ORGANOMETALLICS

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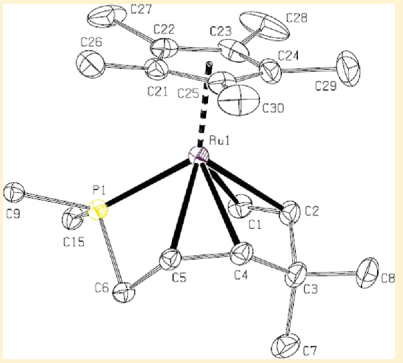
Ruthenium-Mediated Cyclometalation Reactions of Allene and Allylphosphine C=C Bonds: Synthesis of $\kappa(P),\eta^4$-(Hexa-2,5-dien-1-yl) diphenylphosphine−Ruthenium(II) Complexes

Amparo Villar, Josefina Díez, Elena Lastra,* and M. Pilar Gamasa*

Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al C.S.I.C.), Universidad de Oviedo, 33006 Oviedo, Principado de Asturias, Spain

Supporting Information

ABSTRACT: The cyclopentadienyl-containing complex $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa^3\text{-}(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][PF_6]$ (**1**) reacts with allenes, giving regioselectively the η^2-allene complexes $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(\eta^2\text{-}CH_2{=}C{=}CR^1R^2)][PF_6]$ [$R^1 = R^2 = Me$ (**3**); $R^1 = H$, $R^2 = Ph$ (**4**); $R^1R^2 = -(CH_2)_5-$ (**5**)]. On the other hand, the reaction of the pentamethylcyclopentadienyl-containing complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][OTf]$ (**2**) with allenes yields regio- and stereoselectively the complexes $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa(P),\eta^4\text{-}Ph_2PCH_2CH{=}CHC(R^1R^2)CH{=}CH_2\}][OTf]$ [$R^1 = R^2 = Me$ (**6**); $R^1 = H$, $R^2 = Ph$ (**7**); $R^1R^2 = -(CH_2)_5-$ (**8**)] via the intermolecular coupling of allene and allyldiphenylphosphine ligands. The intermediate complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}\{\eta^2\text{-}CH_2{=}C{=}CMe_2\}][OTf]$ (**9**) has been spectroscopically characterized. The structure of complex $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa(P),\eta^4\text{-}Ph_2PCH_2CH{=}CHC(Me)_2CH{=}CH_2\}][\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]$ (**6a**) has been resolved by X-ray diffraction analysis.



INTRODUCTION

Allenes are an important class of building blocks for modern organic synthesis through metal-catalyzed reactions.[1] In the last years, some inter- and intramolecular reactions of allenes with unsaturated compounds have been efficiently undertaken using several ruthenium catalysts. Thus, Ma and Jia have reported the synthesis of 2-vinyl-1,3-cycloalkadienes by intermolecular reactions of cyclic allenes with terminal alkynes,[2] while Trost et al. have studied the intermolecular cyclometalation of several functionalized monosubstituted allenes with α,β-unsaturated enones.[3] On the other hand, Ihara et al. have observed that the complex $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3][PF_6]$ catalyzes dimerization of allenic alcohols.[4] Intramolecular ruthenium-catalyzed (2 + 2) cycloaddition reactions of allenes[5] and of allenynes,[6] and cycloisomerization of δ-enallenes to form 1,3- or 1,4-cyclic dienes[7] have been also reported. In most cases, a η^2-allene intermediate was proposed, although no experimental evidence of its formation could be provided. Continuing our interest in the C−C coupling reactions between alkenylphosphines−ruthenium complexes and alkynes,[8] we now report our studies on the reactivity of complexes $[Ru(\eta^5\text{-}C_5R_5)(MeCN)\{\kappa^3(P,C,C')\text{-}Ph_2PCH_2CH{=}CH_2\}][PF_6]$ ($R^1 = H$ (**1**); $R^2 = Me$ (**2**)) toward allenes. It should be noted that few examples of stoichiometric Ru-assisted coupling reactions have been reported up to now.[9] Moreover, studies on the stoichiometric coupling reactions of allenes with unsaturated substrates would be helpful for a better mechanistic understanding of transition-metal-catalyzed reactions of allenes.

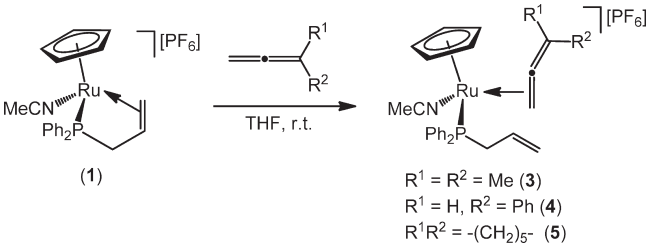
RESULTS AND DISCUSSION

Synthesis of the Complexes $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(\eta^2\text{-}CH_2{=}C{=}CR^1R^2)][PF_6]$ ($R^1 = R^2 = Me$ (3); $R^1 = H$, $R^2 = Ph$ (4); $R^1R^2 = -(CH_2)_5-$ (5)). The complex $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][PF_6]$ (**1**) reacts with allenes at room temperature in THF, affording complexes $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(\eta^2\text{-}CH_2{=}C{=}CR^1R^2)][PF_6]$ (**3**−**5**), isolated as pale yellow solids in moderate-to-good yields (62−95%) (Scheme 1). Complexes **3**−**5** should be kept under a nitrogen atmosphere at low temperature to prevent decomposition. Characteristic features of the spectroscopic data are the following: (i) The NMR spectra (298 K) confirm the $\kappa(P)$ coordination mode of the allylphosphine ligand.[8a] Thus, the $^{31}P\{^1H\}$ NMR spectra exhibit a singlet signal at 42.3 (**3**), 40.6 (**4**), and 42.1 (**5**) ppm; the ^1H NMR spectra show a broad singlet (=CH_2, 5.16−5.10 ppm) and a multiplet (=CH, 5.62−5.51 ppm); and a single $C\{^1H\}$ NMR resonance at 120.6 (t, $^3J_{CP} = 10.6$ Hz) (**3**), 121.6 (t, $^3J_{CP} = 11.4$ Hz) (**4**), and 120.6 (t, $^3J_{CP} = 10.9$ Hz) ppm (**5**) is observed for the methylene carbon =CH_2. (ii) The NMR spectra show a singlet in the range of 2.48−2.22 ppm (^1H NMR) and of 5.2−4.0 ppm ($^{13}C\{^1H\}$ NMR) for the methyl group of acetonitrile. (iii) The $^{13}C\{^1H\}$ NMR spectra of complexes show single resonances for the allene carbon nuclei: terminal sp^2-CH_2 (10.3, 18.4, and

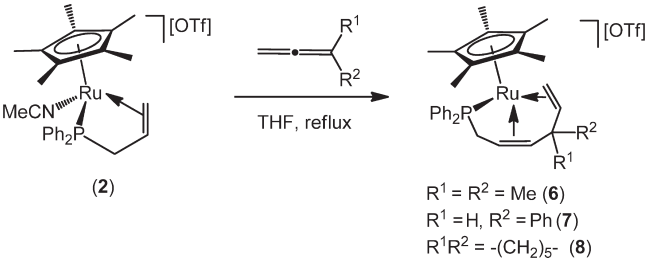
Received: July 22, 2011
Published: October 12, 2011

   dx.doi.org/10.1021/om200668h | *Organometallics* 2011, 30, 5803–5808

Scheme 1



Scheme 2



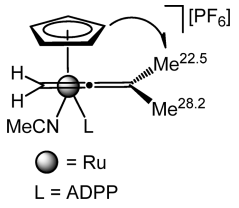


Figure 1

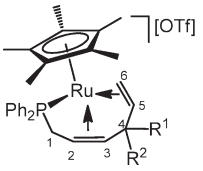


Figure 2

9.7 ppm for **3**, **4**, and **5**, respectively), central carbon sp-C (149.7, 160.2, and 147.3 ppm for **3**, **4**, and **5**, respectively), and terminal sp^2-CHR/CR_2 (117.5, 120.9, and 124.9 ppm for **3**, **4**, and **5**, respectively). The high- and low-field signals observed for the CH_2 and the central carbons of the allene moiety, respectively, indicate that the coordination to ruthenium occurs through the unsubstituted double bond of the allene. These data are in good agreement with those reported for other η^2-allene−metal complexes.[10,11]

The high regio- and diasteroselectivity of these reactions represents the most interesting feature. Although it has been reported that metal allene complexes undergo two fluxional processes, rotation of the allene ligand about the metal−allene bond and migration of the metallic fragment along the orthogonal allene π-systems,[10c,11d,12] the NMR spectra of complexes **3**−**5** show the presence of a unique isomer. Thus, the presence of a single isomer for complex **3** at room temperature is evidenced by the observation of a singlet (42.3 ppm, ^{31}P NMR) and two methyl resonances (2.15 and 2.03 ppm, ^{1}H NMR; 28.2 and 22.5 ppm, ^{13}C NMR). Moreover, no evidence of a fluxional processes is observed on the NMR time scale in the range of 298−213 K. The cross-peak (2D, NOESY) between a methyl group and the cyclopentadienyl ligand indicates the spatial proximity of both groups (Figure 1), thus confirming the syn orientation of the methyl group toward the ruthenium center. The stereochemistry of the double bond in the case of **4** could not be established on the basis of NOESY experiments. Tentatively, the structure of **4** has been assigned as the isomer with the Ph group anti to the ruthenium center on the basis of the ^{1}H NMR shift of the benzylidene hydrogen (C=C*H*Ph) and is in accordance with the steric effects reported in the literature.[11d,12a,12b,13] Unfortunately, an X-ray analysis could not be performed because all attempts to crystallize complexes **3**−**5** have been unsuccessful.

The alkene−allene exchange process from the complex [Ru(η^5-C_5H_5)(MeCN)\{κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH{=}CH_2$\}][PF_6] (**1**) leading to **3**−**5** reflects the well-known hemilabile character of the allyldiphenylphosphine,[8] a fact that has been corroborated by kinetic studies.[8c]

Further attempts directed to promote the coupling of the unsaturated ligands within the metal coordination sphere were unsuccessful. Thus, warming solutions of complexes **3**−**5** in refluxing THF resulted in mixtures of unidentified products.

Synthesis of the Complexes [Ru(η^5-C_5Me_5)\{κ(*P*),η^4-$Ph_2PCH_2CH{=}CHC(R^1R^2)CH{=}CH_2$\}][OTf] ($R^1$ = R^2 = Me (6); R^1 = H, R^2 = Ph (7); R^1R^2 = −$(CH_2)_5$− (8)). In contrast to the above results, when the allene partners were treated with the pentamethylcyclopentadienyl-containing complex [Ru(η^5-C_5Me_5)(MeCN)\{κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH{=}CH_2$\}][OTf] (**2**) in refluxing THF, the complexes [Ru(η^5-C_5Me_5)\{κ(*P*),η^4-$Ph_2PCH_2CH{=}CHC(R^1R^2)CH{=}CH_2$\}][OTf] (**6**−**8**) were formed in a regio- and stereoselective manner. Compounds **6**−**8** were isolated as orange air-stable solids in good yield (76−96%) (Scheme 2).

The most significant spectroscopic data are the following: (i) The IR spectra show the expected absorptions for the OTf^- anion (ca. 1264, 1150, 1030 cm^{-1}). (ii) The $^{31}P\{^{1}H\}$ NMR spectra exhibit a characteristic high-field singlet at −60.9 (**6**), −60.9 (**7**), and −60.8 ppm (**8**).[14] (iii) The ^{1}H NMR spectra show signals for the olefinic protons of both η^2-alkenes (see the *P*-hexa-2,5-dien-1-yl substituent) in the ranges of 4.12−4.02 (H-2), 2.98−2.84 (H-5), 2.20−1.77 (H-3), and 2.57−2.31 and 1.53−1.39 (2 × H-6) ppm (see Figure 2). (iv) The $^{13}C\{^{1}H\}$ NMR spectra show singlet signals for the terminal olefinic carbons (C-6, 52.6−49.1 ppm; C-5, 47.8−38.8 ppm) and doublet signals for the internal olefinic carbons C-2 and C-3 (C-2/C-3, 57.5−47.9 ppm; $^{2}J_{CP}$ = 19.8−19.6 Hz, $^{3}J_{CP}$ = 8.2−7.9 Hz).

All the attempts to obtain single crystals of complexes **6**−**8** suitable for X-ray analysis failed. However, slow diffusion of hexane into an ethereal solution of complex [Ru(η^5-C_5Me_5)\{κ(*P*),η^4-$Ph_2PCH_2CH{=}CHCMe_2CH{=}CH_2$\}][\{3,5-$(CF_3)_2C_6H_3$\}$_4$B] (**6a**) (obtained from **6** via TfO^-/3,5-$(CF_3)_2C_6H_3$\}$_4B^-$ anion exchange using the Brookhart's salt[15]) allowed us to collect suitable crystals for X-ray diffraction studies.

X-ray Crystal Structure of the Complex 6a. An ORTEP-type representation of the cation of complex **6a** is shown in Figure 3. Selected bonding data are collected in Table 1. The crystal belongs to the centrosymmetric space group $P\bar{1}$, indicating the presence of a racemic mixture. The asymmetric unit consists of two molecules with the same absolute configuration. Because the more relevant structural parameters are similar in both molecules, only a single data set is discussed. Figure 3 shows the

dx.doi.org/10.1021/om200668h |*Organometallics* 2011, 30, 5803–5808

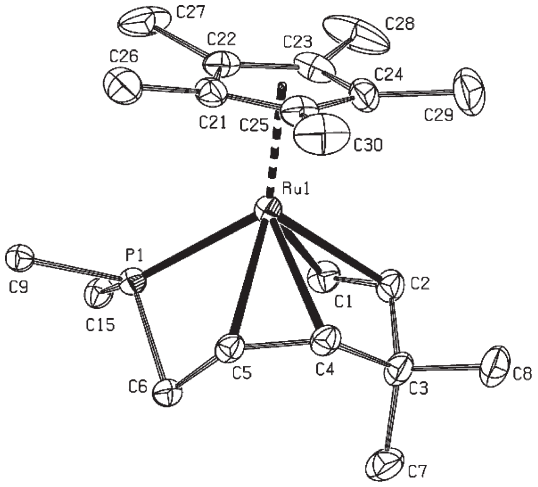


Figure 3. ORTEP drawing of complex **6a** showing atom-labeling scheme. Thermal ellipsoids are shown at 10% probability. Hydrogen atoms and the $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]$ anion are omitted for clarity. Only the C_{ipso}-aryl of the PPh_3 ligand is drawn.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 6a·0.25C_6H_{14}

bond	distance	bond	distance
Ru(1)−C*[a]	1.8703(6)	Ru(1)−C(4)	2.302(6)
Ru(1)−P(1)	2.3178(15)	Ru(1)−C(5)	2.308(5)
Ru(1)−C(1)	2.245(6)	C(1)−C(2)	1.354(9)
Ru(1)−C(2)	2.243(6)	C(4)−C(5)	1.365(9)
C(2)−C(3)	1.543(10)	C(3)−C(4)	1.515(9)
angle	**value**	**angle**	**value**
C(1)−C(2)−C(3)	125.5(6)	C(3)−C(4)−C(5)	131.3(6)
C(2)−C(3)−C(4)	97.7(5)	C(4)−C(5)−C(6)	72.6(3)
C(5)−C(6)−P(1)	93.5(4)	C*−Ru(1)−P(1)	127.32(4)
C*−Ru(1)−C(5)	135.06(15)	C*−Ru(1)−C(1)	127.73(19)
C*−Ru(1)−C(4)	126.45(18)	C*−Ru(1)−C(2)	119.67(18)

[a] CT01 = C* = centroid of C(21), C(22), C(23), C(24), C(25).

enantiomer with configuration *S* at the ruthenium center and the terminal olefin being coordinated through the *re*-face.

Complex **6a** exhibits a three-legged piano stool geometry with the ruthenium atom bonded to the cyclopentadienyl ring and to the tridentate ligand, (*Z*)-(4,4-dimethylhexa-2,5-dien-1-yl)diphenylphosphine. The bond distances around the ruthenium atom are in accordance with previously reported structures.[8a] Thus, the Ru(1)−C(1) (2.245(6) Å), Ru(1)−C(2) (2.243(6) Å), Ru(1)−C(4) (2.302(6), and Ru(1)−C(5) (2.308(5) Å) bond distances as well as the C(1)−C(2) (1.354(9) Å) and C(4)−C(5) (1.365(9) Å) olefinic bond distances reflect the coordination of the two olefins of this pentadiene fragment to the ruthenium center.

The formation of an η^2-allene intermediate complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(\eta^2\text{-}CH_2{=}C{=}CMe_2)][OTf]$ (**9**) is assessed by $^{31}P\{^1H\}$ NMR monitoring the reaction of **2** with 1,1-dimethylallene in $CDCl_3$. After 1 h at 298 K, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows a broad signal at 38.1 ppm, confirming the $\kappa(P)$ coordination mode of the allylphosphine ligand in the new complex **9**, along

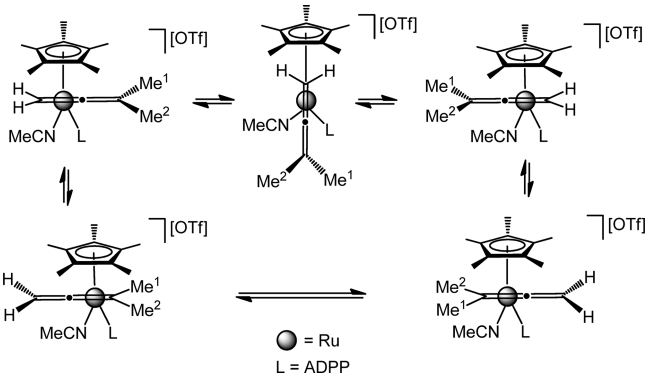
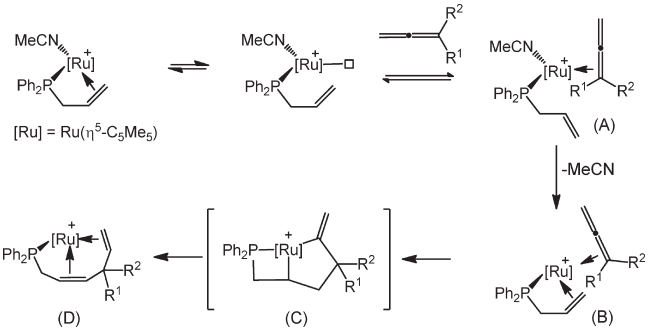


Figure 4

Scheme 3



with two less-intense signals corresponding to complexes **2** (−54.6 ppm) and **6** (−60.9 ppm). The analysis of the NMR (^1H, ^{31}P, ^{13}C) spectra of this mixture allowed the spectroscopic characterization of complex **9** (see the Experimental Section). When the reaction mixture is kept at room temperature during several hours, increasing of the amount of **6** and the total disappearance of **2** and **9** were observed. Unlike complexes **3**−**5** (see above), variable-temperature $^{31}P\{^1H\}$ NMR studies (298−213 K) confirm the dynamic behavior of complex **9** in solution. Thus, the broad resonance signal (38.1 ppm) observed at room temperature splits at low temperature (213 K) into three singlets (41.2, 38.4, and 35.9 ppm; relative intensity, 5:2:1) corresponding with species with $\kappa(P)$-coordination of the alkenylphosphine ligand. It is conceivable that two distinct, typical dynamic processes of η^2-allene complexes (metal−olefin rotation and orthogonal 1,2,2-shift of the organometallic fragment)[12] take place at room temperature (see Figure 4).

A plausible reaction mechanism for the formation of complexes **6**−**8** is shown in Scheme 3. The process would initiate by generation of a coordination vacancy by dissociation of the coordinated olefin group of allylphosphine ligand, followed by metal−η^2 allene coordination to give complex (**A**). Once the allene is coordinated, the dissociation of the acetonitrile and recoordination of the olefin group of allylphosphine would give the coordination complex (**B**). This intermediate species would undergo an oxidative cyclometalation to provide the ruthenacyclopentene intermediate (**C**), which would form the final complex (**D**) via a β-hydride elimination/reductive elimination sequence. The observed regiochemistry (see X-ray structure) implies that, among the species participating in the fluxional process (see Figure 4), only the complex with the metal coordinated to the more substituted

dx.doi.org/10.1021/om200668h |*Organometallics* 2011, 30, 5803–5808

C═C moiety of the allene (complex **A**, scheme 3) behaves as the productive species.

SUMMARY

The ruthenium-assisted coupling reaction of allenes with tethered C═C double bonds of the allyldiphenylphosphine ligand in the complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][OTf]$ (**2**) yields the complexes $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa(P),\eta^4\text{-}Ph_2PCH_2CH{=}CHC(R^1R^2)CH{=}CH_2\}][OTf]$ [$R^1 = R^2 = Me$ (**6**); $R^1 = H$, $R^2 = Ph$ (**7**); $R^1R^2 = -(CH_2)_5-$ (**8**)] in a regio- and stereoselective manner. The η^2-allene complex intermediate $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(\eta^2\text{-}CH_2{=}C{=}CMe_2)][OTf]$ (**9**) has been detected by NMR spectroscopy, and a plausible reaction mechanism for the formation of complexes **6**−**8** is proposed. Moreover, the η^2-allene complexes $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(\eta^2\text{-}CH_2{=}C{=}CR^1R^2)][PF_6]$ [$R^1 = R^2 = Me$ (**3**); $R^1 = H$, $R^2 = Ph$ (**4**); $R^1R^2 = -(CH_2)_5-$ (**5**)] are exclusively isolated using the complex $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][PF_6]$ (**1**) as a precursor.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)_3][OTf]$[16] $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][PF_6]$ (**1**)[14] and $Ph_2PCH_2CH{=}CH_2$[17] were prepared by previously reported methods. Other reagents were obtained from commercial suppliers and used without further purification. Infrared spectra were recorded on a PerkinElmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a PerkinElmer 240-B microanalyzer. A correct elemental analysis could not be obtained for complexes **3**−**5**, probably as a consequence of their high air sensitivity. The conductivities were measured at room temperature, in acetone solutions (ca. 5×10^{-4} M), with a Jenway PCM3 conductimeter. Mass spectra (FAB) were recorded using a VG-AUTOSPEC spectrometer, operating in the positive mode, and using 3-nitrobenzyl alcohol (NBA) as the matrix. Mass spectra (MALDI-TOF) were determined with a MICROFLEX Bruker spectrometer, operating in the positive mode, and using dihydroxyanthranol as the matrix. NMR spectra were recorded on Bruker spectrometers (AC400 operating at 400.13 (^{1}H), 100.61 (^{13}C) and 161.95 (^{31}P) MHz or 300 DPX or AC300 operating at 300.13 (^{1}H), 75.48 (^{13}C), and 121.49 (^{31}P) MHz). DEPT experiments were carried out for all the compounds. 2D-NMR (NOESY, HSQC) were performed in selected complexes. Chemical shifts are reported in parts per million and referenced to TMS or 85% H_3PO_4 as standards. Coupling constants J are given in hertz. Figure 2 shows the atom labels used for the ^{1}H and $^{13}C\{^1H\}$ spectroscopic data of complexes **6**−**8**.

Synthesis of the Complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][OTf]$ (2). Allyldiphenylphosphane (116 μL, 0.54 mmol) was added to a solution of the complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)_3][OTf]$ (250 mg, 0.49 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The resulting solution was stirred for 0.75 h. The solution was then concentrated to ca. 3 mL, and a mixture of diethyl ether/hexane (1:1, 30 mL) was added. The resulting yellow solid was washed with diethyl ether/hexane (1:1, 2 × 30 mL) and vacuum-dried. Yield: 256 mg, 80%. IR (Nujol, ν(CN), ν(OTf) cm^{-1}): 2288 (w), 1264 (vs), 1151 (m), 1031 (s). Molar conductivity (acetone, S cm^2 mol^{-1}, 293 K): 99. Anal. Calcd for $C_{28}H_{33}F_3NO_3PRuS$ (652.67 g/mol): C, 51.53; H, 5.10; N, 2.15. Found: C, 50.93; H, 4.89; N, 1.97. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ = 7.33 (m, 10H, Ph), 4.32 (m, 1H, P-CH_2), 3.63 (m, 1H, ═CH), 3.41 (m, 1H, ═CH_2), 3.09 (m, 1H, P-CH_2), 2.76 (m, 1H, ═CH_2), 2.16 (s, 3H, CH_3), 1.49 (s, 15 H, C_5Me_5). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 293 K): δ = −54.6 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, acetone-d_6, 293 K): δ = 132.5−129.0 (CN, Ph), 121.0 (q, J_{CF} = 320.3 Hz, CF_3SO_3), 93.4 (s, C_5Me_5), 60.1 (d, J_{CP} = 7.0 Hz, =CH_2), 50.7 (d, J_{CP} = 22.5 Hz, ═CH), 34.6 (d, J_{CP} = 33.8 Hz, P-CH_2), 9.1 (s, C_5Me_5), 4.1 (s, CH_3).

Synthesis of the Complexes $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa(P)\text{-}Ph_2PCH_2CH{=}CH_2\}\{\eta^2\text{-}CH_2{=}C{=}CR^1R^2\}][PF_6]$ ($R^1 = R^2 = Me$ (3); $R^1 = H$, $R^2 = Ph$ (4); $R^1R^2 = -(CH_2)_5-$ (5). The corresponding allene (0.3 mmol) was added to a solution of the complex $[Ru(\eta^5\text{-}C_5H_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH_2CH{=}CH_2\}][PF_6]$ (116 mg, 0.2 mmol) in THF (10 mL). The resulting solution was stirred at room temperature for 2 h. The solution was then concentrated to ca. 3 mL, and a mixture of diethyl ether/hexane (1:1, 30 mL) was added. The resulting pale yellow solid was washed with diethyl ether (2 × 10 mL) and vacuum-dried. (**3**) Yield: 0.123 g, 95%. IR (KBr, $\nu(PF_6)$, cm^{-1}): 838 (s). Λ_M = 116 S cm^2 mol^{-1} (acetone, 293 K). MS-MALDI: m/z 461 ($[Ru(C_5H_5)(Ph_2PCH_2CH{=}CH_2)(CH_2{=}C{=}CMe_2)]^+$). ^{1}H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ = 7.69−7.23 (m, 10H, Ph), 5.54 (m, 1H, ═CH), 5.10 (m, 2H, ═CH_2), 4.95 (s, 5H, C_5H_5), 3.40 (m, 2H, P-CH_2), 2.49 (m, 2H, $CH_{2\text{-allene}}$), 2.22 (s, 3H, CH_3CN), 2.15 (s, 3H, $CH_{3\text{-anti}}$), 2.03 (s, 3H, $CH_{3\text{-syn}}$) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 293 K): δ = 42.3 (s) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 293 K): δ = 149.7 (s, $C{=}CMe_2$), 133.1−128.8 (═CH, CN, Ph), 120.6 (d, $^3J_{CP}$ = 10.6 Hz, ═CH_2), 117.5 (s, $C{=}CMe_2$), 86.0 (s, C_5H_5), 36.9 (d, J_{CP} = 28.2 Hz, P-CH_2), 28.2 (s, $CH_{3\text{-anti}}$), 22.5 (s, $CH_{3\text{-syn}}$), 10.3 (broad, $CH_{2\text{-allene}}$), 4.0 (s, CH_3CN) ppm. (**4**) Yield: 0.130 g, 94%. IR (KBr, $\nu(PF_6)$, cm^{-1}): 839 (s). Λ_M = 107 S cm^2 mol^{-1} (acetone, 293 K). MS-MALDI: m/z 509 ($[Ru(C_5H_5)(Ph_2PCH_2CH{=}CH_2)(CH_2{=}C{=}CHPh)]^+$). ^{1}H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ = 7.56−7.21 (m, 15H, Ph), 6.26 (broad, ═C*H*Ph), 5.51 (m, 1H, ═CH), 5.22 (s, 5H, C_5H_5), 5.14 (m, 2H, ═CH_2), 3.37−3.18 (m, 3H, P-CH_2, $CH_{2\text{-allene}}$), 2.53 (m, 1H, $CH_{2\text{-allene}}$), 2.48 (s, 3H, CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 293 K): δ = 40.6. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 293 K): δ = 160.2 (s, *C*═CHPh), 138.0 (s, C_{ipso} Ph), 133.5−127.1 (═CH, Ph, CN), 121.6 (d, $^3J_{CP}$ = 11.4 Hz, ═CH_2), 120.9 (s, C═CHPh), 88.7 (s, C_5H_5), 36.0 (d, J_{CP} = 28.7 Hz, P-CH_2), 18.4 (broad, $CH_{2\text{-allene}}$), 5.2 (s, CH_3CN) ppm. (**5**) Yield: 0.085 g, 62%. IR (KBr, $\nu(PF_6)$, cm^{-1}): 834. Λ_M = 118 S cm^2 mol^{-1} (acetone, 293 K). MS-MALDI: m/z 501 ($[Ru(C_5H_5)(Ph_2PCH_2CH{=}CH_2)(CH_2{=}C{=}C(CH_2)_5))]^+$). ^{1}H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ = 7.60−7.33 (m, 10H, Ph), 5.62 (m, 1H, ═CH), 5.16 (m, 2H, ═CH_2), 4.99 (s, 5H, C_5H_5), 3.45 (m, 2H, P-CH_2), 2.56 (m, 4H, $-(CH_2)_5-$), 2.27 (s, 3H, CH_3CN), 2.13 (m, 2H, $CH_{2\text{-allene}}$), 1.71−1.58 (m, 6H, $-(CH_2)_5-$) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 293 K): δ = 42.1 (s) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 293 K): δ = 147.3 (s, *C*═CH$(CH_2)_5$), 133.7−128.4 (═CH, Ph, CN), 124.9 (s, C═*C*H$(CH_2)_5$), 120.6 (d, $^3J_{CP}$ = 10.9 Hz, ═CH_2), 86.0 (s, C_5H_5), 40.5 (s, $-(CH_2)_5-$), 36.9 (d, J_{CP} = 26.7 Hz, P-CH_2), 33.9, 28.6, 28.5, 26.5 (4s, $-(CH_2)_5-$), 9.7 (broad, $CH_{2\text{-allene}}$), 4.1 (s, CH_3CN) ppm.

Synthesis of the Complexes $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa(P),\eta^4\text{-}Ph_2PCH_2CH{=}CHC(R^1R^2)CH{=}CH_2\}][OTf]$ ($R^1 = R^2 = Me$ (6); $R^1 = H$, $R^2 = Ph$ (7); $R^1R^2 = -(CH_2)_5-$ (8)). The allene (0.17 mmol) was added to a solution of the complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH_2CH{=}CH_2\}][OTf]$ (100 mg, 0.15 mmol) in THF (10 mL). The mixture was heated at 60 °C for 1 h in a sealed tube. The solution was then evaporated to dryness, the crude product extracted with dichloromethane, and the extract filtered. Concentration of the resulting solution to ca. 3 mL, followed by addition of a mixture of diethyl ether/hexane (1:1, 30 mL), afforded complexes **6**−**8** as orange solids, which were washed with diethyl ether (2 × 5 mL) and vacuum-dried. (**6**) Yield: 0.097 g, 96%. IR (KBr, ν(OTf), cm^{-1}): 1264 (vs), 1149 (vs), 1031 (vs). Λ_M = 113 S cm^2 mol^{-1} (acetone, 293 K). Anal. Calcd for

$C_{31}H_{38}F_3O_3PRuS$ (679.74 g/mol): C, 54.78; H, 5.63. Found: C, 54.90; H, 5.76. MS-MALDI: *m/z* 531 ($[Ru(C_5Me_5)(Ph_2PCH_2CH{=}CHCMe_2CH{=}CH_2)]^+$). ^1H NMR (300.13 MHz, $CDCl_3$, 293 K): δ = 7.57−7.39 (m, 10H, Ph), 4.13 (m, 1H, H-1), 4.02 (m, 1H, H-2), 3.12 (m, 1H, H-1), 2.98 (m, 1H, H-5), 2.31 (d, J_{HH} = 8.4 Hz, 1H, H-6), 2.20 (m, 1H, H-3), 1.53 (m, 1H, H-6), 1.51 (s, 15H, C_5Me_5), 1.48 (s, 3H, CH_3), 0.78 (s, 3H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 293 K): δ = −60.9 ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 293 K): δ = 132.9−129.2 (Ph), 121.1 (q, J_{CF} = 320.6 Hz, CF_3SO_3), 95.6 (s, C_5Me_5), 57.5 (d, J_{CP} = 8.2 Hz, C-3), 56.5 (d, J_{CP} = 19.8 Hz, C-2), 49.8 (s, C-6), 47.8 (s, C-5), 34.0 (s, CH_3), 32.2 (s, C-4), 28.1 (d, J_{CP} = 34.2 Hz, C-1), 23.7 (s, CH_3), 9.2 (s, C_5Me_5) ppm. (**7**) Yield: 0.083 g, 76%. IR (KBr, ν(OTf), cm^{-1}): 1264 (vs), 1150 (m) and 1030 (vs). Λ_M = 101 S cm^2 mol^{-1} (acetone, 293 K). Anal. Calcd for $C_{35}H_{38}F_3O_3PRuS\cdot CH_2Cl_2$ (727.78 g/mol): C, 53.20; H, 4.96. Found: C, 53.30; H, 4.39. MS-MALDI: *m/z* 579 ($[Ru(C_5Me_5)(Ph_2PCH_2CH{=}CHCHPhCH{=}CH_2)]^+$). ^1H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ = 7.59−7.08 (m, 15H, Ph), 4.43 (m, 1H, H-1), 4.12 (m, 1H, H-2), 2.97 (m, 2H, H-5, H-1), 2.65 (m, 1H, H-4), 2.57 (d, J_{HH} = 6.5 Hz, 1H, H-6), 1.77 (m, 1H, H-3), 1.50 (s, 15H, C_5Me_5), 1.39 (m, 1H, H-6) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 293 K): δ = −60.9 ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 293 K): δ = 141.6−126.1 (Ph), 120.1 (q, J_{CF} = 321.0 Hz, CF_3SO_3), 95.8 (s, C_5Me_5), 55.0 (d, J_{CP} = 19.6 Hz, C-2), 52.6 (s, C-6), 47.9 (d, J_{CP} = 7.9 Hz, C-3), 39.7, 38.8 (2s, C-4, C-5), 27.6 (d, J_{CP} = 34.2 Hz, C-1), 9.2 (s, C_5Me_5), ppm. (**8**) Yield: 0.095 g, 88%. IR (KBr, ν(OTf), cm^{-1}): 1264 (vs), 1151 (vs) and 1031 (s). Λ_M = 111 S cm^2 mol^{-1} (acetone, 293 K). Anal. Calcd for $C_{34}H_{42}F_3O_3PRuS$ (719.80 g/mol): C, 56.73; H, 5.63. Found: C, 56.50; H, 5.78. MS-MALDI: *m/z* 571 ($[Ru(C_5Me_5)\{Ph_2PCH_2CH{=}CHC(-(CH_2)_5-)CH{=}CH_2\}]^+$). ^1H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ = 7.60−7.45 (m, 10H, Ph), 4.20 (m, 1H, H-1), 4.02 (m, 1H, H-2), 3.10 (m, 1H, H-1), 2.84 (m, 1H, H-5), 2.34 (d, J_{HH} = 6.3 Hz, 1H, H-6), 2.06 (m, 1H, H-3), 1.97 (broad, 2H, $-(CH_2)_5-$), 1.76 (broad, 8H, $-(CH_2)_5-$), 1.50 (broad, 16H, C_5Me_5, H-6) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 293 K): δ = −60.8 ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 293 K): δ = 133.0−129.4 (Ph), 121.0 (q, J_{CF} = 321.0 Hz, CF_3SO_3), 95.6 (s, C_5Me_5), 57.0, 56.8 (2 × br s, C-2, C-3), 49.1 (s, C-6), 47.0 (s, C-5), 42.6 (s, $-(CH_2)_5-$), 37.4 (s, C-4), 31.7 (s, $-(CH_2)_5-$), 28.5 (d, J_{CP} = 34.0 Hz, C-1), 25.7, 21.3, 20.3 (3s, $-(CH_2)_5-$), 9.4 (s, C_5Me_5) ppm.

Synthesis and Spectroscopic Characterization of Complex [Ru(η^5-C_5Me_5)(MeCN){κ(*P*)-$Ph_2PCH_2CH{=}CH_2$}{η^2-$CH_2{=}C{=}CMe_2$}][OTf] (9). To an NMR tube containing the complex [Ru(η^5-C_5Me_5)(MeCN){κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH{=}CH_2$}][OTf] (**1**) (0.060 g, 0.09 mmol) dissolved in 0.5 mL of $CDCl_3$ at room temperature was added 3-methyl-1,2-butadiene (32 μL, 0.18 mmol). After 1 h at room temperature, the complex [Ru(η^5-C_5Me_5)(MeCN){κ(*P*)-$Ph_2PCH_2CH{=}CH_2$}{η^2-$CH_2{=}C{=}CMe_2$}][OTf] (**9**) was formed as majority product and characterized by NMR spectroscopy: ^1H NMR (300.13 MHz, $CDCl_3$, 293 K): δ = 7.55−7.20 (m, 10H, Ph), 5.43 (m, 1H, =CH), 5.00 (m, 2H, $=CH_2$), 3.18 (m, 2H, P-CH_2), 2.63 (s, 3H, CH_3CN), 2.33 (m, 2H, $CH_{2\text{-allene}}$), 2.27 (s, 3H, $CH_{3\text{-anti}}$), 1.97 (s, 3H, $CH_{3\text{-syn}}$), 1.39 (s, 15H, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 293 K): δ = 38.1 (broad) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 293 K): δ = 158.5 (s, $C{=}CMe_2$), 133.4−129.1 (=CH, Ph), 121.5 (q, J_{CF} = 320.6 Hz, CF_3SO_3), 120.5 (d, $^3J_{CP}$ = 9.9 Hz, $=CH_2$), 116.3 (s, CN), 98.1 (s, C_5Me_5), 96.1 (s, $C{=}CMe_2$), 35.0 (d, J_{CP} = 25.8 Hz, P-CH_2), 30.5 (s, $CH_{3\text{-anti}}$), 22.0 (s, $CH_{3\text{-syn}}$), 17.4 (s, $CH_{2\text{-allene}}$), 9.7 (s, C_5Me_5), 5.2 (s, CH_3CN).

X-ray Diffraction. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of the complex **6a** in dichloromethane. In the asymmetric unit of complex **6a**, half a hexane molecule per two formula units of the complex was found. The most relevant crystal and refinement data are collected in Table 2. Diffraction data were recorded on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu−Kα radiation (λ = 1.5418 Å). Images were collected at a 65 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and a variable exposure time per image (1.5−2s). The data collection strategy was calculated with the program CrysAlis Pro CCD.[18] Data reduction and cell refinement were performed with the program CrysAlis Pro RED.[18] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[18]

Table 2. Crystal Data and Refinement for 6a·0.25C_6H_{14}

chem formula	$C_{63.5}H_{53.5}BF_{24}PRu$
fw	2830.83
T (K)	293(2)
wavelength (Å)	1.5418
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	12.868(2)
b (Å)	21.135(4)
c (Å)	25.841(9)
α (deg)	107.61(2)
β (deg)	96.99(2)
γ (deg)	104.684(16)
V (Å^3)	6328(3)
Z	4
ρ_{calcd} (g cm^{-3})	1.486
μ (mm^{-1})	3.231
F(000)	2858
cryst size (mm^3)	0.22 × 0.16 × 0.1
θ range (deg)	3.41−74.91
index ranges	$-14 \le h \le 15$
	$-25 \le k \le 26$
	$-31 \le l \le 31$
no. of reflns collected	78915
no. of independent reflns	25 038 [*R*(int) = 0.0283]
completeness to θ = 74.91° (%)	96.2
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	25 038/0/1601
GOF on F^2	1.118
R_1 [$I > 2\sigma(I)$][a]	R_1 = 0.0779, wR_2= 0.2382
R (all data)	R_1 = 0.0949, wR_2 = 0.2620
largest diff. peak and hole (e Å^{-3})	1.259 and −0.723

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

The software package WINGX was used for space group determination, structure solution, and refinement.[19] The structure was solved by Patterson intepretation and phase expansion using DIRDIF.[20] Isotropic least-squares refinement on F^2 using SHELXH97 was performed.[21] During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined except some highly disordered fluorine (these atoms were found in two positions and isotropically refined). The H atoms were geometrically placed, and their coordinates were refined riding on their parent atoms. The function minimized was $([\Sigma wF_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a = 0.1635, b = 3.5661) with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography International.[22] Geometrical calculations were made with PARST.[23] The crystallographic plots were made with PLATON.[24]

dx.doi.org/10.1021/om200668h |*Organometallics* 2011, 30, 5803–5808

■ ASSOCIATED CONTENT

Supporting Information. CIF/PLATON report, CIF data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: pgb@uniovi.es (M.P.G), elb@uniovi.es (E.L.).

■ ACKNOWLEDGMENT

This work was supported by the Ministerio de Educación y Ciencia of Spain (Projects BQU2003-00255, CTQ2006-08485, and Consolider Ingenio 2010 (CSD2007-00006)). A.V. thanks the Spanish Ministerio de Educación y Ciencia for a Ph.D. fellowship.

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