring oriented *trans* to the carbonyl group, as shown by the dihedral angle (1.14°) between the planes C*–C**–Ru and C*–Ru–C(10).[15]

The Ru–C(10) [1.840(4) Å] and C(10)–O(1) [1.132(5) Å] bond lengths are comparable to those found in other indenyl carbonyl ruthenium(II) complexes such as [RuI(η⁵-C_9H_7)(CO)(PCy_3)] [1.817(13) and 1.142(15) Å][16] and [Ru(η⁵-1,2,3-$Me_3C_9H_4$)(CO)(PPh_3)(C=C=CPh_2)][BF_4] [1.83(1) and 1.15(1) Å].[17]

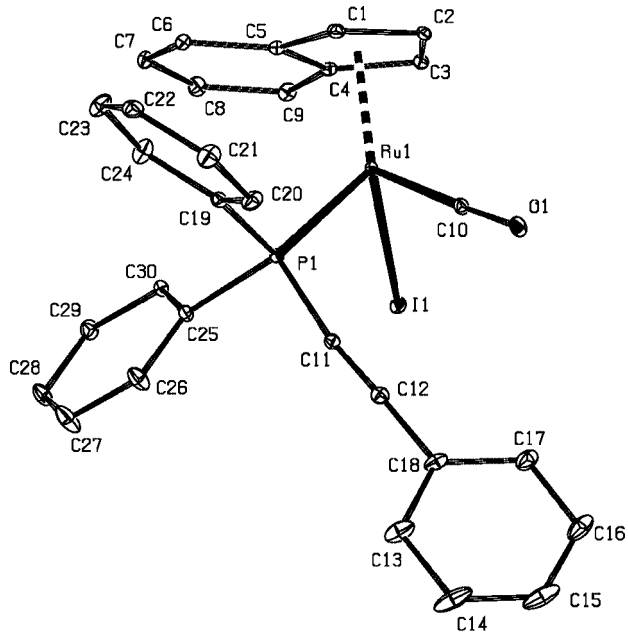


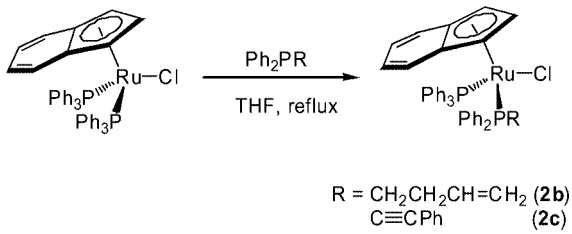
Figure 1. Molecular structure and atom-labelling scheme for complex **1c**. Non-hydrogen atoms are represented by their 10% probability ellipsoids. Hydrogen atoms and phenyl rings have been omitted for clarity. Selected bond lengths [Å]: Ru(1)–I(1) = 2.7224(4), Ru(1)–P(1) = 2.3087(9), Ru(1)–C(10) = 1.840(4), Ru(1)–C* = 1.9170, C(10)–O(1) = 1.132(5), P(1)–C(11) = 1.755(4), C(11)–C(12) = 1.210(6). Selected bond angles [°]: P(1)–Ru(1)–I(1) = 90.17(3), P(1)–Ru(1)–C(10) = 87.53(12), I(1)–Ru(1)–C(10) = 92.42(13), C*–Ru(1)–I(1) = 121.81, C*–Ru(1)–P(1) = 129.53, C*–Ru(1)–C(10) = 124.44, P(1)–C(11)–C(12) = 172.0(4), C(11)–C(12)–C(18) = 176.9(4). C* represents the centroid of atoms C(1), C(2), C(3), C(4), and C(5).

The alkynyl carbon–carbon bond length C(11)–C(12) [1.210(6) Å] is in the typical range for a carbon–carbon triple bond (1.205 Å in the free acetylene) and slightly longer than in other alkynylphosphaneruthenium complexes[7a] such as [$RuCl_2$(η⁶-*p*-cymene)($Ph_2PC\equiv CC_6H_4$-4-CH_3-κ*P*)] [1.198(3) Å] or [RuCl(η⁶-*p*-cymene)($Ph_2PC\equiv CtBu$-κ*P*)][OTf] [1.196(6) Å]. The alkynyl fragment of the phosphane displays a nearly linear geometry [C(11)–C(12)–C(18) = 176.9(4)°].

Both enantiomers are present in equal numbers in the crystal, as the crystal belongs to the centric space group $P\bar{1}$. The (*R*) enantiomer is shown in Figure 1.

Synthesis of [RuCl(η⁵-C₉H₇)(Ph₂PR-κP)(PPh₃)] [R = CH₂CH₂CH=CH₂ (2b), C≡CPh (2c)]

The reaction of the complex [RuCl(η⁵-C_9H_7)$(PPh_3)_2$] with the corresponding phosphane in refluxing THF results in the formation of the complexes [RuCl(η⁵-C_9H_7)(Ph_2PR-κ*P*)(PPh_3)] [R = $CH_2CH_2CH=CH_2$ (**2b**), C≡CPh (**2c**)], which were isolated as air-stable, red solids in 60% yield (Scheme 2). Complexes **2b**,**c** are soluble in dichloromethane and diethyl ether and insoluble in hexane, and were characterized by analytical and spectroscopic techniques (See Experimental Section for details).



Scheme 2.

The most remarkable features of those complexes are (a) the ν(C≡C) absorption at 2168 cm^{-1} in the IR spectrum for complex **2c**, (b) the expected doublets in the $^{31}P\{^1H\}$ NMR spectra at δ = 49.0 and 45.6 ppm ($^2J_{P,P}$ = 42.9 Hz) for **2b** and δ = 48.1 and 29.1 ppm ($^2J_{P,P}$ = 45.0 Hz) for **2c**, and (c) the $^{13}C\{^1H\}$NMR spectrum of **2c** shows two doublets at δ = 109.1 ($^2J_{C,P}$ = 11.5 Hz) and 87.2 ppm ($^2J_{C,P}$ = 80.7 Hz) for the acetylene carbons. One olefinic carbon appears at δ = 113.8 ppm in the $^{13}C\{^1H\}$NMR spectrum of **2b**, while the other one is overlapped by aromatic carbons.

Complexes with Alkenylphosphanes $Ph_2P(CH_2)_nCH=CH_2$ (n = 1, 2) Acting as κ^3P,C,C Chelate Ligands: Synthesis of the Complexes $[Ru(\eta^5\text{-}C_9H_7)(L)(Ph_2PR\text{-}\kappa^3P,C,C)][X]$ [L = CO, X = SbF_6, R = $CH_2CH=CH_2$ (3a), $CH_2CH_2CH=CH_2$ (3b); L = PPh_3, X = PF_6, R = $CH_2CH_2CH=CH_2$ (4b)]

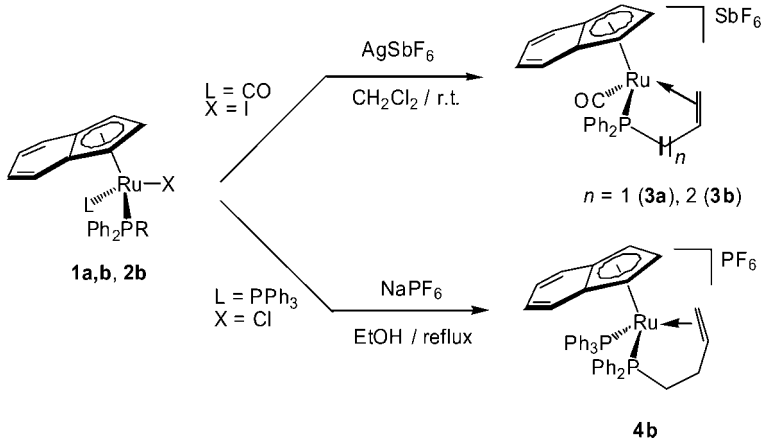
Due to the interest of the reactions carried out with the complex $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)(Ph_2PCH_2CH=CH_2\text{-}\kappa^3P,C,C)][PF_6]$,[11–13] our interest focused on the synthesis of novel complexes with allyl- and homoallylphosphanes coordinated in a κ^3P,C,C mode, which can be formed from complexes **1a**,**b** and **2b** by halide abstraction and subsequent olefin coordination to the metal. Thus, the treatment of complexes **1a**,**b** with $AgSbF_6$ in dichloromethane leads almost quantitatively to the complexes $[Ru(\eta^5\text{-}C_9H_7)(CO)(Ph_2PR\text{-}\kappa^3P,C,C)][SbF_6]$ [R = $CH_2CH=CH_2$ (**3a**), $CH_2CH_2CH=CH_2$ (**3b**)]. Similarly, the reaction of the complex **2b** with $NaPF_6$ in refluxing ethanol affords the complex $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)(Ph_2PCH_2CH_2CH=CH_2\text{-}\kappa^3P,C,C)][PF_6]$ (**4b**) in 67% yield (Scheme 3).

Complexes **3a**,**b** and **4b** were isolated as air-stable, yellow solids that are soluble in dichloromethane and insoluble in diethyl ether and hexane. They were characterized analytically and spectroscopically (IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy; see Experimental Section for details).

The $^{31}P\{^1H\}$ NMR spectra show a singlet resonance for the complexes **3a** (δ = –56.4 ppm) and **3b** (δ = 74.6 ppm), while two doublet signals at δ = 69.3 [$Ph_2P(CH_2)_2CH=CH_2$] and 47.3 ppm (PPh_3; $^2J_{P,P}$ = 29.5 Hz) are found for complex **4b**. The phosphorus resonance of the allyldiphenylphosphane is clearly shifted upfield in the complex **3a** (δ = 74.6 ppm) in comparison with its precursor **1a** (δ = 45.0 ppm) wherein the allylphosphane acts as a monodentate ligand. However, the phosphorus resonances of the homoallyldiphenylphosphane in complexes **3b** and **4b** are shifted downfield with respect to those of the corresponding monodentate phosphanes in the complexes **1b** (δ = 44.0 ppm) and **2b** (δ = 45.6 ppm). The formation of five- (**3a**) and six-membered (**3b**, **4a**) ruthenaphosphacycles may account for the observed shift differences.[18]

Although the two olefin faces are diastereotopic when the alkenylphosphane ligands are bound in a didentate manner, the coordination to the metal is found to be completely selective, affording a sole diastereoisomer, as revealed by the analysis of the $^{31}P\{^1H\}$ NMR spectra of complexes **3a**,**b** and **4b**. Such a selectivity has also been reported previously for the complexes $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)(Ph_2PCH_2CH=CH_2\text{-}\kappa^3P,C,C)][PF_6]$[11] and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(Ph_2PCH_2CH=CH_2\text{-}\kappa^3P,C,C)][PF_6]$.[13] In addition, the $^{31}P\{^1H\}$ NMR spectra remain unchanged over a wide temperature range, thus ruling out a dynamic process between the two diastereoisomers on the NMR time scale. Contrary to these results, the analogous derivative $[Ru(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CH=CH_2\text{-}\kappa P)(Ph_2PCH_2CH=CH_2\text{-}\kappa^3P,C,C)][PF_6]$ was found to be fluxional, giving rise to a rapid equilibrium between the two diastereomeric conformations present in solution.[5c]

The relatively large difference of the ^1H NMR chemical shifts for the CH_2 geminal protons of the olefin in complexes **3a**,**b** and **4** points to a parallel orientation of the



Scheme 3.

olefin with respect to the indenyl ring. Similar data have been reported in other cyclopentadienyl and indenyl π-olefin complexes.[19]

In order to compare the structure of the derivatives **3a** and **4b** with that of the complex $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)(Ph_2PCH_2CH{=}CH_2\text{-}\kappa^3P,C,C)][PF_6]$,[11] and to find out which of the two olefin faces in the $Ph_2P(CH_2)_n\text{-}CH{=}CH_2\text{-}\kappa P$ ligand is most favored for coordination, an X-ray diffraction study was carried out. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a solution of complexes **3a** and **4b** in dichloromethane. The crystals belong to the centrosymmetric space groups $P\bar{1}$ (**3a**) and $P2_1/c$ (**4b**), thereby indicating the presence of a racemic mixture.

In both cases, the asymmetric unit consists of two molecules. For complex **4b**, the two molecules are conformers with identical stereochemistry, the relative configuration at the ruthenium center being R_{Ru} and the olefin being coordinated through the *re* face (R_{Ru}*re*). However, in the case of complex **3a** the two molecules in the asymmetric unit are a pair of diastereoisomers with relative configuration (R_{Ru}*si*) and (S_{Ru}*re*) (Figure 2). For both **3a** and **4b** the more relevant structural parameters are similar in both molecules,[20] and thus only the data corresponding to one molecule will be discussed.

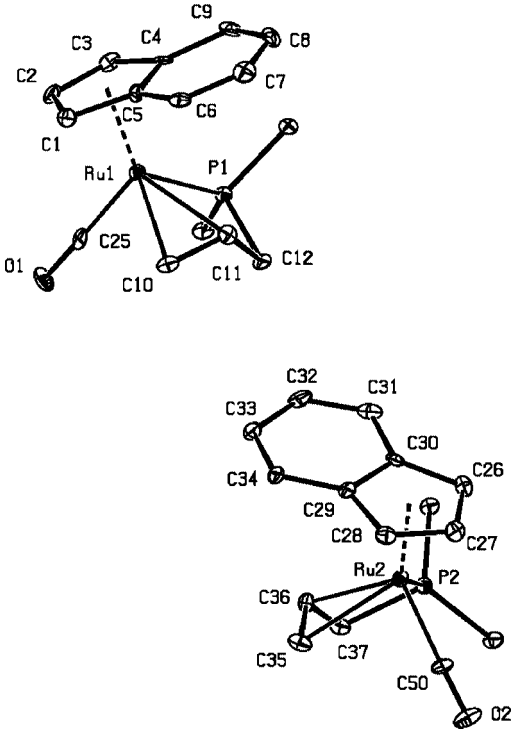


Figure 2. The two diastereoisomers found in the asymmetric unit for the cation of complex **3a** with configurations R_{Ru}*si* and S_{Ru}*re*. Non-hydrogen atoms are represented by their 20% probability ellipsoids. Hydrogen atoms and phenyl rings have been omitted for clarity.

ORTEP-type representations of the cations of one of the molecules for complexes **3a** and **4b** are shown in Figures 3 and 4, respectively. Selected bonding data are collected in Table 1.

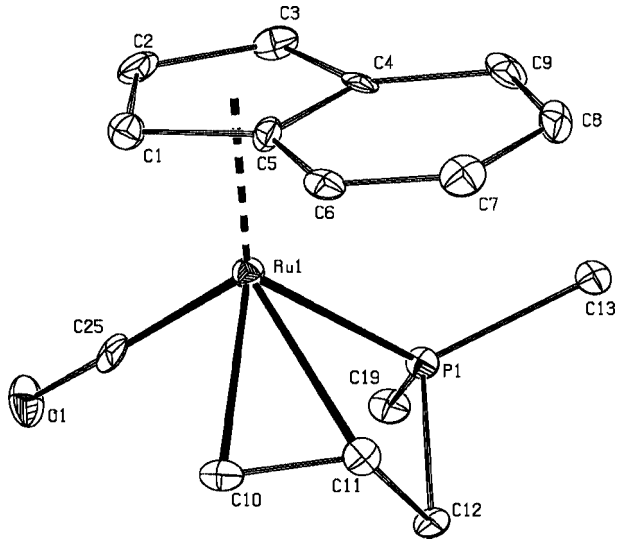


Figure 3. Molecular structure and atom-labelling scheme for the cation of complex **3a**. Non-hydrogen atoms are represented by their 10% probability ellipsoids. Hydrogen atoms and phenyl rings have been omitted for clarity.

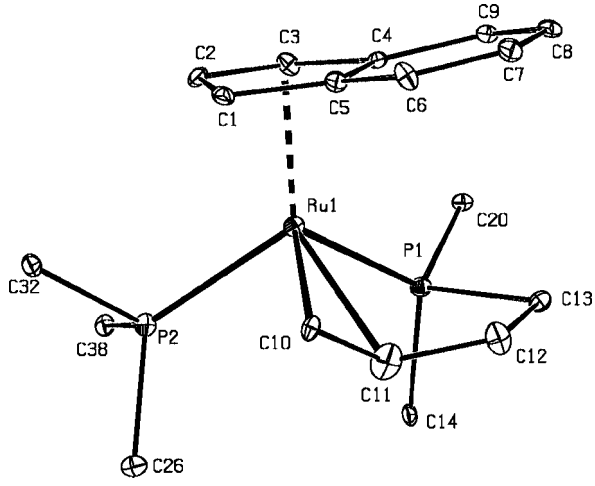


Figure 4. Molecular structure and atom-labelling scheme for the cation of complex **4b**. Non-hydrogen atoms are represented by their 10% probability ellipsoids. Hydrogen atoms and phenyl rings have been omitted for clarity.

Both structures exhibit a three-legged piano-stool geometry with the η^5-indenyl ligand displaying the usual allylene coordination mode. The Ru(1)–C(10) and Ru(1)–C(11) bond lengths reflect the coordination of the olefin to the metal center[20] [2.276(11) and 2.230(11) (**3a**) and 2.228(7) and 2.245(9) (**4b**)]. The C(10)–C(11) bond length is 1.389(17) Å in **3a** and 1.363(11) Å in **4b**, similar to that found in the complex $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)(Ph_2PCH_2CH{=}CH_2\text{-}\kappa^3P,C,C)][PF_6]$.[11] It is also interesting to note that the benzo ring of the indenyl ligand is oriented almost *trans* to the CO group for complex **3a** and *trans* to the PPh_3 ligand for complex **4b**, as is shown by the dihedral angle between the planes C**–C*–Ru(1) and C*–Ru(1)–C(25) of 12.45° (**3a**) and C**–C*–Ru(1) and C*–Ru(1)–P(2)

Table 1. Selected bond lengths [Å] and bond angles [°] for **3a** and **4b**.[a]

3a		4b	
Ru(1)–C(10)	2.276(11)	Ru(1)–C(10)	2.228(7)
Ru(1)–C(11)	2.230(11)	Ru(1)–C(11)	2.245(9)
C(10)–C(11)	1.389(17)	C(10)–C(11)	1.363(11)
Ru(1)–C*	1.9117	Ru(1)–C*	1.9298
Ru(1)–P(1)	2.322(3)	Ru(1)–P(1)	2.344(2)
Ru(1)–C(25)	1.860(14)	Ru(1)–P(2)	2.301(2)
C(25)–O(1)	1.148(15)		
C(25)–Ru(1)–P(1)	90.1(3)	P(1)–Ru(1)–P(2)	102.45(8)
C(25)–Ru(1)–C(10)	94.62(2)	P(2)–Ru(1)–C(10)	88.2(2)
C(25)–Ru(1)–C(11)	103.8(5)	P(2)–Ru(1)–C(11)	96.5(3)
P(1)–Ru(1)–C(10)	94.0(3)	P(1)–Ru(1)–C(10)	107.0(2)
P(1)–Ru(1)–C(11)	65.5(3)	P(1)–Ru(1)–C(11)	71.5(3)
C(25)–Ru(1)–C*	124.65	P(2)–Ru(1)–C*	121.41
P(1)–Ru(1)–C*	129.62	P(1)–Ru(1)–C*	119.18
C(10)–Ru(1)–C*	122.73	C(10)–Ru(1)–C*	113.8
C(11)–Ru(1)–C*	125.76	C(11)–Ru(1)–C*	133.40

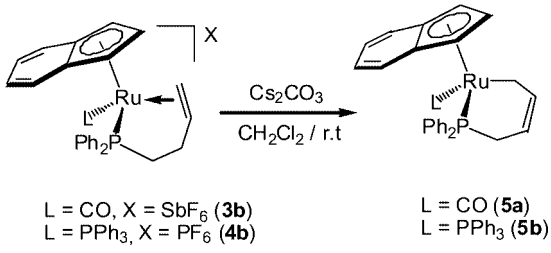
[a] C* = centroid of C(1), C(2), C(3), C(4), and C(5).

11.94° (**4b**).[15] The Ru(1)–C(25) [1.860(14) Å] and C(25)–O(1) [1.148(15) Å] bond lengths for complex **3a** are similar to those found in complex **1c**.

Reactivity of the Complexes [Ru(η^5-C_9H_7)(L)(Ph_2PR-κ^3*P,C,C*)][X]

*Deprotonation Reactions: Synthesis of [Ru(η^5-C_9H_7)(L)(Ph_2PCH_2CH=$CHCH_2$-κ^2*P,C*)] [L = CO (5a), PPh_3 (5b)]*

The complexes [RuCl(η^5-C_9H_7)(L)($Ph_2PCH_2CH_2CH$=CH_2-κ^3*P,C,C*)][X] [X = SbF_6, L = CO (**3b**); X = PF_6, L = PPh_3 (**4b**)] undergo deprotonation reactions in the presence of base. Thus, the treatment of **3b** and **4b** with KO*t*Bu or Cs_2CO_3 in CH_2Cl_2 gives the neutral allylruthenium complexes [Ru(η^5-C_9H_7)(L)(Ph_2PCH_2CH=$CHCH_2$-κ^2*P,C*)] [L = CO (**5a**), PPh_3 (**5b**)], which were isolated as yellow solids in 80–86% yield (Scheme 4).

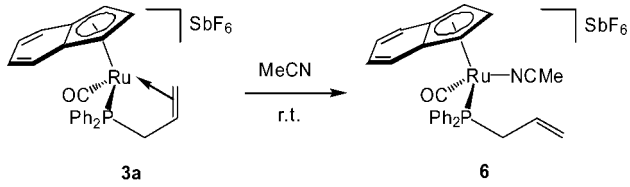


Scheme 4.

Their analytical and spectroscopic data support the proposed formulations (see Experimental Section for details).[21] The most significant spectroscopic features are (a) the IR spectrum of **5a** shows the ν(CO) absorption at 1920 cm^{-1}, (b) the $^{31}P\{^1H\}$ spectra of **5a** and **5b** show the resonance of the chelate-ring phosphorus atom at δ = 101.3 (singlet) and 91.8 ppm (doublet, $^2J_{P,P}$ = 33.7 Hz), respectively, and (c) the $^{13}C\{^1H\}$ NMR spectra show a high-field signal for the Ru–CH_2 carbon (δ = –4.1 ppm for **5a**; δ = –0.7 ppm for **5b**) and two signals for the olefinic carbons of **5a** (δ = 116.4 and 146.0 ppm; $^2J_{C,P}$ = 14.4 Hz) and **5b** (δ = 115.3 and 147.0 ppm; $^2J_{C,P}$ = 13.6 Hz). Moreover, the analogous complexes [Ru(η^5-C_9H_7)(L)(Ph_2PCH_2CH=CH_2-κ^3*P,C,C*)][X] [L = CO, X = SbF_6 (**3a**); L = PPh_3, X = PF_6[11]] do not suffer deprotonation and are recovered unaltered after treatment with KO*t*Bu or Cs_2CO_3 under similar reaction conditions.

*π-Olefin Exchange Reactions: Synthesis of the Complex [Ru(η^5-C_9H_7)(CO)(MeCN)(Ph_2PCH_2CH=CH_2-κ*P*)]-[SbF_6] (6)*

The complex **3a** reacts with acetonitrile to generate the complex [Ru(η^5-C_9H_7)(CO)(MeCN)(Ph_2PCH_2CH=CH_2-κ*P*)][SbF_6] (**6**), which was isolated as a yellow solid in 91% yield (Scheme 5).



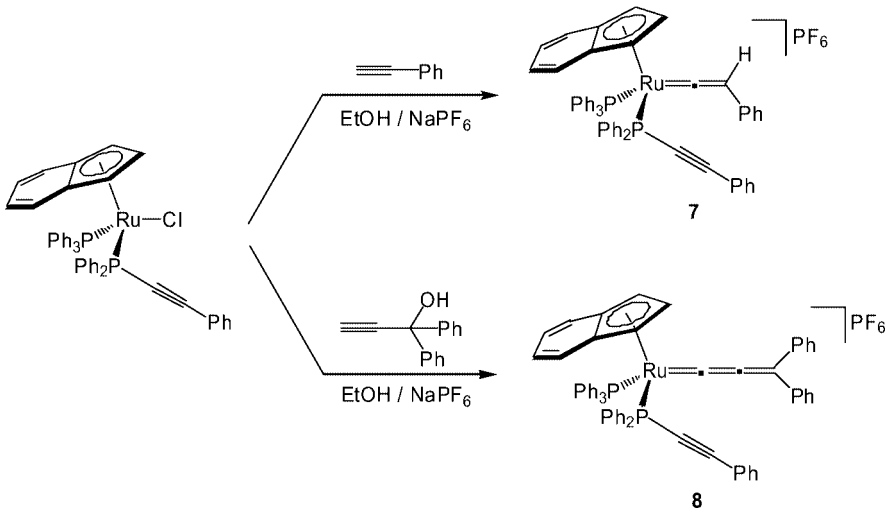
Scheme 5.

Complex **6** was characterized analytically and spectroscopically (see Experimental Section for details). In particular, its IR spectrum shows a strong ν(CO) absorption at 1977 cm^{-1}, a broad singlet resonance is observed at δ = 2.2 ppm for the methyl group of the acetonitrile ligand in the ^1H NMR spectrum, a singlet signal appears in the $^{31}P\{^1H\}$ NMR spectrum at δ = 46.9 ppm, which is in the typical range for monodentate coordination of the phosphane and in agreement with the value found for complex **1a** (δ = 45.0 ppm), and the $^{13}C\{^1H\}$ NMR spectrum shows a singlet signal at δ = 3.7 ppm for the methyl group of the acetonitrile and a low-field doublet signal at δ = 200.2 ppm ($^2J_{C,P}$ = 18.9 Hz) for the CO ligand.

This result agrees with that reported recently for the derivative [Ru(η^5-C_9H_7)(PPh_3)(Ph_2PCH_2CH=CH_2-κ^3*P,C,C*)]-[PF_6], which reacts with acetonitrile to generate a Ph_2CH_2CH=CH_2-κ*P* complex, thus emphasizing the hemilabile character of the allylphosphane.[11,14] However, all attempts to open the $Ph_2PCH_2CH_2CH$=CH_2-κ^3*P,C,C* chelate ring of derivatives **3b** and **4b** by treatment with acetonitrile were unsuccessful, probably due to the higher stability of the six-membered ring.

*Reaction of [RuCl(η^5-C_9H_7)(PPh_3)(Ph_2PC≡CPh-κ*P*)] (2c) with Alkynes: Synthesis of Vinylidene [Ru(η^5-C_9H_7)-(PPh_3)(Ph_2PC≡CPh-κ*P*){C=C(Ph)H}][PF_6] (7) and Allenylidene [Ru(η^5-C_9H_7)(PPh_3)(Ph_2PC≡CPh-κ*P*)-(C=C=CPh_2)][PF_6] (8) Derivatives*

Complex **2c** reacts with terminal alkynes to give cumulenylidene complexes. Thus, the reaction of **2c** with PhC≡CH or Ph_2C(OH)C≡CH in the presence of $NaPF_6$ in refluxing ethanol leads to the expected vinylidene [Ru(η^5-



Scheme 6.

C_9H_7)(PPh_3)($Ph_2PC{\equiv}CPh$-κ*P*){C=C(Ph)H}] (**7**; 82% yield) and allenylidene complexes [Ru(η^5-C_9H_7)(PPh_3)(Ph_2P-C≡CPh-κ*P*)(C=C=CPh_2)] (**8**; 76% yield) as orange and purple solids, respectively (Scheme 6).

Complexes **7** and **8** are soluble in CH_2Cl_2 and THF and insoluble in diethyl ether and hexane. Both complexes were characterized analytically and spectroscopically (see Experimental Section for details). In particular, some data should be noted: (a) the IR spectra show the ν(C≡C) absorption at 2171 (**7**) and 2169 cm^{-1} (**8**) and the ν(C=C=C) absorption at 1931 cm^{-1}; (b) the $^{31}P\{^1H\}$ NMR spectra show two doublets at δ = 20.6 and 41.7 ppm ($^2J_{P,P}$ = 27.2 Hz) for complex **7** and δ = 26.0 and 48.3 ppm ($^2J_{P,P}$ = 28.7 Hz) for complex **8**; (c) the $^{13}C\{^1H\}$ NMR spectra show two signals for the alkynyl carbons at δ = 112.9 and 81.6 (**7**) and 111.3 and 81.7 ppm (**8**). A low-field pseudotriplet signal ($^2J_{C,P}$ = 18.5–16.4 Hz) is observed for the C_α nuclei of the cumulenic group at δ = 355.4 (**7**) and 293.2 ppm (**8**).

Conclusions

In summary, the present work describes the synthesis of a series of chiral-at-ruthenium indenyl complexes containing alkynyl- and alkenylphosphane ligands. In the case of alkenylphosphane complexes both κ*P* and κ^3*P*,*C*,*C* coordination modes have been shown to occur. In complexes with κ^3*P*,*C*,*C*-alkenylphosphane coordination, an effective chiral recognition of a prochiral allyl group has been achieved, the olefin being coordinated to the metal in a diastereoselective way.[22]

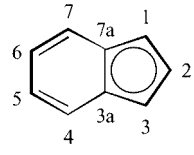
The X-ray structure analysis of representative derivatives showing the κ^3*P*,*C*,*C* coordination mode has been performed and their structure compared with that of the previously described allylphosphane complexes [Ru(η^5-C_9H_7)(PPh_3){$Ph_2PCH_2CR{=}CH_2$-κ^3*P*,*C*,*C*}][PF_6] (R = H, Me).[11] Moreover, these complexes can be used as model systems to study the diastereoselective coordination found for the alkenylphosphane ligand in $Ph_2P(CH_2)_nCH{=}CH_2$-κ^3*P*,*C*,*C* complexes.

The reactivity of the alkenylphosphane ligand is highly dependent on the size of the chelate ring. Thus, the complex **3a**, which contains the allylphosphane ligand $Ph_2PCH_2CHCH_2$-κ^3*P*,*C*,*C*, undergo ring opening upon reaction with two-electron ligands, thus emphasizing the hemilabile character of the ligand, while complexes **3b** and **4b**, with the six-membered chelate ring $Ph_2PCH_2CH_2CHCH_2$-κ^3*P*,*C*,*C*, undergo no transformation in acetonitrile.

The alkynylphosphane complex **1c** is able to activate terminal alkynes, leading to the formation of vinylidene [Ru(η^5-C_9H_7)(PPh_3)($Ph_2PC{\equiv}CPh$-κ*P*){C=C(Ph)H}][PF_6] (**7**) and allenylidene [Ru(η^5-C_9H_7)(PPh_3)($Ph_2PC{\equiv}CPh$-κ*P*)(C=C=CPh_2)][PF_6] (**8**) derivatives.

Experimental Section

General: All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds [RuCl(η^5-C_9H_7)(PPh_3)$_2$],[23] [RuI(η^5-C_9H_7)(CO)$_2$],[24] Ph_2PCH_2-$CH{=}CH_2$,[25] $Ph_2PCH_2CH_2CH{=}CH_2$,[26] and $Ph_2PC{\equiv}CPh$[27] were prepared by previously reported methods. Infrared spectra were recorded with a Perkin–Elmer 1720-XFT or a Perkin–Elmer 599 IR spectrometer. The C, H, and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. NMR spectra were recorded with Bruker AC 300 and 300 DPX instruments at 300 (^{1}H), 121.5 (^{31}P), or 75.4 MHz (^{13}C) or a Bruker AC 400 instrument at 400.1 (^{1}H), 161.9 (^{31}P), or 100.6 MHz (^{13}C) with $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments were carried out for all the complexes. The following atom labels have been used for the ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic data.



Synthesis of [RuI(η^5-C_9H_7)(CO)(Ph_2PR-κ*P*)] [R = $CH_2CH{=}CH_2$ (1a), $CH_2CH_2CH{=}CH_2$ (1b), C≡CPh (1c)]: Previously sublimed Me_3NO (188 mg, 2.50 mmol) was added to a solution of [RuI(η^5-C_9H_7)$(CO)_2$] (500 mg, 1.25 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 10 min at room temperature. After this time, the initial orange solution turned nearly black, and the complex [Ru(η^5-C_9H_7)(NMe_3)(CO)] had formed (checked by IR spectroscopy in solution). The corresponding phosphane ligand was then added (1.5 mmol) and the reaction mixture stirred for 15–30 min. The resulting solution was evaporated to dryness and the residue extracted with toluene (2 × 20 mL) and vacuum-dried. The solid residue was then recrystallized from CH_2Cl_2/hexane and complexes **1a**–**c** were obtained as red solids.

1a: Time: 15 min. Yield: 596 mg (80%). IR (KBr): ν(CO) = 1940 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 18 °C): δ = 3.33 (m, 1 H, P–CH_2), 3.51 (m, 1 H, P–CH_2), 3.58 (s, 1 H, 1-H or 3-H), 4.92 (m, 2 H, =CH_2), 5.28 (m, 1 H, 2-H), 5.58 (m, 2 H, =CH, 1-H or 3-H), 7.29 (m, 14 H, 4,5,6,7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 18 °C): δ = 38.1 (d, $J_{C,P}$ = 30.3 Hz, P–CH_2), 70.4 (s, C-1 or C-3), 71.3 (d, $^2J_{C,P}$ = 7.1 Hz, C-1 or C-3), 89.4 (s, C-2), 110.5, 111.9 (s, C-3a, C-7a), 119.3 (d, $^2J_{C,P}$ = 11.1 Hz, =CH_2), 123.0–137.4 (=CH, C-4,5,6,7, Ar), 203.0 (d, $^2J_{C,P}$ = 21.2 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 18 °C): δ = 45.0 ppm (s). $C_{25}H_{22}IOPRu$ (597.39): calcd. C 50.26, H 3.71; found C 51.38, H 3.95.

1b: Time: 30 min. Yield: 596 mg (78%). IR (KBr): ν(CO) = 1930 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 18 °C): δ = 1.85 (m, 1 H, CH_2), 2.07 (m, 1 H, CH_2), 2.52 (m, 1 H, P–CH_2), 2.74 (m, 1 H, P–CH_2), 4.57 (s, 1 H, 1-H, 2-H or 3-H), 4.91 (m, 2 H, =CH_2), 5.28 (s, 1 H, 1-H, 2-H or 3-H), 5.60 (s, 1 H, 1-H, 2-H or 3-H), 5.69 (m, 1 H, =CH), 6.69 (d, $J_{H,H}$ = 8.26 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 6.86 (t, $J_{H,H}$ = 7.4 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 7.14–7.63 (m, 12 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 18 °C): δ = 28.4 (s, CH_2), 32.1 (d, $J_{C,P}$ = 30.5 Hz, P–CH_2), 70.6 (s, C-1 or C-3), 72.0 (d, $^2J_{C,P}$ = 7.4 Hz, C-1 or C-3), 89.7 (s, C-2), 111.0, 112.3 (s, C-3a, C-7a), 114.8 (s, =CH_2), 123.2–137.5 (=CH, C-4,5,6,7, Ar), 203.5 (d, $^2J_{C,P}$ = 21.3 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 18 °C): δ = 44.0 ppm (s). $C_{26}H_{24}IOPRu$ (611.42): calcd. C 51.08, H 3.96; found C 52.47, H 4.44.

1c: Time 30 min. Yield: 797 mg (97%). IR (KBr): ν(C≡C) = 2176, ν(CO) = 1940 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 18 °C): δ = 4.82 (br. s, 1 H, 1-H or 3-H), 5.57 (pseudo t, $J_{H,H}$ = 2.6 Hz, 1 H, 2-H), 5.79 (br. s, 1 H, 1-H or 3-H), 6.95–7.73 (m, 19 H, 4,5,6,7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 18 °C): δ = 71.0 (s, C-1 or C-3), 73.7 (d, $^2J_{C,P}$ = 9.9 Hz, C-1 or C-3), 84.1 (d, $J_{C,P}$ = 93.6 Hz, P–*C*≡C), 90.0 (s, C-2), 108.9 (d, $^2J_{C,P}$ = 14.4 Hz, P–C≡*C*), 111.0, 111.7 (s, C-3a, C-7a), 121.2–134.1 (C-4,5,6,7, Ar), 202.4 (d, $^2J_{C,P}$ = 20.7 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 18 °C): δ = 22.5 ppm (s). $C_{30}H_{22}IOPRu$ (657.44): calcd. C 54.81, H 3.37; found C 53.26, H 2.90.

Synthesis of [RuCl(η^5-C_9H_7)(PPh_3)($Ph_2PCH_2CH_2CH{=}CH_2$-κ*P*)] (2b): A solution of [RuCl(η^5-C_9H_7)$(PPh_3)_2$] (500 mg, 0.64 mmol) and homoallyldiphenylphosphane (168 mg, 0.70 mmol) in THF (40 mL) was refluxed for 20 min. It was then concentrated to about 10 mL and CuI (183 mg, 0.96 mmol) was added. After 30 min at room temperature, the solution was evaporated to dryness and the residue extracted with diethyl ether (2 × 20 mL), vacuum-dried, and recrystallized from diethyl ether/hexane (1:10) to obtain complex **2b** as a red solid. Yield: 290 mg (60%). ^1H NMR (300 MHz, $CDCl_3$, 18 °C): δ = 0.81 (m, 1 H, CH_2), 0.97 (m, 1 H, CH_2), 1.50 (m, 1 H, CH_2), 2.56 (m, 1 H, CH_2), 4.67 (m, 4 H, 1-H, 3-H, =CH_2), 4.84 (t, $J_{H,H}$ = 2.0 Hz, 2-H), 5.33 (m, 1 H, =CH), 6.30 (d, $J_{H,H}$ = 8.2 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 6.81–8.00 (m, 28 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 18 °C): δ = 20.3 (d, $J_{C,P}$ = 22.9 Hz, P–CH_2), 28.7 (d, $^2J_{C,P}$ = 8.3 Hz, CH_2), 61.6 (s, C-1 or C-3), 69.4 (d, $^2J_{C,P}$ = 11.4 Hz, C-1 or C-3), 90.6 (s, C-2), 109.8, 111.3 (s, C-3a, C-7a), 113.8 (s, =CH_2), 123.3–138.2 (=CH, C-4,5,6,7, Ar) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 18 °C): δ = 45.6 (d, $^2J_{P,P}$ = 42.9 Hz), 49.0 (d, $^2J_{P,P}$ = 42.9 Hz) ppm. $C_{43}H_{39}ClP_2Ru$ (754.24): calcd. C 68.47, H 5.21; found C 67.05, H 4.30.

Synthesis of [RuCl(η^5-C_9H_7)(PPh_3)($Ph_2PC{\equiv}CPh$-κ*P*)] (2c): A solution of [RuCl(η^5-C_9H_7)$(PPh_3)_2$] (500 mg, 0.64 mmol) and phenylalkynyldiphenylphosphane (161 mg, 0.77 mmol) in THF (55 mL) was refluxed for 10 min. The solution was then evaporated to dryness and the solid residue extracted with diethyl ether (2 × 20 mL). The solution was concentrated under vacuum and the product precipitated as a red solid upon addition of hexane; it was vacuum-dried. Yield: 307 mg (60%). IR (KBr): ν(C≡C) = 2168 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 18 °C): δ = 3.80, 4.29, 4.87 (s, 4 H, 1,2,3-H and 4-H, 5-H, 6-H, or 7-H), 6.84–7.87 (m, 33 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 18 °C): δ = 66.6 (s, C-1 or C-3), 69.5 (d, $^2J_{C,P}$ = 9.5 Hz, C-1 or C-3), 87.2 (d, $J_{P,C}$ = 80.7 Hz, P–*C*≡C), 91.8 (s, C-2), 109.1, (d, $J_{C,P}$ = 11.5 Hz, P–C≡*C*), 110.5 (s, C-3a or C-7a), 111.8 (d, $^2J_{C,P}$ = 3.8 Hz, C-3a or C-7a), 122.5–134.7 (C-4,5,6,7, Ar) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 18 °C): δ = 29.1 (d, $^2J_{P,P}$ = 45.0 Hz), 48.1 (d, $^2J_{P,P}$ = 45.0 Hz) ppm. $C_{47}H_{37}ClP_2Ru{\cdot}CH_2Cl_2$ (800.27): calcd. C 65.13, H 4.44; found C 66.41, H 4.04.

Synthesis of [Ru(η^5-C_9H_7)(CO)(Ph_2PR-κ^3*P*,*C*,*C*)][SbF_6] [R = $CH_2CH{=}CH_2$ (3a), $CH_2CH_2CH{=}CH_2$ (3b)]: A solution of the complex [RuCl(η^5-C_9H_7)(Ph_2PR-κ^1*P*)(CO)] [R = $CH_2CH{=}CH_2$ (**1a**), $CH_2CH_2CH{=}CH_2$ (**1b**)] (0.82 mmol) and $AgSbF_6$ (337 mg, 0.98 mmol) in CH_2Cl_2 (80 mL) was stirred for 1 h at room temperature in the absence of light. A change of color from red to yellow was observed. After this time, the suspension was exposed to light for 1 h, then filtered through kieselguhr and the solvents evaporated to dryness. The solid residue was recrystallized from CH_2Cl_2/hexane (1:10), washed with hexane (2 × 20 mL), and vacuum-dried.

3a: Yield: 562 mg (97%). IR (KBr): ν(CO) = 2012, ν(SbF_6) = 658 cm^{-1}. Conductivity (acetone): 123 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (400.1 MHz, CD_2Cl_2, 18 °C): δ = 2.36 (m, 1 H, =CH_2), 2.82 (m, 1 H, P–CH_2), 3.47 (m, 1 H, =CH_2), 3.92 (m, 1 H, =CH), 4.43 (m, 1 H, P–CH_2), 5.47 (pseudo t, $J_{H,H}$ = 2.5 Hz, 1 H, 2-H), 5.85, 6.05 (s, 1 H each, 1-H, 3-H), 6.78 (d, $J_{H,H}$ = 8.6 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 7.16–7.71 (m, 13 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 18 °C): δ = 34.0 (d, $J_{C,P}$ = 38.2 Hz, P–CH_2), 55.1 (d, $J_{C,P}$ = 20.1 Hz, =CH), 57.0 (d, $J_{C,P}$ = 6.0 Hz, =CH_2), 73.8, 76.3 (s, C-1, C-3), 93.9 (s, C-2), 106.9, 108.9 (s, C-3a, C-7a), 122.6–134.7 (C-4,5,6,7, Ar), 202.0 (d, $^2J_{C,P}$ = 16.1 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 18 °C): δ = –56.4 ppm (s). $C_{25}H_{22}F_6OPRuSb$ (706.24): calcd. C 42.52, H, 3.14; found C 42.12, H 3.09.

3b: Yield: 561 mg (95%). IR (KBr): ν(CO) = 2001, ν(SbF_6) = 659 cm^{-1}. Conductivity (acetone): 144 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (400.1 MHz, CD_2Cl_2, 18 °C): δ = 1.73 (m, 1 H, CH_2), 2.11 (d, $J_{H,H}$ = 8.6 Hz, 1 H, =CH_2), 2.66 (m, 2 H, CH_2 and P–CH_2), 3.06 (m, 1 H, P–CH_2), 3.13 (d, $J_{H,H}$ = 13.0 Hz, 1 H, =CH_2), 4.48 (m, 1 H, =CH), 5.61 (m, 1 H, 2-H), 5.87 (s, 1 H, 1-H or 3-H), 6.27 (s, 1 H, 1-H or 3-H), 6.60 (dd, $J_{H,H}$ = 8.6, $J_{H,H}$ = 1.0 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 7.27–7.69 (m, 13 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 18 °C): δ = 28.1 (d, $J_{C,P}$ = 6.0 Hz, CH_2), 38.8 (d, $J_{C,P}$ = 34.2 Hz, P–CH_2), 54.9 (s, =CH_2), 74.6, 77.8 (s, C-1, C-3), 85.2 (d, $J_{C,P}$ = 5.0 Hz, =CH), 94.7 (s, C-2), 107.5, 110.0 (s, C-3a, C-7a), 121.7–134.7 (C-4,5,6,7, Ar), 200.2 (d, $^2J_{C,P}$ = 18.1 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz,

CD_2Cl_2, 18 °C): δ = 74.6 ppm (s). $C_{26}H_{24}F_6OPRuSb{\cdot}CH_2Cl_2$ (720.26): calcd. C 40.28, H 3.25; found C 40.18, H 2.78.

Synthesis of [Ru(η⁵-C₉H₇)(PPh₃)(Ph₂PCH₂CH₂CH=CH₂-κ³*P*,*C*,*C*)][PF₆] (4b): A solution of the complex [RuCl(η⁵-C_9H_7)(PPh_3)($Ph_2PCH_2CH_2CH=CH_2$-κ*P*)] (500 mg, 0.66 mmol) and $NaPF_6$ (222 mg, 1.32 mmol) in EtOH (30 mL) was refluxed for 5 min. After this time, the solution was evaporated to dryness and the residue extracted with CH_2Cl_2 (2×20 mL). The solvent was then concentrated to about 2 mL and diethyl ether (20 mL) was added. The yellow solid obtained was washed with diethyl ether (2×10 mL) and vacuum-dried. Yield: 382 mg (67%). IR (KBr): ν(PF_6) = 838 cm^{-1}. Conductivity (acetone): 97 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300.1 MHz, CD_2Cl_2, 18 °C): δ = 1.78 (d, $J_{H,H}$ = 8.8 Hz, 1 H, =CH_2), 2.24 (m, 2 H, CH_2), 2.54 (m, 2 H, CH_2), 3.57 (m, 1 H, =CH_2), 5.10 (s, 1 H, 1-H, 2-H or 3-H), 5.30 (m, 1 H, =CH), 5.37 (s, 1 H, 1-H, 2-H or 3-H), 5.51 (s, 1 H, 1-H, 2-H or 3-H), 6.79–7.69 (m, 29 H, 4,5,6,7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 18 °C): δ = 24.4 (d, $^2J_{C,P}$ = 6.7 Hz, P–CH_2), 40.0 (d, $J_{C,P}$ = 33.5 Hz, CH_2), 79.3 (s, C-1 or C-3), 82.1 (d, $^2J_{C,P}$ = 12.0 Hz, C-1 or C-3), 87.6 (s, C-2), 97.5, 103.6 (s, C-3a, C-7a), 107.4 (d, $J_{C,P}$ = 3.4 Hz, =CH_2), 122.5–133.6 (=CH, C-4,5,6,7, Ar) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 18 °C): δ = 47.3 (d, $^2J_{P,P}$ = 29.5 Hz), 69.3 (d, $^2J_{P,P}$ = 29.5 Hz) ppm. MS (FAB+): *m*/*z* = 719 [M^+].

Synthesis of [Ru(η⁵-C₉H₇)(L)(Ph₂PCH₂CH=CHCH₂-κ²*P*,*C*)] [L = CO (5a), PPh₃ (5b)]: A solution of [Ru(η⁵-C_9H_7)(L)-($Ph_2PCH_2CH_2CH=CH_2$-κ³*P*,*C*,*C*)][X] [X = SbF_6, L = CO (**3b**); X = PF_6, L = PPh_3 (**4b**)] (0.14 mmol) and Cs_2CO_3 (228 mg, 0.7 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 h at room temperature. After this time the solution was filtered through kieselguhr and the solvents evaporated to dryness. The solid residue was extracted with 20 mL of diethyl ether and precipitated with hexane. The yellow solid obtained was washed with hexane (2×10 mL) and vacuum-dried.

5a: Yield: 46 mg (86%). IR (KBr): ν(CO) = 1920 cm^{-1}. ^1H NMR (400.1 MHz, C_6D_6, 18 °C): δ = 2.19 (m, 1 H, Ru–CH_2) 2.35 (m, 1 H, Ru–CH_2), 2.69 (m, 2 H, P–CH_2), 4.82 (s, 1 H, 1-H or 3-H), 5.04 (s, 1 H, 2-H), 5.34 (s, 1 H, 1-H or 3-H), 5.51 (m, 1 H, =CH), 6.46 (d, $J_{H,H}$ = 8.1 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 6.78 (m, 1 H, =CH), 6.97–7.27 (m, 13 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 18 °C): δ = –4.1 (d, $J_{C,P}$ = 8.8 Hz, Ru–CH_2), 26.8 (d, $J_{C,P}$ = 22.4 Hz, CH_2), 72.0 (d, $^2J_{C,P}$ = 7.2 Hz, C-1 or C-3), 74.3 (s, C-1 or C-3), 98.3 (s, C-2), 108.1 (s, C-3a, C-7a), 116.4 (s, =CH), 122.5–141.6 (C-4,5,6,7, Ar), 146.0 (d, $J_{C,P}$ = 14.4 Hz, =CH), 205.4 (d, $^2J_{C,P}$ = 16.8 Hz, CO) ppm. $^{31}P\{^1H\}$(162.0 MHz, C_6D_6, 18 °C): δ = 101.3 ppm (s). MS (FAB+): *m*/*z* = 485 [M^+ + 1].

5b: Yield: 80 mg (80%). ^1H NMR (400.1 MHz, CD_2Cl_2, –50 °C): δ = 0.79 (m, 1 H, Ru–CH_2), 1.62 (m, 1 H, P–CH_2), 2.43 (m, 1 H, Ru–CH_2), 3.30 (m, 1 H, P–CH_2), 3.99 (s, 1 H, 1-H or 3-H), 4.19 (s, 1 H, 1-H or 3-H), 5.15 (s, 1 H, 2-H), 5.51 (m, 1 H, =CH), 6.67 (m, 1 H, =CH), 6.92–7.66 (m, 29 H, 4,5,6,7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, –50 °C): δ = –0.7 (br. s, Ru–CH_2), 25.8 (d, $J_{C,P}$ = 20.4 Hz, P–CH_2), 71.1 (s, C-1 or C-3), 74.0 (d, $^2J_{C,P}$ = 5.4 Hz, C-1 or C-3), 93.5 (pseudo t, $^2J_{C,P}$ = 4.7 Hz, C-2), 103.8, 109.7 (s, C-3a, C-7a), 115.3 (s, =CH), 121.0–144.9 (C-4,5,6,7, Ar), 147.0 (d, $J_{C,P}$ = 13.6 Hz, =CH) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 18 °C): δ = 56.2 (d, $^2J_{P,P}$ = 33.7 Hz), 91.8 (d, $^2J_{P,P}$ = 33.7 Hz) ppm. MS (FAB+): *m*/*z* = 719 [M^+ + 1].

Synthesis of [Ru(η⁵-C₉H₇)(MeCN)(CO)(Ph₂PCH₂CH=CH₂-κ*P*)]-[SbF₆] (6): A solution of [Ru(η⁵-C_9H_7)(CO)($PPh_2CH_2CH=CH_2$-κ³*P*,*C*,*C*)][SbF_6] (500 mg, 0.7 mmol) in MeCN (100 mL) was stirred at room temperature for 2.5 h. The solution was then evaporated to dryness and the residue extracted with CH_2Cl_2 (2×20 mL). The solvent was then concentrated to about 2 mL and hexane (20 mL) was added. The yellow solid obtained was washed with hexane (2×10 mL) and vacuum-dried. Yield: 530 mg (91%). IR (KBr): ν(CO) = 1977, ν(SbF_6) = 658 cm^{-1}. Conductivity (acetone): 123 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, $CDCl_3$, 18 °C): δ = 2.23 (br. s, 3 H, CH_3), 3.35 (m, 2 H, P–CH_2), 5.15 and 5.28 (2×m, 5 H, =CH_2 and 1,2,3-H), 5.48 (m, 1 H, =CH), 7.22–7.68 (m, 14 H, 4,5,6,7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 18 °C): δ = 3.7 (s, CH_3), 36.6 (d, $J_{C,P}$ = 30.2 Hz, P–CH_2), 65.8, 67.1 (s, C-1, C-3), 93.3 (s, C-2), 109.3, 112.9 (s, C-3a, C-7a), 121.4 (d, $J_{C,P}$ = 12.1 Hz, =CH_2), 123.5–132.3 (C-4,5,6,7, Ar), 200.2 (d, $^2J_{C,P}$ = 18.9 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 18 °C): δ = 46.9 ppm (s). $C_{27}H_{25}F_6OPNRuSb$ (747.29): calcd. C 43.40, H 3.37, N 1.87; found C 42.48, H 3.67, N 1.90.

Synthesis of [Ru(η⁵-C₉H₇)(PPh₃)(Ph₂PC≡CPh-κ*P*){=C=C(Ph)H}]-[PF₆] (7): A solution of [RuCl(η⁵-C_9H_7)(PPh_3)($Ph_2PC{\equiv}CPh$-κ*P*)] (50 mg, 0.07 mmol), $NaPF_6$ (23 mg, 0.14 mmol), and phenylacetylene (36 mg, 0.35 mmol) in EtOH (8 mL) was refluxed for 15 min. After this time the solution was evaporated to dryness and the residue was extracted with CH_2Cl_2 (2×10 mL). The solvent was then concentrated to about 2 mL and hexane (20 mL) was added. The orange solid obtained was washed with hexane (2×10 mL) and vacuum-dried. Yield: 58 mg (82%). IR (KBr): ν(C≡C) = 2171, ν(PF_6) = 838 cm^{-1}. Conductivity (acetone): 96 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2, 18 °C): δ = 5.30, 5.54, 5.74 (s, 1 H each, 1,2,3-H), 5.94 (d, $J_{H,H}$ = 8.3 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 6.21 (s, 1 H, =CH), 6.37 (d, $J_{H,H}$ = 8.3 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 6.78–7.58 (m, 37 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $(CD_3)_2CO$, 18 °C): δ = 81.6 (d, $J_{C,P}$ = 95.0 Hz, P–*C*≡C), 82.5 (s, C-1 and C-3), 100.6 (s, C-2), 112.9 (d, $^2J_{C,P}$ = 12.3 Hz, P–C≡*C*), 115.1 (s, C-3a or C-7a), 117.2 (s, C_β), 120.9 (d, $J_{C,P}$ = 2.6 Hz, C-3a or C-7a), 123.9–135.2 (Ar), 355.4 (pseudo t, $^2J_{C,P}$ = 16.4, C_α) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 18 °C): δ = 20.6 (d, $^2J_{P,P}$ = 27.2 Hz), 41.7 (d, $^2J_{P,P}$ = 27.2 Hz) ppm.

Synthesis of [Ru(η⁵-C₉H₇)(PPh₃)(Ph₂PC≡CPh-κ*P*)(=C=C=CPh₂)]-[PF₆] (8): A solution of [RuCl(η⁵-C_9H_7)(PPh_3)($Ph_2PC{\equiv}$CPh-κ*P*)] (50 mg, 0.07 mmol), $NaPF_6$ (23 mg, 0.14 mmol), and 1,1-diphenylprop-2-yn-1-ol (72 mg, 0.35 mmol) in EtOH (8 mL) was refluxed for 20 min. After this time the solution was evaporated to dryness and the residue was extracted with CH_2Cl_2 (2×10 mL). The solution was concentrated under vacuum and the product precipitated and washed with hexane (2×10 mL). The violet solid obtained was vacuum-dried. Yield: 59 mg (76%). IR (KBr): ν(C≡C) = 2169, ν(C=C=C) = 1931, ν(PF_6) = 837 cm^{-1}. Conductivity (acetone): 133 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, $CDCl_3$, 18 °C): δ = 5.24, 5.66, 5.72 (s, 3 H, 1,2,3-H), 6.22 (d, $J_{H,H}$ = 8.0 Hz, 1 H, 4-H, 5-H, 6-H, or 7-H), 6.88–7.84 (m, 43 H, 4-H, 5-H, 6-H, or 7-H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 18 °C): δ = 80.8 (d, $J_{C,P}$ = 5.8 Hz, C-1 or C-3), 81.7 (dd, $J_{C,P}$ = 92.5, $^3J_{C,P}$ = 3.5 Hz, P–*C*≡C), 82.6 (d, $J_{C,P}$ = 7.0 Hz, C-1 or C-3), 98.4 (s, C-2), 111.3 (d, $^2J_{C,P}$ = 10.4 Hz, P–C≡*C*), 113.5 (s, C-3a or C-7a), 119.5 (d, $^2J_{C,P}$ = 2.3 Hz, C-3a or C-7a), 122.6–142.8 (Ar), 158.5 (s, C_γ), 204.9 (s, C_β), 293.2 (pseudo t, $^2J_{C,P}$ = 18.5 Hz, C_α) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 18 °C): δ = 26.0 (d, $^2J_{P,P}$ = 28.7 Hz), 48.3 (d, $^2J_{P,P}$ = 28.7 Hz) ppm.

X-ray Crystal Structure Determination of Complexes 1c, 3a, and 4b: Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane (**1c**) or pentane (**3a** and **4b**) into a saturated solution of the complexes in dichloromethane. The most relevant crystal and refinement data are collected in Table 2. Diffraction data for **1c** were recorded with a Bruker Smart 6k CCD area-

Table 2. Crystal data and structure refinement for **1c**, **3a**, and **4b**.

	1c	**3a**	**4b**
Chemical formula	$C_{30}H_{22}IOPRu$	$C_{25}H_{22}F_6OPRuSb$	$C_{43}H_{39}F_6P_3Ru$
Mol. mass	657.42	706.22	863.72
T [K]	296(2)	293(2)	293(2)
Wavelength [Å]	1.54184	1.54184	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	8.71010(10)	12.1110(9)	10.8581(13)
b [Å]	17.1308(3)	13.2257(8)	36.732(4)
c [Å]	17.7376(3)	16.0508(10)	19.627(2)
α [°]	81.6670(10)	80.581(4)	90
β [°]	77.1680(10)	86.865(4)	105.209(2)
γ [°]	83.3500(10)	89.774(4)	90
V [Å^3]	2543.69(7)	2532.5(3)	7553.9(14)
Z	4	4	8
$\rho_{calcd.}$ [g cm^{-3}]	1.717	1.852	1.519
μ [mm^{-1}]	15.268	14.442	0.603
F(000)	1288	1376	3520
Crystal size [mm]	0.25 × 0.15 × 0.12	0.125 × 0.05 × 0.025	0.25 × 0.21 × 0.19
θ range [°]	2.57 to 70.62	2.79 to 70.06	1.54 to 26.12
Index ranges	$-13 \le h \le 12$	$-14 \le h \le 14$	$-13 \le h \le 12$
	$0 \le k< \le 45$	$-15 \le k \le 16$	$0 \le k \le 45$
	$0 \le l \le 24$	$0 \le l \le 19$	$0 \le l \le 24$
No. of reflns. collected	16413	50571	37632
No. of unique reflns.	8462 [R(int) = 0.0295]	9308 [R(int) = 0.066]	14418 [R(int) = 0.10]
Completeness to θ_{max}	86.6%	96.7%	95.8%
No. of parameters/restraints	613/0	616/0	955/0
Goodness-of-fit on F^2	0.984	0.959	0.998
Weight function (a, b)		0.0546,13.5440	0.0694, 0.1691
R_1[a] [$I > 2\rho(I)$]	0.0312	0.0619	0.0916
wR_2[a] [$I > 2\rho(I)$]	0.0772	0.1544	0.1061
R_1 (all data)	0.0360	0.1074	0.2105
wR_2 (all data)	0.0800	0.1977	0.1283
Largest diff peak and hole [e Å^{-3}]	1.218 and-0.565	2.668 and –1.042	0.6166 and –1.115

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}$½.

detector three-circle diffractometer (Cu-K_α radiation, λ = 1.5418 Å). The data were collected using 0.3°-wide ω scans with a crystal-to-detector distance of 40 mm. The diffraction frames were integrated using the SAINT package[28] and corrected for absorption with SADABS.[29] For **3a** diffraction data were recorded with a Nonius Kappa CCD single crystal diffractometer using Cu-K_α radiation (λ = 1.5418 Å) − the crystal-to-detector distance was fixed at 29 mm − and using the oscillation method, with 2° oscillation and 40 s exposure time per frame. The data collection strategy was calculated with the program Collect.[30] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack[31] and absorption correction was applied by means of SORTAV.[32] Data for **4b** were collected on a Bruker Smart CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were collected using 0.3°-wide ω scans with a crystal-to-detector distance of 40 mm. The diffraction frames were integrated using the SAINT package[28] and corrected for absorption with SADABS.[29]

The software package WINGX was used for space group determination, structure solution, and refinement.[33] The structures were solved by Patterson interpretation and phase expansion using DIRDIF.[34] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[35] For all the complexes, during the final stages all non-hydrogen atoms were refined with anisotropic displacement parameters and the H atoms were geometrically located and their coordinates were refined riding on their parent atoms. The maximum residual electron density is located near to heavy atoms (Ru, I) for **1c** and near to the disordered PF_6^- ions for **3a**.

The function minimized was $[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a = 0.0512 and b = 0 for **1c**, a = 0.0899 and b = 0 for **3a**, a = 0.0228 and b = 0 for **4b**) 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 from the International Tables for X-ray Crystallography.[36] Geometrical calculations were made with PARST.[37] The crystallographic plots were made with PLATON.[38] CCDC-276224 (**1c**), -276225 (**3a**), and -276226 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] For representative examples of complexes with $R_2PCH{=}CH_2$, see the following: [M] = [Cr] and [Mo] a) P. G. Edwards, J. S. Fleming, S. S. Liyanage, S. J. Coles, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1996**, 1801–1807; [Os]: b) M. Baya, M. L. Buil, M. A. Esteruelas, E. Oñate, *Organometallics* **2005**, *24*, 2030–2038; c) M. A. Esteruelas, A. I. González, A. M.

López, E. Oñate, *Organometallics* **2004**, *23*, 4858–4869; [Rh]: d) L. P. Barthel-Rosa, V. J. Catalano, K. Maitra, J. H. Nelson, *Organometallics* **1996**, *15*, 3924–3934. For representative examples of complexes with $R_2PCH_2CH=CH_2$, see the following: [M] = [Cr] and [Mo], see ref.[1a]; [W]: e) X. Morise, M. L. H. Green, P. C. McGowan, S. J. Simpson, *J. Chem. Soc., Dalton Trans.* **1994**, 571–578; [Pd]: f) S. J. Coles, P. Faulds, M. B. Hursthouse, D. G. Kelly, G. C. Ranger, A. J. Toner, N. M. Walker, *J. Organomet. Chem.* **1999**, *586*, 234–240. For examples of complexes with $R_2PCH_2CH_2CH=CH_2$, see the following: [M] = [Ni]: g) K. Issleib, M. Haftendorn, *Z. Anorg. Allg. Chem.* **1967**, *351*, 9–17; [Rh] and [Ir]: h) D. V. Krupenya, S. I. Selivanov, S. P. Tunik, M. Haukka, T. A. Pakkanen, *Dalton Trans.* **2004**, 2541–2549; i) P. W. Clark, G. E. Hartwell, *J. Organomet. Chem.* **1975**, *102*, 387–396.

[2] For representative examples of alkynylphosphane complexes, see the following: [M] = [Fe]: a) E. Louattani, J. Suades, A. Álvarez-Larena, J. F. Piniella, G. Germain, *J. Organomet. Chem.* **1996**, *506*, 121–127; [Mo]: b) E. Louattani, J. Suades, *J. Organomet. Chem.* **2000**, *604*, 234–240; [Rh], [Ir], and [Pt]: c) J. R. Berenguer, M. Bernechea, J. Forniés, A. García, E. Lalinde, M. T. Moreno, *Inorg. Chem.* **2004**, *43*, 8185–8198; d) J. Forniés, A. García, B. Gil, E. Lalinde, M. T. Moreno, *Dalton Trans.* **2004**, 3854–3863; e) J. Forniés, A. García, J. Gómez, E. Lalinde, M. T. Moreno, *Organometallics* **2002**, *21*, 3733–3743; [Au]: f) M. Bardaji, A. Laguna, P. G. Jones, *Organometallics* **2001**, *20*, 3906–3912.

[3] For recent examples of ruthenium complexes with DCVP see: a) D. Dorota, J. H. Nelson, *Dalton Trans.* **2005**, 92–103; b) K. Y. Ghebreyessus, J. H. Nelson, *Synth. React. Inorg. Met.-Org. Chem.* **2003**, *33*, 1329–1349.

[4] For recent examples of ruthenium complexes with DPVP see: a) D. C. Wilson, J. H. Nelson, *J. Organomet. Chem.* **2003**, *682*, 272–289; b) H. D. Hansen, J. H. Nelson, *Inorg. Chim. Acta* **2003**, *352*, 4–8; c) G. Kesete, J. H. Nelson, *Inorg. Chem. Commun.* **2003**, *6*, 1044–1047; d) D. Dorota, J. H. Nelson, *Dalton Trans.* **2003**, 449–457; e) G. Kesete, J. H. Nelson, *Organometallics* **2000**, *19*, 3387–3392; f) H. Heather, J. H. Nelson, *Organometallics* **2000**, *19*, 4740–4755.

[5] For recent examples of ruthenium complexes with ADPP see: a) D. Cuervo, M. P. Gamasa, J. Gimeno, *Chem. Eur. J.* **2004**, *10*, 425–432; b) K. D. Redwine, J. H. Nelson, *J. Organomet. Chem.* **2000**, *613*, 177–199; c) L. P. Barthel-Rosa, K. Maitra, J. Fischer, J. H. Nelson, *Inorg. Chem.* **1998**, *37*, 633–639.

[6] C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1999**, *18*, 1011–1017.

[7] a) J. R. Berenguer, M. Bernechea, J. Forniés, A. García, E. Lalinde, *Organometallics* **2004**, *23*, 4288–4300; b) J. R. Berenguer, M. Bernechea, J. Forniés, J. Gómez, E. Lalinde, *Organometallics* **2002**, *21*, 2314–2324; c) C. J. Adams, M. I. Bruce, B. W. Skelton, A. H. White, *Inorg. Chem.* **1992**, *31*, 3336–3338; d) G. Mohamed, B. Demerseman, P. H. Dixneuf, *J. Organomet. Chem.* **1992**, *424*, 65–70.

[8] a) F. Hong, Y. Ho, Y. Chang, Y. Lai, *Tetrahedron* **2004**, *60*, 2639–2645; b) T. Baumgartner, K. Huynth, S. Schleidt, A. J. Lough, I. Manners, *Chem. Eur. J.* **2002**, *8*, 4622–4632; c) T. De Simone, R. S. Dickson, B. W. Skelton, A. W. White, *Inorg. Chim. Acta* **1995**, *240*, 323–333; d) I. Moldes, J. Ros, *Inorg. Chim. Acta* **1995**, *232*, 75–81.

[9] J. E. Davies, M. J. Mays, P. R. Raithby, K. Sarveswaran, G. A. Solan, *J. Chem. Soc., Dalton Trans.* **2001**, 1269–1277.

[10] I. Ara, J. Forniés, A. García, J. Gómez, E. Lalinde, M. T. Moreno, *Chem. Eur. J.* **2002**, *8*, 3698–3716.

[11] P. Álvarez, E. Lastra, J. Gimeno, P. Braña, J. A. Sordo, J. Gómez, L. R. Falvello, M. Bassetti, *Organometallics* **2004**, *23*, 2956–2966.

[12] P. Álvarez, E. Lastra, J. Gimeno, M. Bassetti, L. R. Falvello, *J. Am. Chem. Soc.* **2003**, *125*, 2386–2387.

[13] J. Díez, M. P. Gamasa, J. Gimeno, E. Lastra, A. Villar, *Organometallics* **2005**, *24*, 1410–1418.

[14] M. Bassetti, P. Álvarez, J. Gimeno, E. Lastra, *Organometallics* **2004**, *23*, 5127–5134.

[15] C* represents the centroid of atoms C(1), C2), C(3), C(4), and C(5); C** represents the centroid of atoms C(4), C(5), C(6), C(7), C(8), and C(9).

[16] S. García-Granda, M. Pérez-Priede, J. F. Van der Maelen, personal communication.

[17] M. P. Gamasa, J. Gimeno, C. González-Bernardo, J. Borge, S. García-Granda, *Organometallics* **1997**, *16*, 2483–2485.

[18] P. Garrou, *Chem. Rev.* **1981**, *81*, 229–266.

[19] a) J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1989**, *122*, 1645–1647; b) J. W. Faller, B. V. Johnson, *J. Organomet. Chem.* **1975**, *88*, 101–113; c) J. A. Miguel-García, H. Adams, P. M. Maitlis, *J. Organomet. Chem.* **1991**, *413*, 427–444.

[20] Significant distance differences are only found in the cases of the coordination of the olefin to the ruthenium center, probably due to steric requirements. **3a**: Ru–C(10) 2.276(11) and 2.289(13); Ru–C(11) 2.230(11) and 2.263(11); C(10)–C(11) 1.389(17) and 1.395(16). **4b**: Ru–C(10) 2.228(7) and 2.253(8); Ru–C(11) 2.245(9) and 2.235(8); C(10)–C(11) 1.363(11) and 1.363(10).

[21] Complex **5b** is unstable in solution at room temperature and the NMR spectra were therefore recorded at low temperature (–50 °C).

[22] J. A. Gladysz, B. I. Boone, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 550–583.

[23] L. A. Oro, M. A. Ciriano, M. Campo, C. Foces-Foces, F. H. Cano, *J. Organomet. Chem.* **1985**, *289*, 117–131.

[24] M. S. Loonat, L. Carlton, J. C. A. Boeyens, N. J. Coville, *J. Chem. Soc., Dalton Trans.* **1989**, 2407–2414.

[25] P. Clark, J. L. S. Curtis, P. E. Garrou, G. E. Hartwell, *Can. J. Chem.* **1974**, *52*, 1714–1720.

[26] R. S. Dickson, T. De Simona, E. M. Campi, W. R. Jackson, *Inorg. Chim. Acta* **1994**, *220*, 187–192.

[27] E. Louattani, J. Suades, R. Mathieu, *J. Organomet. Chem.* **1991**, *421*, 335–340.

[28] SAINT version 6.02 Bruker Analytical X-ray Systems, Madison, WI, **2000**.

[29] G. M. Sheldrick, *SADABS empirical absorption program*, University of Göttingen, **1996**.

[30] Collect, Nonius BV, Delft, The Netherlands, **1997**–**2000**.

[31] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.

[32] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

[33] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[34] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The DIRDIF Program System*, Technical Report of the Crystallographic Laboratory, University of Nijmegen, Nijmegen, The Netherlands, **1999**.

[35] G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, **1997**.

[36] *Tables for X-ray Crystallography*, Kynoch Press, Birminghan, U. K., **1974**, vol. IV (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).

[37] M. Nardelli, *Comput. Chem.* **1983**, *7*, 95–98.

[38] A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*, University of Utrecht, The Netherlands, **2005**.

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