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Nucleophilic Additions to Allenylidene Ruthenium Complexes

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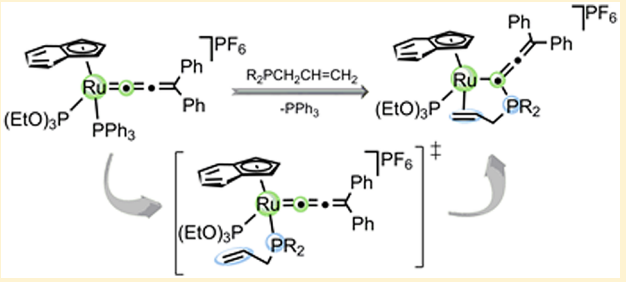
Supporting Information

ABSTRACT: Allenylidene complexes $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OR)_3\}(PPh_3)][PF_6]$ (R = Et (**1**), Me (**2**)) have been synthesized by the reaction of the complexes $[Ru(\eta^5\text{-}C_9H_7)Cl\{P(OR)_3\}(PPh_3)]$ with 1,1-diphenyl-2-propyn-1-ol in the presence of $NaPF_6$. Addition of different nucleophiles to complex **1** allows the synthesis of new allenyl or alkynyl ruthenium complexes depending on the regiochemistry of the reaction. Unexpected complexes $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(C,C,C)\text{-}C(R_2PCH_2CH=CH_2)=C=CPh_2\}\{P(OEt)_3\}][PF_6]$ (R = ^{i}Pr (**9a**), Ph (**9b**)), containing an unusual $\kappa^3(C,C,C)$-ligand have been obtained from the reaction of the allenylidene complex **1** with alkenylphosphane $Ph_2PCH_2CH=CH_2$ (ADPP) or $^iPr_2PCH_2CH=CH_2$ (ADIP). The formation of these complexes is proposed to proceed through an intermediate, $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OR)_3\}\{\kappa^1(P)\text{-}R_2PCH_2CH=CH_2\}][PF_6]$.



INTRODUCTION

Transition metal allenylidene complexes display a versatile chemistry,[1] which makes them useful intermediates in stoichiometric and catalytic processes.[2] In particular, the reactivity of ruthenium(II) allenylidene complexes has been widely studied.[3]

It is well known that electrophilic attacks to allenylidene complexes take place at the β-carbon atom of the allenylidene chain, while C_α and C_γ atoms react with nucleophiles. This reactivity agrees with theoretical calculations[4] indicating the contributions for the HOMO (mainly C_β atom) and the LUMO (mainly C_α and C_γ atoms) orbitals.

The regioselectivity of the nucleophilic addition reactions to the allenylidene chain depends on both electronic and steric factors of (i) the metallic fragment; (ii) the substituents on the allenylidene chain; and (iii) the nucleophile. Thus, anionic nucleophiles tend to react through the C_γ atoms, leading to neutral alkynyl complexes.[5,6] In fact, stereoselective nucleophilic attack on the C_γ atom has been used in the stoichiometric formation of optically active alkynyl complexes,[7] and recently diastereoselective nucleophilic attacks on a chiral-at-metal ruthenium allenylidene complex have been reported to give alkynyl complexes in diasteromeric ratios up to 84:16.[8] However, these nucleophilic attacks are not always regioselective, and mixtures of complexes resulting from the attack to both C_α and C_γ can be obtained.[9]

When neutral nucleophiles containing acidic hydrogens such alcohols, amines, and thiols are used, vinylcarbene complexes, resulting from the initial addition of the nucleophile to the α-carbon and protonation of the β-carbon, are usually the reaction products.[10,11] However, depending on the metal fragment and the substituents on the allenylidene chain, the less frequent addition to C_γ can be obtained. This reaction occurs especially for electron-rich allenylidene ruthenium complexes, leading to vinylidene complexes.[6,12]

On the other hand, when phosphanes are used as nucleophiles, both regioisomers can be obtained depending on the reactants.[11,13] Moreover, isomerization processes from the kinetically controlled alkynyl complexes, resulting from the attack to the γ-carbon, to the thermodynamically controlled allenyl products, resulting from the attack to the α-carbon, are observed for some complexes.[14]

In order to clarify the regioselectivity of nucleophilic attacks on the allenylidene chain, in this paper we look into the reaction of a number of neutral and anionic nucleophiles toward the allenylidene $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OEt)_3\}(PPh_3)][PF_6]$ (**1**), bearing the phosphite ligand $P(OEt)_3$, which presents a π-acceptor character intermediate between the CO and phosphanes, which are commonly used as ancillary ligands in the study of the reactivity of allenylidene complexes.[15]

On the other hand, the reaction of the allenylidene **1** with alkenylphosphanes $Ph_2PCH_2CH=CH_2$ (ADPP) or $^iPr_2PCH_2CH=CH_2$ (ADIP) allows the synthesis and characterization of unexpected complexes $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(C,C,C)\text{-}C(R_2PCH_2CH=CH_2)=C=CPh_2\}\{P(OEt)_3\}][PF_6]$, containing an unusual $\kappa^3(C,C,C)$-ligand.

RESULTS AND DISCUSSION

Synthesis of $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OR)_3\}(PPh_3)][PF_6]$ (R = Et (1), Me (2)). Complexes $[Ru(\eta^5\text{-}C_9H_7)Cl\{P(OR)_3\}(PPh_3)]$ (R = Et, Me) were synthesized in 88% and 92% yield, respectively, by reaction of complex

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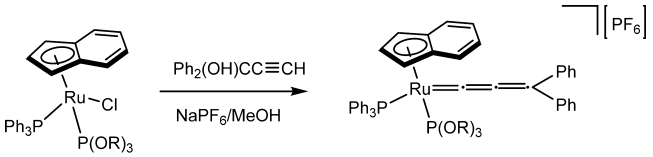
$[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ with the stoichiometric amount of phoshites, $P(OEt)_3$ or $P(OMe)_3$, in refluxing toluene. These complexes have been recently synthesized in 75% yield when the same reaction is carried out in refluxing THF. Analytical and spectroscopic data agree with those reported in the literature.[16]

The reaction of these complexes with 1,1-diphenyl-2-propyn-1-ol and $NaPF_6$, in refluxing methanol, gives rise to allenylidene complexes $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OR)_3\}(PPh_3)][PF_6]$ (R = Et (**1**), Me (**2**)) in 85% (**1**) and 93% (**2**) yield (Scheme 1). Both complexes are purple, air-stable solids. Elemental analyses and electrospray (ES) mass spectra agree with the proposed stoichiometry.

Scheme 1. Synthesis of Complexes 1 and 2



Complexes **1** and **2** have been fully characterized by spectroscopic methods. Characteristic features of the spectroscopic data for these complexes are the following: (i) The IR spectra show the $\nu(C=C=C)$ absorption at 1936 (**1**) and 1939 (**2**) cm^{-1} along with the expected absorption for the PF_6 group at 838 cm^{-1}; (ii) the $^{31}P\{^1H\}$ NMR spectra in dichloromethane show two doublets, one for the phosphane ligand at 51.0 ppm ($^2J_{PP}$ = 50.2 Hz) (**1**) and 51.3 ppm ($^2J_{PP}$ = 51.8 Hz) (**2**) and another for the phosphite ligand at 135.9 ppm (**1**) and 141.3 ppm (**2**); (iii) the ^1H and $^{13}C\{^1H\}$ NMR spectra of both complexes show the expected signals for the indenyl ligand; (iv) the $^{13}C\{^1H\}$ NMR spectra of these complexes display the characteristic low-field resonances for the C_α atom at 295.0 ppm (**1**) and 295.5 ppm (**2**) as a doublet of doublets and two singlets for the C_β and C_γ atoms of the allenylidene group at 204.1 and 156.2 ppm (**1**) and 202.6 and 157.0 ppm (**2**), respectively (see Experimental Section).

The structure of complex **2** was determined by single-crystal X-ray diffraction analysis. Slow diffusion of hexane into a solution of **2** in dichloromethane allowed us to collect suitable crystals for X-ray diffraction studies. An ORTEP-type representation of the cation of complex **2**·$2CH_2Cl_2$ is shown in Figure 1, and selected bonding data are collected in the caption.

The molecule exhibits a three-legged piano-stool geometry, with the η^5-indenyl ligand displaying the usual allylene coordination mode. The benzo ring of the indenyl ligand is oriented over the allenylidene chain, as shown by the dihedral angle between the planes C*−C**−Ru and C*−Ru−C(1)[17] of 20.61(2)°. The diphenylallenylidene ligand is bound to the metal in a nearly linear fashion (C(1)−C(2)−C(3) bond angle 177.60(70)°) with bond lengths Ru−C(1) 1.898(6) Å, C(1)−C(2) 1.247(9) Å, and C(2)−C(3) 1.366(9) Å. As expected, the observed distances in the allenylidene chain indicate a contribution of the canonical form $[M]-C\equiv C-CPh_2$. These bonding parameters can be compared with those shown by other ruthenium(II) allenylidene complexes, i.e., $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(PMe_3)_2]^+$[18] and $[Ru(\eta^5\text{-}C_9H_7)\{=C=C=C\text{-}(C_{13}H_{20})\}(PPh_3)_2]^+$.[19]

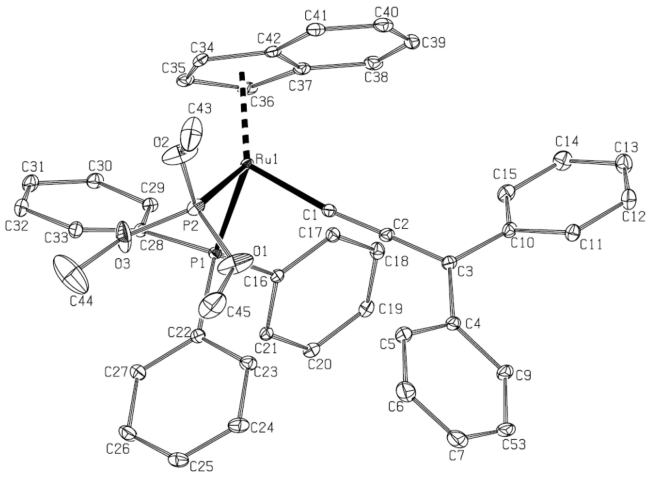
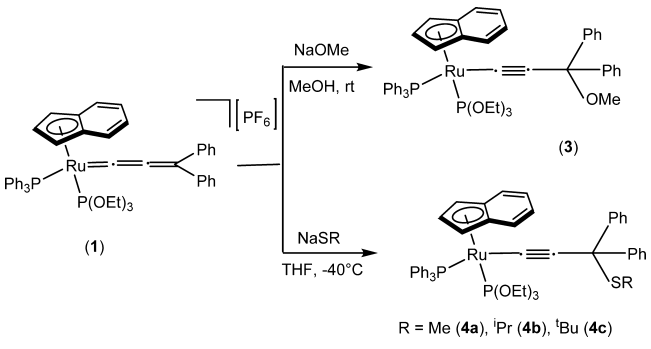


Figure 1. Molecular structure and atom-labeling scheme for the cation of complex $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OMe)_3\}(PPh_3)][PF_6]\cdot 2CH_2Cl_2$ (**2**·$2CH_2Cl_2$). Solvent molecules and hydrogen atoms have been omitted for clarity. Non-hydrogen atoms are represented by their 20% probability ellipsoids. Selected bond lengths (Å): Ru(1)−P(1) = 2.301(2), Ru(1)−P(2) = 2.233(2), Ru(1)−C* = 1.936(1), Ru(1)−C(1) = 1.898(6), C(1)−C(2) = 1.247(9), C(2)−C(3) = 1.366(9). Selected bond angles (deg): Ru(1)−C(1)−C(2) = 172.20(50), C(1)−C(2)−C(3) = 177.60(70), C*−Ru(1)−C(1) = 124.78(18), C*−Ru(1)−P(1) = 123.05(4), C*−Ru(1)−P(2) = 124.70(5), P(1)−Ru(1)−P(2) = 93.56(6), P(1)−Ru(1)−C(1) = 89.07(18), P(2)−Ru(1)−C(1) = 91.85(19), C* = centroid of C(34), C(35), C(36), C(37), C(42). C** = centroid of C(37), C(38), C(39), C(40), C(41), C(42).

Reaction of $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OEt)_3\}(PPh_3)][PF_6]$ (1) with Anionic Nucleophiles: Synthesis of Alkynyl Complexes $[Ru(\eta^5\text{-}C_9H_7)\{C\equiv C\text{-}C(OMe)Ph_2\}\{P(OEt)_3\}(PPh_3)]$ (3) and $[Ru(\eta^5\text{-}C_9H_7)\{C\equiv C\text{-}C(SR)Ph_2\}\{P(OEt)_3\}(PPh_3)]$ (R = Me (4a), ^{i}Pr (4b), ^{t}Bu (4c)). The reaction of complex **1** with sodium methoxide at room temperature or sodium alkylsulfides at low temperature leads respectively to neutral alkynyl complexes $[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(OMe)Ph_2\}\{P(OEt)_3\}(PPh_3)]$ (**3**) and $[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(SR)Ph_2\}\{P(OEt)_3\}(PPh_3)]$ (R = Me (**4a**), ^{i}Pr (**4b**), ^{t}Bu (**4c**)), which were isolated as orange solids (Scheme 2). Even when

Scheme 2. Synthesis of Complexes 3 and 4a−c



complexes **4b,c** were detected as pure complexes in the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy, they were isolated as a mixture with small amounts (5−15%) of allenyl complexes (see below) due to isomerization processes during the reaction workup.

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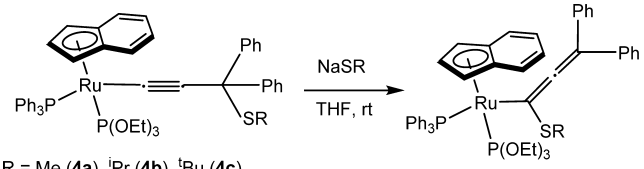
Complexes **3** and **4a−c** have been fully characterized by spectroscopic methods. In particular, it must be noted that (i) IR spectra show the ν(C≡C) absorption in the range 2073−2078 cm^{-1}. (ii) The ^{31}P{^{1}H} NMR spectra show two doublets ($^{2}J_{PP}$ = 65.6−66.8 Hz), one low field corresponding to the phosphite ligand in the range 150.8−151.5 ppm and the other corresponding to the phosphane ligand in the range 54.7−56.8 ppm. (iii) The ^{1}H NMR spectra show singlet signals at 3.58 ppm (OMe) and 2.22 ppm (SMe) for complexes **3** and **4a**, respectively. The hydrogen atoms for the ^{i}Pr and ^{t}Bu groups appear at 1.25, 1.39, and 3.71 ppm (**4b**) and 1.68 ppm (**4c**), respectively. (iv) The ^{13}C{^{1}H} NMR spectra exhibit signals corresponding to the C_α and the C_β at 104.2 and 110.8 ppm (**3**), 101.2 and 109.4 ppm (**4a**), and 99.5 and 110.7 ppm (**4b**), respectively. The ^{13}C{^{1}H} NMR spectra for complex **4c** could not be registered since this complex evolves readily, even at low temperature, to the corresponding allenyl complex (see below).

Synthesis of the Allenyl Complexes [Ru(η^5-C_9H_7){C(SR)=C=CPh_2}{P(OEt)$_3$}(PPh_3)] (R = Me (5a), ^{i}Pr (5b), ^{t}Bu (5c)). When the reaction of complex **1** with sodium alkylsulfides is carried out at room temperature, the thermodynamically stable allenyl complexes [Ru(η^5-C_9H_7){C(SR)=C=CPh_2}{P(OEt)$_3$}(PPh_3)] (R = Me (**5a**), ^{i}Pr (**5b**), ^{t}Bu (**5c**)) are isolated. These complexes can also be obtained by stirring THF solutions of the alkynyl complexes **4a−c** overnight at room temperature, as the result of formal 1,3-migration of alkylsulfide from the C_γ to the C_α of the allenylidene chain (Scheme 3). Analogous migration of the methoxide group in complex **3** does not occur even at refluxing temperature.

Scheme 3. Synthesis of Complexes 5a−c



R = Me (**4a**), ^{i}Pr (**4b**), ^{t}Bu (**4c**)

R = Me (**5a**), ^{i}Pr (**5b**), ^{t}Bu (**5c**)

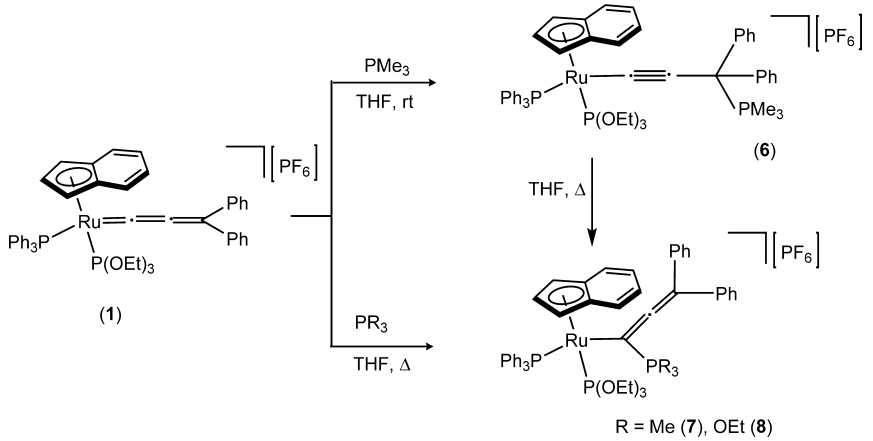
Complexes **5a−c** are isolated as orange, stable solids, and they have been fully characterized by spectroscopic methods.[20] The IR spectra show the ν(C=C=C) absorption at 1958 (**5a**), 1957 (**5b**), and 1956 (**5c**) cm^{-1}. ^{31}P{^{1}H} NMR spectra are indicative of the presence of both phosphane and phosphite ligands, showing two doublets ($^{2}J_{PP}$ = 64.4−64.8 Hz) in the range 51.7−52.6 ppm and 144.0−145.4 ppm, respectively. ^{1}H and ^{13}C{^{1}H} NMR spectra indicate the presence of the alkyl groups of the corresponding thiolate ligands (see Experimental Section). ^{13}C{^{1}H} NMR spectra also show the signals corresponding to the carbon atoms of the allenyl chain at 96.7 (**5a**), 94.8 (**5b**), and 90.8 ppm (**5c**) for C_α, 198.1 (**5a**), 197.6 (**5b**), and 197.2 ppm (**5c**) for C_β, and 103.7 (**5a**), 102.4 (**5b**), and 100.7 ppm (**5c**) for C_γ.

As shown, the kinetically stable alkynyl products isomerize to the thermodynamically stable allenyl products depending on the electronic and steric properties of the nucleophile, and the migration from C_γ to C_α is easier for the bulkier substituents. For example, the complete isomerization of complex **4a** to **5a** requires stirring a THF solution of **4a** for 2 days at room temperature, while complexes **5b** and **5c**, bearing ^{i}Pr and ^{t}Bu groups, were obtained by stirring THF solutions of the corresponding complexes **4b,c** overnight. A possible explanation for this isomerization can be found in the small cone angle of the phosphite auxiliary ligand. Analogous behavior has been reported for complexes [Ru(η^5-C_9H_7){C(PMe_2Ph)=C=CPh_2}(dppm)], bearing dpppm as auxiliary ligand.[14b]

Reaction of [Ru(η^5-C_9H_7)(=C=C=CPh_2){P(OEt)$_3$}(PPh_3)][PF_6] (1a) with Neutral P-Donor Nucleophiles: Synthesis of [Ru(η^5-C_9H_7){C≡C−C(PMe_3)Ph_2}{P(OEt)$_3$}(PPh_3)] (6), [Ru(η^5-C_9H_7){C(PMe_3)=C=CPh_2}{P(OEt)$_3$}(PPh_3)] (7), and [Ru(η^5-C_9H_7){C{P(OEt)$_3$}=C=CPh_2}{P(OEt)$_3$}(PPh_3)] (8). In the same way, allenylidene complex **1** reacts with neutral P-donor nucleophiles, giving rise to γ-phosphonio alkynyl or α-phosphonio allenyl complexes depending on the nucleophile and the reaction conditions. Thus, the reaction of complex **1** with PMe_3 at room temperature allows the synthesis of complex [Ru(η^5-C_9H_7){C≡C−C(PMe_3)Ph_2}{P(OEt)$_3$}(PPh_3)] (**6**) as a yellow solid. When complex **6** is heated in THF, irreversible isomerization to thermodynamically stable α-phosphonio allenyl **7** occurs. Complex **7** can also be obtained directly from complex **1**. Thus, when the reaction of **1** with PMe_3 is carried out in refluxing THF, the regioisomer α-phosphonio allenyl complex [Ru(η^5-C_9H_7){C(PMe_3)=C=CPh_2}{P(OEt)$_3$}(PPh_3)] (**7**) is directly obtained (Scheme 4).

Complex **1** reacts with the stronger π-acceptor P(OEt)$_3$ in refluxing THF, to give complex [Ru(η^5-C_9H_7){C{P(OEt)$_3$}=C=CPh_2}{P(OEt)$_3$}(PPh_3)] (**8**) (Scheme 4). However, the

Scheme 4. Synthesis of Complexes 6−8



R = Me (**7**), OEt (**8**)

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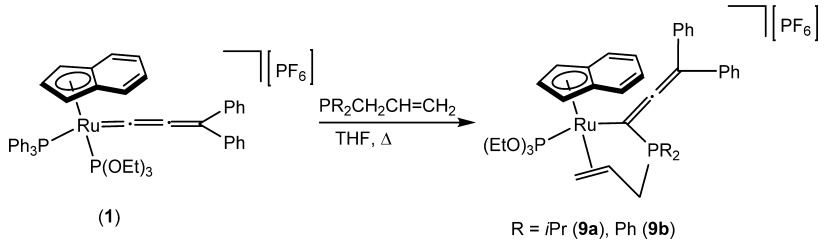
Scheme 5. Synthesis of Complexes 9a,b



reaction did not take place at room temperature, and complex **1** was recovered unaltered.

Complexes **6**, **7**, and **8** have been fully characterized analytically and spectroscopically. The most significant spectroscopic features for these complexes are as follows. (i) The IR spectrum of the alkynyl complex **6** shows the absorption for the ν(C≡C) bond at 2072 cm^{-1}, and IR spectra of complexes **7** and **8** show the ν(C=C=C) absorption at 1859 (**7**) and 1864 (**8**) cm^{-1} along with the expected absorption for the PF_6 group at 840 cm^{-1}. (ii) $^{31}P\{^1H\}$ NMR spectra are indicative of the presence of three phosphorus in the molecule. Phosphorus−phosphorus coupling constants in these complexes agree with the proposed structure. Thus, for complex **6** the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 30.6 ppm for the phosphorus atom of the PMe_3 ligand and two doublets ($^2J_{PP}$ = 64.8 Hz) at 54.4 and 148.3 ppm for the PPh_3 and $P(OEt)_3$ ligands, respectively. For complex **7**, the phosphite bonded to the metal appears, in the $^{31}P\{^1H\}$ NMR spectrum, as a doublet of doublets at 141.0 ppm coupled with both the PPh_3 ($^2J_{PP}$ = 71.3 Hz) ligand and PMe_3 ($^3J_{PP}$ = 21.1 Hz). However, the signals for the phosphane ligand (59.2 ppm) and the phosphonium group (30.5 ppm) appear as doublets, and no coupling between these phosphorus atoms is observed. For complex **8**, due to the larger coupling constants observed for phosphite ligands,[21] the signals for the three phosphorus appear as doublet of doublets with coupling constants $^2J_{PP}$ = 72.9 Hz and $^3J_{PP}$ = 9.7 and 7.3 Hz (see Experimental Section). (iii) The $^{13}C\{^1H\}$ NMR spectrum for complex **6** shows the signal corresponding to the C_α of the alkynyl group as a multiplet at 98.7 ppm, while C_β is masked by the indenyl signals. $^{13}C\{^1H\}$ NMR spectra for complexes **7** and **8** show the allenyl chain at 75.7 and 74.2 ppm (C_α), 209.1 and 215.9 ppm (C_β), and 96.6 and 98.9 ppm (C_γ) for complexes **7** and **8**, respectively. (iv) Other signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra agree with the proposed structure.

Synthesis of [Ru(η^5-C_9H_7){κ^3(*C,C,C*)-C(R_2PCH_2CH=CH_2)=C=CPh_2}{$P(OEt)_3$}][PF_6] (R = ^{i}Pr (9a), R = Ph (9b)). Complex **1** does not react with alkenylphosphanes R_2PCH_2CH=CH_2 (R = ^{i}Pr, Ph) at room temperature. However, the reaction of **1** with these alkenylphosphanes in a sealed tube at 110−120 °C leads to complexes [Ru(η^5-C_9H_7){κ^3(*C,C,C*)-C(R_2PCH_2CH=CH_2)=C=CPh_2}{$P(OEt)_3$}][PF_6] (R = ^{i}Pr (**9a**), R = Ph (**9b**)), containing a κ^3(*C,C,C*)-ligand (Scheme 5).

Complexes **9a,b** are air-stable solids, and both have been analytically and spectroscopically characterized. The most significant spectroscopy data are the following. (i) IR spectra show the absorption at 1937 (**9a**) and 1931 (**9b**) for the allenyl group and at 1437 (**9a**) and 1436 (**9b**) cm^{-1} for the coordinated olefin. (ii) The $^{31}P\{^1H\}$ NMR spectra exhibit two doublets ($^3J_{PP}$ = 4.9 Hz) at 147.8 (**9a**) and 146.5 ppm (**9b**) for the $P(OEt)_3$ ligand and δ 82.2 (**9a**) and 60.0 ppm (**9b**) for the phosphonium group. (iii) $^{13}C\{^1H\}$ NMR spectra show the signals corresponding to the allenyl chain at 78.6 (C_α), 208.7 (C_β), and 100.5 ppm ($C\gamma$) for complex **9a** and at δ 81.2 (C_α), 214.8 (C_β), and 103.5 ppm ($C\gamma$) for complex **9b**. (iv) Other signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra agree with the proposed structures.

The structure of complex **9a** was determined by single-crystal X-ray diffraction analysis. Suitable crystals were obtained by slow diffusion of hexane into a solution of complex **9a** in $CHCl_3$. An ORTEP representation is shown in Figure 2, and selected bonding data are collected in the caption.

The molecule exhibits a pseudooctahedral three-legged piano stool geometry with the η^5-indenyl ligand displaying the usual allylene coordination mode. The angles between the five-membered-ring centroid C* and the legs show values typical of a pseudooctahedron (see the caption to Figure 2). The Ru−C(17) and Ru−C(18) bond distances reflect the coordination

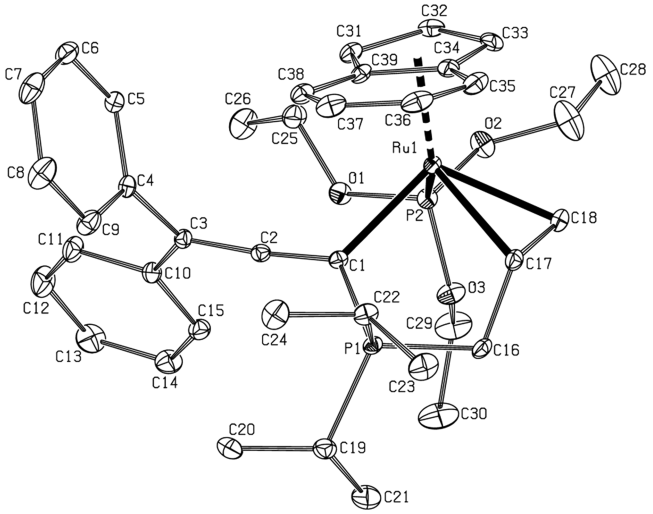


Figure 2. Molecular structure and atom-labeling scheme for the cation of complex [Ru(η^5-C_9H_7){κ^3-(*C,C,C*)-C($^iPr_2PCH_2CH$=CH_2)=C=CPh_2}{$P(OEt)_3$}][PF_6] (**9a**). Hydrogen atoms except those of the coordinated olefin have been omitted for clarity. Non-hydrogen atoms are represented by their 20% probability ellipsoids. Selected bond lengths (Å): Ru(1)−C(1) = 2.137(4), Ru(1)−P(2) = 2.207(1), Ru(1)−C(17) = 2.205(3), Ru(1)−C(18) = 2.214(4), Ru(1)−C* = 1.923(1), C(17)−C(18) = 1.402(5), C(1)−P(1) = 1.779(3), C(1)−C(2) = 1.296(5), C(2)−C(3) = 1.327(5). Selected bond angles (deg): C*−Ru(1)−C(1) = 121.74(9), C*−Ru(1)−P(2) = 124.34(3), C*−Ru(1)−C(17) = 124.14(10), C*−Ru(1)−C(18) = 120.16(11), Ru(1)−C(1)−C(2) = 125.50(30), C(1)−C(2)−C(3) = 174.50(40), Ru(1)−C(1)−P(1) = 112.42(17), C(1)−P(1)−C(16) = 100.69(17), C(16)−C(17)−C(18) = 121.80(40), P(2)−Ru(1)−C(1) = 84.31(9), C(1)−Ru(1)−C(17) = 83.55(13), C(18)−Ru(1)−P(2) = 84.23(11). C* = centroid of C(31), C(32), C(33), C(34), C(39). C** = centroid of C(34), C(35), C(36), C(37), C(38), C(39).

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of the olefin to the metal center, and the C(17)−C(18) bond distance, 1.401(5) Å, is similar to that found in complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)][PF_6]$ (1.391(8) Å).[22] It is also interesting to note that the benzo ring of the indenyl ligand is oriented trans to the phosphite ligand, as shown by the dihedral angle between the planes Ru−C*−C** and C*−Ru−P(2)[23] of 18.48(2)°. Figure 2 shows the complex with relative configuration S_{Ru} and olefin coordination through the *re* enantioface. However, both enantiomers are present in equal proportion in the crystal, which belongs to the centrosymmetric space group $P\bar{1}$.

Nelson et al. reported the synthesis of the analogous complex $[RuCl(\eta^6\text{-}C_6Me_6)\{\kappa^3\text{-}(C,C,C)\text{-}C(Ph_2PCH{=}CH_2){=}C{=}CPh_2\}][PF_6]$ obtained, in 24% yield, through the reaction of complex $[RuCl(\eta^6\text{-}C_6Me_6)(NCMe)(Ph_2PCH{=}CH_2)][PF_6]$ with 1,1-diphenyl-2-propyn-1-ol (Figure 3). In this reaction, migration of the coordinated vinyl phosphane to the previously formed allenylidene takes place.[24]

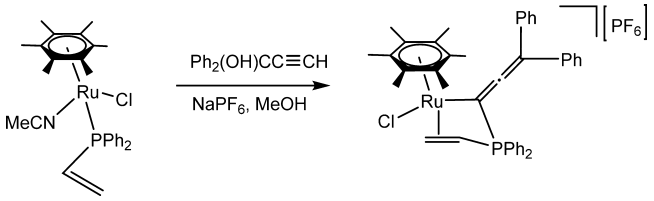


Figure 3. Synthesis of complex $[RuCl(\eta^6\text{-}C_6H_6)(NCMe)(Ph_2PCH{=}CH_2)][PF_6]$.

According to this reaction and taking into account the high temperatures needed for the synthesis of complexes **9a,b**, a mechanism can be proposed for the formation of complexes **9a,b**. Thus, the first step for the transformation from **1** into **9a,b** would be the PPh_3 substitution for the alkenylphosphane, followed by an intramolecular attack of the phosphane to the C_α of the allenylidene chain (Scheme 6). The phosphane substitution step would explain the high temperatures needed for this reaction, in contrast with the low temperature observed for the nucleophilic addition of PMe_3 to the allenylidene chain observed in the synthesis of complex **6**.

SUMMARY

In summary, the nucleophilic attacks to the allenylidene complex $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C{=}C(Ph)_2\}\{P(OEt)_3\}(PPh_3)][PF_6]$ (**1**) allow synthesizing the regioisomers' alkynyl or allenyl complexes depending on the reaction conditions. The kinetically stable alkynyl complexes resulting from nucleophilic addition to the C_γ evolve to the thermodynamically stable allenyl complexes depending on the size and electronic properties of the nucleophile.

Complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(C,C,C)\text{-}C(R_2PCH_2CH{=}CH_2){=}C{=}CPh_2\}\{P(OEt)_3\}][PF_6]$, containing an unusual $\kappa^3(C,C,C)$-ligand, was obtained by the addition of alkenylphosphanes to the allenylidene complex **1**. The proposed mechanism for this transformation starts with substitution of PPh_3 followed by an intramolecular attack of the phosphane to the C_α of the allenylidene chain.

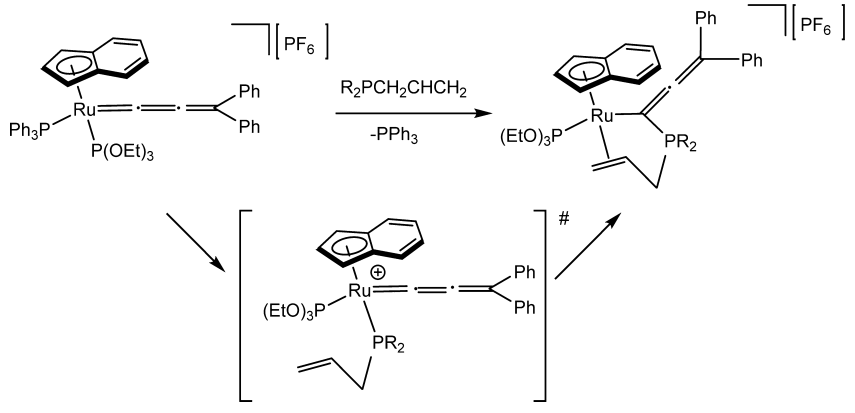
EXPERIMENTAL SECTION

General Procedures. All manipulations were perfomed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. The reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The phosphane $Ph_2PCH_2CH{=}CH_2$[25] was prepared by a previously reported procedure. $^iPr_2PCH_2CH{=}CH_2$ was synthesized following the same experimental procedure.

Infrared spectra were recorded on a PerkinElmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a PerkinElmer 240-B and a LECO CHNS-TruSpec microanalyzer. Mass spectra (ESI) were determined with a Bruker Esquire 6000 spectrometer, operating in positive mode and using dichloromethane and methanol solutions. NMR spectra were recorded on Bruker spectrometers AV400 operating at 400.13 (^{1}H), 100.61 (^{13}C), and 161.95 (^{31}P) MHz, AV300 operating at 300.13 (^{1}H), 75.45 (^{13}C), and 121.49 (^{31}P) MHz, and AV600 operating at 600.15 (^{1}H) MHz and 150.91 (^{13}C) MHz. DEPT and 2D COSY HH, HSQC, and HMBC experiments were carried out for all the compounds. 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. Abbreviations used: s, singlet; d, doublet; dd, double doublet; t, triplet; sept, septuplet; m, multiplet. For complexes **5a−c**, analytically pure samples could not be obtained. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of these complexes are provided as Supporting Information.

*Synthesis of Complexes $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)\{P(OR)_3\}(PPh_3)][PF_6]$ (R = Et (**1**); R = Me (**2**)).* To a solution of the complex $[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)\{P(OR)_3\}]$ (0.3 mmol; R = Et, 204 mg; R = Me, 191 mg) and $NaPF_6$ (1.5 mmol, 252 mg) in MeOH (10 mL) was added 1,1-diphenyl-2-propyn-1-ol (1.5 mmol, 312 mg). The initial orange solution was stirred at reflux temperature for 30 min, after which it turned to deep purple. Solvent was eliminated to dryness. The residue was extracted with CH_2Cl_2 and filtered through kieselghur. Solvents were evaporated, and the addition of hexane (30 mL) afforded a deep purple solid, which was washed with hexane (2 × 15

Scheme 6. Proposed Mechanism for the Synthesis of Complexes 9a,b



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mL) and vacuum-dried. R = Et (**1**): yield 85%. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, CD_2Cl_2, 20 °C): δ 135.9 (d, $^{2}J_{PP}$ = 50.2 Hz, $P(OEt)_3$), 51.0 (d, $^{2}J_{PP}$ = 50.2 Hz, PPh_3), −144.4 (sept, $^{1}J_{PF}$ = 711.2 Hz, PF_6). ^{1}H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 1.19 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 3.50 (m, 6H, $P(OCH_2CH_3)_3$), 5.38, 5.47, 5.79 (3s, 3 × 1H, C_9H_7), 7.09−7.65 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 15.7 (d, $^{3}J_{CP}$ = 7.3 Hz, $P(OCH_2CH_3)_3$), 63.2 (d, $^{2}J_{CP}$ = 8.9 Hz, $P(OCH_2CH_3)_3$), 80.1, 84.2, 95.9, 111.5, 112.7 (5s, C_9H_7), 123.7−144.7 (PPh_3, Ph_2, C_9H_7), 156.2 (s, C_γ), 204.1 (s, C_β), 295.0 (dd, $^{2}J_{CP}$ = 15.8 Hz, $^{2}J_{CP}$ = 26.4 Hz, Ru=C_α). Conductivity (acetone, 20 °C): Λ = 130 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν (C=C=C) 1936 (s), ν (PF_6) 838 (s). MS (ESI) *m*/*z*: 835 ([M]$^+$, 100%). Anal. Calcd for $C_{48}H_{47}F_6O_3P_3Ru$: C, 58.84; H, 4.83. Found: C, 59.12; H, 4.76.

R = Me (**2**): yield 93%. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, CD_2Cl_2, 20 °C): δ 141.3 (d, $^{2}J_{PP}$ = 51.8 Hz, $P(OMe)_3$), 51.3 (d, $^{2}J_{PP}$ = 51.8 Hz, PPh_3), −144.4 (sept, $^{1}J_{PF}$ = 711.2 Hz, PF_6). ^{1}H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 3.50 (d, $^{3}J_{HP}$ = 11.6 Hz, 9H, $P(OMe)_3$), 5.32, 5.54, 5.86 (3s, 3 × 1H, C_9H_7), 7.08−7.64 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 53.5 (d, $^{2}J_{CP}$ = 8.7 Hz, $P(OMe)_3$), 79.4, 84.1, 95.2, 111.6, 111.7 (5s, C_9H_7), 123.5−144.7 (PPh_3, Ph_2, C_9H_7), 157.0 (s, C_γ), 202.6 (s, C_β), 295.5 (dd, $^{2}J_{CP}$ = 13.8 Hz, $^{2}J_{CP}$ = 26.0 Hz, Ru=C_α). Conductivity (acetone, 20 °C): Λ = 115 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν (C=C=C) 1939 (s), ν (PF_6) 838 (s). MS (ESI) *m*/*z*: 793 ([M]$^+$, 100%), 293 ([M − PPh_3 − $P(OEt)_3$]$^+$, 28%). Anal. Calcd for $C_{45}H_{41}F_6O_3P_3Ru$: C, 57.63; H, 4.41. Found: C, 57.48; H, 4.55.

*Synthesis of Complex [Ru(η^5-C_9H_7){C≡CC(OMe)Ph_2}{P(OEt)$_3$}(PPh$_3$)] (**3**).* NaH (0.12 mmol, 3 mg) was dissolved in MeOH, then evaporated to dryness to isolate the NaOMe formed. It was solved again in THF (10 mL), and the complex [Ru(η^5-C_9H_7)(=C=C=CPh_2){$P(OEt)_3$}(PPh_3)][PF_6] (**1**) (0.06 mmol, 58 mg) was added. The initial purple solution was stirred at room temperature for 20 min, until it turned yellow. Solvent was removed, and the residue was extracted with diethyl ether (2 × 15 mL). Solvent was evaporated to dryness, affording an orange solid: yield 62%. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 20 °C): δ 151.5 (d, $^{2}J_{PP}$ = 65.6 Hz, $P(OEt)_3$), 56.8 (d, $^{2}J_{PP}$ = 65.6 Hz, PPh_3). ^{1}H NMR (400.1 MHz, C_6D_6, 20 °C): δ 1.05 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 3.58 (s, 3H, OMe), 3.84 (m, 6H, $P(OCH_2CH_3)_3$), 4.45, 5.23, 5.49 (3s, 3 × 1H, C_9H_7), 6.93−8.08 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 20 °C): δ 16.0 (d, $^{3}J_{CP}$ = 6.0 Hz, $P(OCH_2CH_3)_3$), 51.2 (s, OMe), 60.8 (d, $^{2}J_{CP}$ = 6.3 Hz, $P(OCH_2CH_3)_3$), 68.8 (d, $^{2}J_{CP}$ = 7.7 Hz, C_9H_7), 72.4, 93.2 (2s, C_9H_7), 82.1 (s, C_γ), 104.2 (m, C_α), 109.0 C_9H_7), 110.8 (C_β), 123.0−148.1 (PPh_3, Ph_2, C_9H_7). IR (KBr, cm^{-1}): ν (C≡C) 2074 (w). Anal. Calcd for $C_{49}H_{50}O_4P_2Ru$: C, 67.96; H, 5.82. Found: C, 67.62; H, 5.66.

*Synthesis of Complex [Ru(η^5-C_9H_7){C≡CC(SMe)Ph_2}{P(OEt)$_3$}(PPh$_3$)] (**4a**).* To a solution of the complex [Ru(η^5-C_9H_7)(=C=C=CPh_2){$P(OEt)_3$}(PPh_3)][PF_6] (**1**) (0.06 mmol, 58 mg) in THF (10 mL) at −40 °C was added NaSMe (0.12 mmol, 8.4 mg). The initial purple solution was stirred at this temperature for 15 min, until it turned orange. Solvent was removed, and the residue was extracted with hexane (2 × 15 mL). Solvent was evaporated to dryness, affording an orange solid: yield 59%. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, C_6D_6, 20 °C): δ 151.3 (d, $^{2}J_{PP}$ = 66.5 Hz, $P(OEt)_3$), 56.4 (d, $^{2}J_{PP}$ = 66.5 Hz, PPh_3). ^{1}H NMR (400.1 MHz, C_6D_6, 20 °C): δ 1.05 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 2.22 (s, 3H, SMe), 3.86 (m, 6H, $P(OCH_2CH_3)_3$), 4.42, 5.29, 5.50 (3s, 3 × 1H, C_9H_7), 6.90−8.18 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 0 °C): δ 14.7 (s, SMe), 16.0 (d, $^{3}J_{CP}$ = 6.7 Hz, $P(OCH_2CH_3)_3$), 60.8 (d, $^{2}J_{CP}$ = 6.7 Hz, $P(OCH_2CH_3)_3$), 68.7 (d, $^{2}J_{CP}$ = 7.6 Hz, C_9H_7), 72.1, 93.1 (2s, C_9H_7), 75.2 (s, C_γ), 101.2 (dd, $^{2}J_{CP}$ = 29.4 Hz, $^{2}J_{CP}$ = 20.9 Hz, C_α), 109.4 (s, C_β), 111.0, 111.2 (2d, $^{2}J_{CP}$ = 5.7 Hz, $^{2}J_{CP}$ = 4.7 Hz, C_9H_7), 122.8−147.1 (PPh_3, Ph_2, C_9H_7). IR (KBr, cm^{-1}): ν (C≡C) 2078 (w). MS (ESI) *m*/*z*: 835 ([M − SMe]$^+$, 100%). Anal. Calcd for $C_{49}H_{50}O_3P_2RuS$: C, 66.73; H, 5.71; S, 3.64. Found: C, 66.56; H, 5.72; S, 3.36.

*Synthesis of Complexes [Ru(η^5-C_9H_7){C≡CC(SR)Ph_2}{P(OEt)$_3$}(PPh$_3$)] (R = ^{i}Pr (**4b**); R = ^{t}Bu (**4c**)).* By stirring NaOH (0.12 mmol, 4.8 mg) and the thiol (0.12 mmol) in THF (10 mL) for 30 min, the corresponding thiolate was formed. Then, it was cooled at −40 °C, and the complex [Ru(η^5-C_9H_7)(=C=C=CPh_2){$P(OEt)_3$}(PPh_3)][PF_6] (**1**) (0.06 mmol, 58 mg) was added. The mixture was stirred at this temperature for 40 min, until it turned orange. Once the reaction was completed, the solution was evaporated to dryness. The residue was extracted with hexane and filtered. The resulting solution was evaporated to dryness, affording an orange solid. R = ^{i}Pr (**4b**): yield 71%. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 20 °C): δ 151.0 (d, $^{2}J_{PP}$ = 66.8 Hz, $P(OEt)_3$), 55.6 (d, $^{2}J_{PP}$ = 66.8 Hz, PPh_3). ^{1}H NMR (400.1 MHz, C_6D_6, 20 °C): δ 1.07 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 1.25 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $SCHMe_2$), 1.39 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $SCHMe_2$), 3.71 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1H, $SCHMe_2$), 3.88 (m, 6H, $P(OCH_2CH_3)_3$), 4.43, 5.34, 5.57 (3s, 3 × 1H, C_9H_7), 6.94−8.09 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, −50 °C): δ 16.3 (d, $^{3}J_{CP}$ = 7.0 Hz, $P(OCH_2CH_3)_3$), 24.4, 24.5 (2s, $SCHMe_2$), 36.8 (s, SCH), 60.7 (d, $^{2}J_{CP}$ = 6.3 Hz, $P(OCH_2CH_3)_3$), 68.3, 71.1, 93.1 (3s, C_9H_7), 76.0 (s, C_γ), 99.5 (m, C_α), 110.7 (s, C_β), 107.8, 111.1 (2s, C_9H_7), 122.2−147.2 (PPh_3, Ph_2, C_9H_7). IR (KBr, cm^{-1}): ν (C≡C) 2075 (w). MS (ESI) *m*/*z*: 835 ([M − S^{i}Pr]$^+$, 100%).

R = ^{t}Bu (**4c**): yield 50%. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 20 °C): δ 150.8 (d, $^{2}J_{PP}$ = 66.8 Hz, $P(OEt)_3$), 54.7 (d, $^{2}J_{PP}$ = 66.8 Hz, PPh_3). ^{1}H NMR (400.1 MHz, C_6D_6, 20 °C): δ 1.09 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 1.68 (s, 9H, $SCMe_3$), 3.92 (m, 6H, $P(OCH_2CH_3)_3$), 4.43, 5.47, 5.68 (3s, 3 × 1H, C_9H_7), 6.93−8.24 (m, 29H, PPh_3, Ph_2, C_9H_7). IR (KBr, cm^{-1}): ν (C≡C) 2073 (w). MS (ESI) *m*/*z*: 835 ([M − S^{t}Bu]$^+$, 100%).

*Synthesis of Complex [Ru(η^5-C_9H_7){C(SMe)=C=CPh_2}{P(OEt)$_3$}(PPh$_3$)] (**5a**).* To a solution of the complex [Ru(η^5-C_9H_7)(=C=C=CPh_2){$P(OEt)_3$}(PPh_3)][PF_6] (**1**) (0.06 mmol, 58 mg) in THF (10 mL) was added NaSMe (0.12 mmol, 8.4 mg). The initial purple solution turned orange and was stirred at room temperature for 2 days (monitored by $^{31}P\{^{1}H\}$ NMR). Solvent was then removed, and the residue was extracted with hexane (2 × 15 mL). Solvent was evaporated to dryness, affording an orange solid: yield 59%. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, C_6D_6, 20 °C): δ 145.4 (d, $^{2}J_{PP}$ = 64.8 Hz, $P(OEt)_3$), 52.6 (d, $^{2}J_{PP}$ = 64.8 Hz, PPh_3). ^{1}H NMR (400.1 MHz, C_6D_6, 20 °C): δ 0.94 (t, $^{3}J_{HH}$ = 6.8 Hz, 9H, $P(OCH_2CH_3)_3$), 2.08 (s, 3H, SMe), 3.58 (m, 3H, $P(OCH_2CH_3)_3$), 3.73 (m, 3H, $P(OCH_2CH_3)_3$), 5.44, 5.55, 5.99 (3s, 3 × 1H, C_9H_7), 6.38 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, C_9H_7), 7.08−7.89 (m, 28H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 20 °C): δ 15.6 (d, $^{3}J_{CP}$ = 6.5 Hz, $P(OCH_2CH_3)_3$), 21.3 (s, SMe), 60.8 (d, $^{2}J_{CP}$ = 9.8 Hz, $P(OCH_2CH_3)_3$), 68.0, 72.9 (2d, $^{2}J_{CP}$ = 8.1 Hz, $^{2}J_{CP}$ = 8.1 Hz, C_9H_7), 96.7 (dd, $^{2}J_{CP}$ = 12.3 Hz, $^{2}J_{CP}$ = 18.0 Hz, C_α), 98.8, 106.2, 111.9 (3s, C_9H_7), 103.7 (s, C_γ), 122.8−147.1 (PPh_3, Ph_2, C_9H_7), 198.1 (d, $^{3}J_{CP}$ = 4.9 Hz, C_β). IR (KBr, cm^{-1}): ν (C=C=C) 1958 (w).

*Synthesis of Complexes [Ru(η^5-C_9H_7){C(SR)=C=CPh_2}{P(OEt)$_3$}(PPh$_3$)] (R = ^{i}Pr (**5b**); R = ^{t}Bu (**5c**)).* By stirring NaOH (0.12 mmol, 4.8 mg) and the thiol (0.12 mmol) in THF (10 mL) for 30 min, the corresponding thiolate was formed. Then, the complex [Ru(η^5-C_9H_7)(=C=C=CPh_2){$P(OEt)_3$}(PPh_3)][PF_6] (**1**) (0.06 mmol, 58 mg) was added. The mixture was stirred at room temperature overnight. Once the reaction was completed (monitored by $^{31}P\{^{1}H\}$ NMR), the solution was evaporated to dryness and the residue was extracted with hexane and filtered. The resulting solution was evaporated to dryness, affording an orange solid. R = ^{i}Pr (**5b**): yield 71%. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 20 °C): δ 144.8 (d, $^{2}J_{PP}$ = 64.4 Hz, $P(OEt)_3$), 52.5 (d, $^{2}J_{PP}$ = 64.4 Hz, PPh_3). ^{1}H NMR (400.1 MHz, C_6D_6, 20 °C): δ 0.84 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, $SCHMe_2$), 0.93 (t, $^{3}J_{HH}$ = 6.8 Hz, 9H, $P(OCH_2CH_3)_3$), 1.36 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, $SCHMe_2$), 3.18 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, $SCHMe_2$), 3.56 (m, 3H, $P(OCH_2CH_3)_3$), 3.72 (m, 3H, $P(OCH_2CH_3)_3$), 5.44, 5.68, 6.07 (3s, 3 × 1H, C_9H_7), 6.27 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, C_9H_7), 7.10−7.95 (m, 28H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 20 °C): δ 15.6 (d, $^{3}J_{CP}$ = 8.7 Hz, $P(OCH_2CH_3)_3$), 23.1, 23.7 (2s, $SCHMe_2$), 41.3 (s, $SCHMe_2$), 60.8 (d, $^{2}J_{CP}$ = 8.9 Hz, $P(OCH_2CH_3)_3$), 67.6, 73.5 (2d, $^{2}J_{CP}$ = 8.8 Hz, $^{2}J_{CP}$ = 15.4 Hz, C_9H_7), 94.8 (dd, $^{2}J_{CP}$ = 16.6 Hz, $^{2}J_{CP}$ = 12.8 Hz, C_α), 102.4 (s, C_γ), 99.3, 105.9, 111.8 (3s, C_9H_7), 122.6−145.3 (PPh_3, Ph_2, C_9H_7), 197.6 (d, $^{3}J_{CP}$ = 5.4 Hz, C_β). IR (KBr, cm^{-1}): ν (C=C=C) 1957 (w).

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R = ^{t}Bu (**5c**): yield 50%. $^{31}P\{^1H\}$ NMR (162.1 MHz, C_6D_6, 20 °C): δ 144.0 (d, $^2J_{PP}$ = 64.8 Hz, $P(OEt)_3$), 51.7 (d, $^2J_{PP}$ = 64.8 Hz, PPh_3). ^1H NMR (400.1 MHz, C_6D_6, 20 °C): δ 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 1.28 (s, 9H, $SCMe_3$), 3.52 (m, 3H, $P(OCH_2CH_3)_3$), 3.63 (m, 3H, $P(OCH_2CH_3)_3$), 5.43, 5.80, 6.03 (3s, 3 × 1H, C_9H_7), 6.35 (d, $^3J_{HH}$ = 8.4 Hz, 1H, C_9H_7), 6.97−8.02 (m, 28H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 20 °C): δ 15.6 (d, $^3J_{CP}$ = 6.5 Hz, $P(OCH_2CH_3)_3$), 30.1 (s, $SCMe_3$), 49.0 (s, $SCMe_3$), 60.7 (d, $^2J_{CP}$ = 9.3 Hz, $P(OCH_2CH_3)_3$), 67.5, 74.0 (2d, $^2J_{CP}$ = 7.2 Hz, $^2J_{CP}$ = 15.6 Hz, C_9H_7), 90.8 (dd, $^2J_{CP}$ = 15.6 Hz, $^2J_{CP}$ = 11.3 Hz, C_α), 100.7 (s, C_γ), 100.6, 106.1, 112.0 (3s, C_9H_7), 122.8−142.3 (PPh_3, Ph_2, C_9H_7), 197.2 (d, $^3J_{CP}$ = 5.3 Hz, C_β). IR (KBr, cm^{-1}): ν (C═C═C) 1956 (w).

*Synthesis of Complex [Ru(η^5-C_9H_7){C≡CC(PMe$_3$)Ph$_2$}{P(OEt)$_3$}(PPh$_3$)][PF$_6$] (**6**).* To a solution of the complex [Ru(η^5-C_9H_7)(═C═C═CPh$_2$){P(OEt)$_3$}(PPh$_3$)][PF_6] (**1**) (0.06 mmol, 58 mg) in THF (10 mL) was added PMe_3 (0.12 mmol, 10.3 μL), and the initial purple solution turned yellow. Solvent was partially evaporated and hexane (20 mL) was added, affording a yellow precipitate. Solvents were decanted, and the solid was washed with hexane (2 × 15 mL) and vacuum-dried: yield 50%. $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 20 °C): δ 148.3 (d, $^2J_{PP}$ = 64.8 Hz, $P(OEt)_3$), 54.4 (d, $^2J_{PP}$ = 64.8 Hz, PPh_3), 30.6 (s, PMe_3), −144.3 (sept, $^1J_{PF}$ = 711.2 Hz, PF_6). ^1H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 1.07 (t, $^3J_{HH}$ = 6.8 Hz, 9H, $P(OCH_2CH_3)_3$), 1.83 (d, $^2J_{HP}$ = 12.8 Hz, 9H, PMe_3), 3.78 (m, 6H, $P(OCH_2CH_3)_3$), 4.28, 5.31, 5.39 (3s, 3 × 1H, C_9H_7), 6.67−7.50 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 8.2 (d, $^1J_{CP}$ = 56.3 Hz, PMe_3), 16.0 (d, $^3J_{CP}$ = 4.5 Hz, $P(OCH_2CH_3)_3$), 52.3 (d, $^1J_{CP}$ = 50.2 Hz, C_γ), 61.0 (d, $^2J_{CP}$ = 7.1 Hz, $P(OCH_2CH_3)_3$), 66.4, 72.1, 93.3 (3s, C_9H_7), 98.7 (m, C_α), 110.7, 111.0, 114.5 (3s, C_β, C_9H_7), 122.7−138.1 (PPh_3, Ph_2, C_9H_7). Conductivity (acetone, 20 °C): Λ = 138 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν (C≡C) 2072 (w), ν (PF_6) 840 (s). Anal. Calcd for $C_{51}H_{56}F_6O_3P_4Ru$: C, 58.01; H, 5.35. Found: C, 57.90; H, 5.41.

*Synthesis of Complex [Ru(η^5-C_9H_7){C(PMe$_3$)═C═CPh$_2$}{P(OEt)$_3$}(PPh$_3$)][PF$_6$] (**7**).*[26] To a solution of the complex [Ru(η^5-C_9H_7)(═C═C═CPh$_2$){P(OEt)$_3$}(PPh$_3$)][PF_6] (**1**) (0.06 mmol, 58 mg) in THF (10 mL) was added PMe_3 (0.12 mmol, 10.3 μL). After the initial formation of complex **6**, the solution was stirred at reflux temperature for 5 h. Then, solvent was partially evaporated and hexane (20 mL) was added, affording a yellow precipitate. The solid was washed with hexane (2 × 15 mL) and vacuum-dried. Analytically pure samples were obtained by recrystallization of CH_2Cl_2/hexane: yield 47%. $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 20 °C): δ 141.0 (dd, $^2J_{PP}$ = 71.3 Hz, $^3J_{PP}$ = 21.1 Hz, $P(OEt)_3$), 59.2 (d, $^2J_{PP}$ = 71.3 Hz, PPh_3), 30.5 (d, $^3J_{PP}$ = 21.1 Hz, PMe_3), −144.3 (sept, $^1J_{PF}$ = 711.3 Hz, PF_6). ^1H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 1.15 (t, $^3J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 1.65 (d, $^2J_{HP}$ = 12.8 Hz, 9H, PMe_3), 3.57 (m, 3H, $P(OCH_2CH_3)_3$), 3.83 (m, 3H, $P(OCH_2CH_3)_3$), 4.75, 4.97, 5.02 (3s, 3 × 1H, C_9H_7), 6.34−7.63 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 13.2 (d, $^1J_{CP}$ = 54.9 Hz, PMe_3), 15.4 (d, $^3J_{CP}$ = 5.7 Hz, $P(OCH_2CH_3)_3$), 62.5 (d, $^2J_{CP}$ = 10.9 Hz, $P(OCH_2CH_3)_3$), 71.0 (d, $^2J_{CP}$ = 16.5 Hz, C_9H_7), 75.7 (m, C_α), 96.6 (d, $^3J_{CP}$ = 23.5 Hz, C_γ), 65.1, 94.3, 107.3, 114.9 (4s, C_9H_7), 123.6−136.6 (PPh_3, Ph_2, C_9H_7), 209.1 (s, C_β). Conductivity (acetone, 20 °C): Λ = 112 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν (C═C═C) 1859 (m), ν (PF_6) 840 (s). Anal. Calcd for $C_{51}H_{56}F_6O_3P_4Ru$: C, 58.01; H, 5.35. Found: C, 57.84; H, 5.29.

*Synthesis of Complex [Ru(η^5-C_9H_7){C(P(OEt)$_3$)═C═CPh$_2$}{P(OEt)$_3$}(PPh$_3$)][PF$_6$] (**8**).* To a solution of the complex [Ru(η^5-C_9H_7)(═C═C═CPh$_2$){P(OEt)$_3$}(PPh$_3$)][PF_6] (**1**) (0.06 mmol, 58 mg) in THF (10 mL) was added $P(OEt)_3$ (0.06 mmol, 10 μL). The initial purple solution was stirred at reflux temperature for 45 min and turned brown. Then, solvent was partially evaporated and hexane (20 mL) was added, affording a brown precipitate. The solid was washed with hexane (2 × 15 mL) and vacuum-dried. Analytically pure samples were obtained by recrystallization of CH_2Cl_2/hexane: yield 68%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 138.5 (dd, $^2J_{PP}$ = 72.9 Hz, $^3J_{PP}$ = 9.7 Hz, Ru-$P(OEt)_3$), 57.9 (dd, $^2J_{PP}$ = 72.9 Hz, $^3J_{PP}$ = 7.3 Hz, PPh_3), 36.4 (dd, $^3J_{PP}$ = 9.7 Hz, $^3J_{PP}$ = 7.3 Hz, C-$P(OEt)_3$), −144.4 (sept, $^1J_{PF}$ = 710.8 Hz, PF_6). ^1H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 1.30 (t, $^3J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 3.57 (m, 6H, $P(OCH_2CH_3)_3$), 3.92 (m, 3H, $P(OCH_2CH_3)_3$), 4.16 (m, 3H, $P(OCH_2CH_3)_3$), 4.84, 4.97, 5.04 (3s, 3 × 1H, C_9H_7), 6.63−7.52 (m, 29H, PPh_3, Ph_2, C_9H_7). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 15.3 (d, $^3J_{CP}$ = 7.1 Hz, $P(OCH_2CH_3)_3$), 15.6 (d, $^3J_{CP}$ = 7.1 Hz, $P(OCH_2CH_3)_3$), 61.8 (d, $^2J_{CP}$ = 10.0 Hz, $P(OCH_2CH_3)_3$), 67.5 (d, $^2J_{CP}$ = 9.2 Hz, $P(OCH_2CH_3)_3$), 67.3, 94.0 (2s, C_9H_7), 69.7 (d, $^2J_{CP}$ = 13.0 Hz, C_9H_7), 74.2 (m, C_α), 98.9 (d, $^3J_{CP}$ = 27.3 Hz, C_γ), 107.9, 111.9 (2s, C_9H_7), 123.8−136.3 (PPh_3, Ph_2, C_9H_7), 215.9 (br s, C_β). Conductivity (acetone, 20 °C): Λ = 116 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν (C═C═C) 1864 (m), ν (PF_6) 840 (s). Anal. Calcd for $C_{54}H_{62}F_6O_6P_4Ru$: C, 56.59; H, 5.45. Found: C, 56.32; H, 5.41.

*Synthesis of [Ru(η^5-C_9H_7){κ^3(C,C,C)-C(R$_2$PCH$_2$CH═CH$_2$)═C═CPh$_2$}{P(OEt)$_3$}][PF$_6$] (R = ^{i}Pr (**9a**), R = Ph (**9b**)).* To a solution of the complex [Ru(η^5-C_9H_7)(═C═C═CPh$_2$){P(OEt)$_3$}(PPh$_3$)][PF_6] (**1**) (0.1 mmol, 98 mg) in THF (10 mL) was added allyldiisopropylphosphane (0.3 mmol, 45 μL) or allyldiphenylphosphane (0.3 mmol, 65 μL). The solution was stirred in a sealed tube at 110 °C overnight (**9a**) or at 120 °C for 24 h (**9b**). The yellow solution was then dropped into stirring hexane (80 mL), affording a brown precipitate. Solvents were decanted, and the solid was washed with hexane (2 × 15 mL) and vacuum-dried. R = ^{i}Pr (**9a**): yield 51%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 147.8 (d, $^3J_{PP}$ = 4.9 Hz, $P(OEt)_3$), 82.2 (d, $^3J_{PP}$ = 4.9 Hz, ADIP), −144.2 (sept, $^1J_{PF}$ = 712.0 Hz, PF_6). ^1H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 1.12−1.50 (m, 14H, Me_2CHP, CHP, PCH_2), 1.22 (t, $^3J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 2.40 (m, 2H, ═CH, $═CH_2$), 2.49 (m, 1H, CHP), 2.63 (m, 1H, PCH_2), 3.47 (m, 1H, $═CH_2$), 4.04 (m, 6H, $P(OCH_2CH_3)_3$), 5.15, 5.53, 5.72 (3s, 3 × 1H, C_9H_7), 6.72 (d, $^3J_{HH}$ = 8.4 Hz, 1H, C_9H_7), 7.04−7.65 (m, 13H, Ph_2, C_9H_7). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 15.3−17.9 (m, Me_2CHP, $P(OCH_2CH_3)_3$), 21.2 (d, $^1J_{CP}$ = 42.0 Hz, CHP), 24.7 (d, $^1J_{CP}$ = 60.0 Hz, PCH_2), 25.6 (d, $^1J_{CP}$ = 27.1 Hz, CHP), 41.6 (dd, $^3J_{CP}$ = 5.2 Hz, $^2J_{CP}$ = 5.9 Hz, $═CH_2$), 56.9 (s, ═CH), 62.4 (d, $^2J_{CP}$ = 7.5 Hz, $P(OCH_2CH_3)_3$), 78.6 (dd, $^1J_{CP}$ = 31.6 Hz, $^2J_{CP}$ = 22.1 Hz, C_α), 73.8, 75.2, 90.2 (3s, C_9H_7), 100.5 (d, $^2J_{CP}$ = 18.9 Hz, C_β), 108.0, 109.6 (2d, $^2J_{CP}$ = 7.0 Hz, $^2J_{CP}$ = 6.2 Hz, C_9H_7), 122.0−136.7 (Ph_2, C_9H_7), 208.7 (s, C_γ). Conductivity (acetone, 20 °C): Λ = 130 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν (C═C═C) 1937 (m), ν (C═C) 1437 (w), ν (PF_6) 839 (s). MS (ESI) m/z: 731 ($[M]^+$, 100%). Anal. Calcd for $C_{39}H_{51}F_6O_3P_3Ru$: C, 53.48; H, 5.87. Found: C, 53.04; H, 5.63. R = Ph (**9b**): yield 55%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 146.5 (d, $^3J_{PP}$ = 4.9 Hz, $P(OEt)_3$), 60.0 (d, $^3J_{PP}$ = 4.9 Hz, ADIP), −144.5 (sept, $^1J_{PF}$ = 710.8 Hz, PF_6). ^1H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 1.18 (t, $^3J_{HH}$ = 7.2 Hz, 9H, $P(OCH_2CH_3)_3$), 2.02 (m, 1H, ═CH), 2.30 (m, 1H, PCH_2), 2.63 (m, 1H, $═CH_2$), 2.75 (m, 1H, $═CH_2$), 3.41 (m, 1H, PCH_2), 3.98 (m, 6H, $P(OCH_2CH_3)_3$), 5.38, 5.53, 5.69 (3s, 3 × 1H, C_9H_7), 6.48−7.72 (m, 24H, PPh_2, Ph_2, C_9H_7). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 15.9 (d, $^3J_{CP}$ = 5.7 Hz, $P(OCH_2CH_3)_3$), 29.8 (d, $^1J_{CP}$ = 72.3 Hz, PCH_2), 46.2 (dd, $^3J_{CP}$ = 5.0 Hz, $^2J_{CP}$ = 8.0 Hz, $═CH_2$), 58.6 (s, ═CH), 62.2 (d, $^2J_{CP}$ = 6.9 Hz, $P(OCH_2CH_3)_3$), 81.2 (dd, $^1J_{CP}$ = 27.6 Hz, $^2J_{CP}$ = 20.7 Hz, C_α), 73.8, 78.1, 89.7 (3s, C_9H_7), 103.5 (d, $^2J_{CP}$ = 22.3 Hz, C_β), 105.9, 107.2 (2d, $^2J_{CP}$ = 8.6 Hz, $^2J_{CP}$ = 6.9 Hz, C_9H_7), 120.5−136.9 (PPh_2, Ph_2, C_9H_7), 214.8 (d, $^3J_{CP}$ = 3.8 Hz, C_γ). Conductivity (acetone, 20 °C): Λ = 116 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν (C═C═C) 1931 (m), ν (C═C) 1436 (w), ν (PF_6) 839 (s). Anal. Calcd for $C_{45}H_{47}F_6O_3P_3Ru$: C, 57.26; H, 5.02. Found: C, 57.03; H, 5.21.

X-ray Crystal Structure Determination of Complexes 2·2CH_2Cl_2 and 9a·$CHCl_3$. Crystals suitable for X-ray diffraction analysis were obtained from dichloromethane/hexane and chloroform/hexane solvent systems for **2** and **9a**, respectively. The most relevant crystal and refinement data are collected in the Supporting Information (Table S1).

In both cases, diffraction data were recorded on an Oxford Diffraction Xcalibur Nova (Agilent) single-crystal diffractometer, using Cu Kα radiation (λ= 1.5418 Å). Images were collected at a 63 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4−20 and 5−30 s,

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respectively). Data collection strategy was calculated with the program CrysAlis Pro CCD.[27] Data reduction and cell refinement were performed with the program CrysAlis Pro RED.[27] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[27]

The software package WINGX[28] was used for space group determination, structure solution, and refinement. The structure of complex **2** was solved by direct methods using SIR2004[29] and **9a** by Patterson interpretation and phase expansion using DIRDIF.[30] In the crystal of **2** two CH_2Cl_2 solvent molecules per unit formula of the complex are present, and for **9a** a $CHCl_3$ solvent molecule per unit formula of the complex was present. Isotropic least-squares refinement on F^2 using SHELXL97[31] was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined, the H atoms were geometrically located, and their coordinates were refined riding on their parent atoms. The maximum residual electron density is located near heavy atoms.

The function minimized was $([\sum wF_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are collected in the Supporting Information Table S1) 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 International.[32] The crystallographic plots were made with PLATON.[33]

■ ASSOCIATED CONTENT

Supporting Information

^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of complexes **5a−c** (Figures S1−S9). Crystal and refinement data for complexes **2**·$2CH_2Cl_2$ and **9a**·$CHCl_3$ (Table S1). X-ray crystallographic data of **2**·$2CH_2Cl_2$ and **9a**·$CHCl_3$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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