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Organoruthenium Complexes Containing New Phosphorus−Carbon and Phosphorus−Carbon−Sulfur Ligands Generated in the Coordination Sphere by Nucleophilic Addition Reactions

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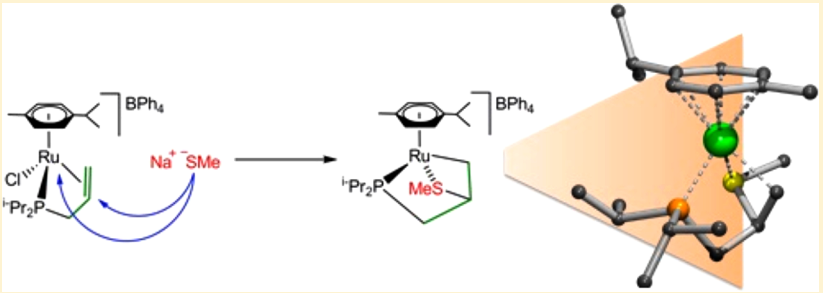
Supporting Information



ABSTRACT: The reaction of the dimeric complex $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$ ($C_{10}H_{14}$ = *p*-cymene) with an excess of allyldiisopropylphosphane (ADIP) leads to the complex $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^2(P,C)\text{-}i\text{Pr}_2PCH_2CH(i\text{Pr}_2PCH_2CH{=}CH_2)CH_2\}]^+$ (**1**$^+$), which presents a new bidentate $\kappa^2(P,C)$ ligand. The same cationic complex can be prepared by nuclephilic attack of 1 equiv of the free ADIP at the coordinated $\kappa^3(P,C,C)\text{-}i\text{Pr}_2PCH_2CH{=}CH_2$ ligand in $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2PCH_2CH{=}CH_2\}]^+$ (**3**$^+$). Addition of different phosphane ligands to complex **3**$^+$ allows to the synthesis of ruthenium complexes with new bidentate ligands $\kappa^2(P,C)$. The unusual complexes $[Ru\{\kappa^3(P,C,S)\text{-}i\text{Pr}_2PCH_2CH(SR)CH_2\}(\eta^6\text{-}C_{10}H_{14})]^+$ (**11a−c**$^+$) containing new $\kappa^3(P,C,S)$ ligands can be obtained by the reaction of **3**$^+$ with anionic nucleophiles RS^-. For comparative purposes, the indenyl complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2PCH_2CH{=}CH_2\}(PPh_3)]^+$ (**8**$^+$) has been also prepared and differences in the reactivities of cationic complexes **3**$^+$ and **8**$^+$ toward nucleophiles are pointed out.

INTRODUCTION

Functionalized phosphanes bearing a multiple carbon−carbon bond display a versatile behavior as ligands in coordination chemistry[1] and have been reasonably well explored to date. One key feature of these hybrid phosphane−olefin ligands is their hemilability, since they are able to easily dissociate the C−C double bond and to allow interaction between the metal center and organic substrates. Indeed, metal-coordinated alkenylphosphanes act as dienophiles in Diels−Alder reactions[2] and can be involved in [2 + 2] cycloaddition reactions[3] and nucleophilic addition reactions onto the C−C double bond.[4]

In the last few years, our interest has been focused on the chemistry of half-sandwich ruthenium complexes bearing alkenylphosphanes. Thus, we have previously described the synthesis and characterization of a series of ruthenium(II) complexes $[Ru(\eta^5\text{-}C_nH_m)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)]^+$ (C_nH_m = C_9H_7, C_5H_5), which feature a $\kappa^3(P,C,C)$ coordination mode of the allyldiphenylphosphane as well as a diastereofacial coordination of the olefin at the ruthenium center. The hemilabile character of alkenylphosphane ligands in ruthenium complexes has been corroborated by kinetic studies.[5] In addition, we have approached the study of their reactivity, particularly as substrates in intramolecular cycloaddition reactions,[6] oxidative coupling reactions,[7] and stereoselective nucleophilic additions to afford ruthenaphosphacyclopentane complexes.[5b]

Continuing with these studies, we report here the synthesis of new half-sandwich arene complexes of ruthenium(II) containing the allyldiisopropylphosphane (ADIP) ligand as well as the nucleophilic addition of neutral P-donor nucleophiles to the $\kappa^3(P,C,C)$ complexes, which lead to the formation of new complexes bearing $\kappa^2(P,C)$ ligands. To our knowledge, these are the first examples of nucleophilic attack of a free phosphane at the allylic group of a coordinated alkenylphosphane. In addition, nucleophilic attack of NaSR at the $\kappa^3(P,C,C)$ complexes leads to the formation of unprecedented complexes with $\kappa^3(P,C,S)$-coordinated ligands.

Comparative studies using the indenyl complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2PCH_2CH{=}CH_2\}(PPh_3)]^+$ (**8**$^+$) have also been performed, and relevant differences in the reactivity toward nucleophiles have been found.

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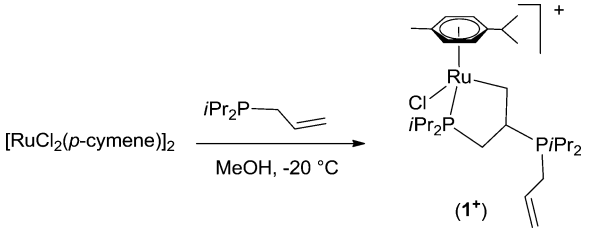
RESULTS AND DISCUSSION

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(*i*Pr$_2$PCH$_2$CH=CH$_2$)CH$_2$}][Cl] (1-Cl). The reaction of the dimeric complex [RuCl(μ-Cl)(η^6-$C_{10}H_{14}$)]$_2$ with an excess of allyldiisopropylphosphane (ADIP) in methanol, at low temperature, leads diastereoselectively to the compound [RuCl(η^6-$C_{10}H_{14}$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(*i*Pr$_2$PCH$_2$CH=CH$_2$)CH$_2$}]-[Cl] (**1-Cl**) (Scheme 1). The complex **1a**$^+$ presents a new tridentate ligand showing a bidentate κ^2(*P*,*C*) coordination mode.

Scheme 1. Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(*i*Pr$_2$PCH$_2$CH=CH$_2$)CH$_2$}]$^+$ (1$^+$)



Compound **1-Cl** is an air-stable yellow solid which has been characterized by analytical and spectroscopic methods. The diastereoselectivity of this reaction is readily assessed by the $^{31}P\{^1H\}$ NMR spectrum, which shows two doublets in accord with the two different phosphorus atoms in the molecule. Thus, the phosphorus atom bonded to ruthenium appears at 86.6 ppm and the phosphorus atom bonded to carbon appears at 36.5 ppm ($^3J_{PP}$ = 63.2 Hz). Other significant spectroscopic features are as follows. (i) The IR spectrum exhibits an absorption corresponding to the C=C double bond at 1635 cm^{-1}. (ii) The ^{1}H NMR spectrum agrees with the presence of the *p*-cymene group and the κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(*i*Pr$_2$PCH$_2$CH=CH$_2$)CH$_2$ ligand. Hydrogen atoms of the olefin of the allylphosphane appear as two doublets at 5.38 and 5.61 ppm (CH$_2$) and a multiplet at 5.81 ppm (CH). (iii) The signals for the RuCH$_2$ protons were unambiguously assigned through HSQC experiments as two multiplets at 2.24 and 3.18 ppm. These chemical shifts agree with those previously reported for the complexes [Ru(η^5-C_9H_7){κ^2(*P*,*C*)-Ph$_2$PCH$_2$CH(R)CH$_2$}(PPh$_3$)][5b] and [Ru(η^5-C_9H_7){κ^2(*P*,*C*)-Ph$_2$PCH$_2$CHCHCH$_2$}(L)].[18] (iv) $^{13}C\{^1H\}$ NMR spectrum shows the CH$_2$ bonded to ruthenium as a broad singlet at 18.2 ppm.The structure of **1-Cl** was determined by single-crystal X-ray diffraction analysis (Figure 1).

The most remarkable feature is the presence of the ruthenaphosphacycle with one allyldiisopropylphosphonium substituent. The bond distance C(12)−P(2) (1.834(2) Å) is typical of a phosphorus−carbon single bond, and the bond distance C(21)−C(22) (1.312(3) Å) and the bond angle C(22)−C(21)−C(20) (122.48(19)°) agree with the presence of the olefin group in the side chain. All of the carbon atoms in the ruthenaphosphacycle present a sp^3 hybridization, as shown by the bond angles around the carbon atoms C(11), C(12), and C(13) in the range 103−115°.

Figure 1 shows the complex with absolute configuration *R* for the ruthenium and *S* for the stereogenic carbon C(12). However, both enantiomers ($R_{Ru}S_C$ and $S_{Ru}R_C$) are present in the crystal in equal proportion, as the crystal belongs to the centric space group $P2_1/n$.

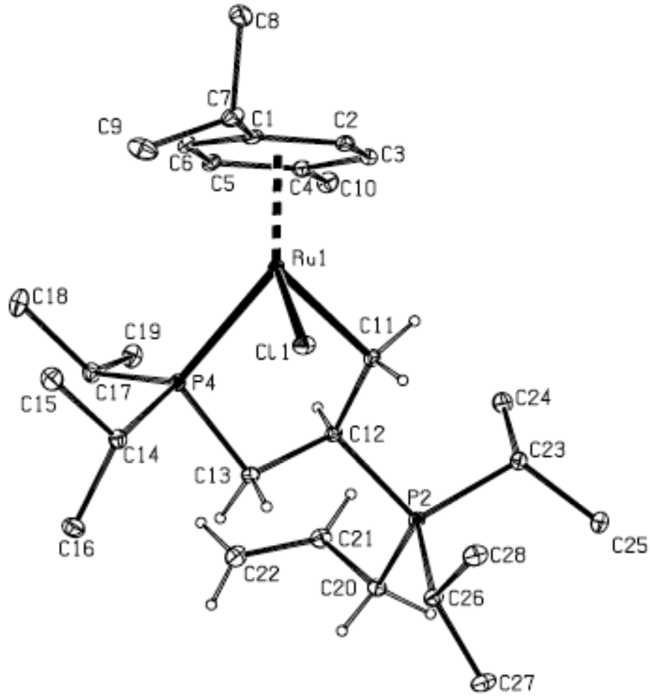


Figure 1. Molecular structure and atom-labeling scheme for the cationic complex [RuCl(η^6-$C_{10}H_{14}$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(*i*Pr$_2$PCH$_2$CH=CH$_2$)CH$_2$}]$^+$ (**1**$^+$). Hydrogen atoms of arene and isopropyl groups (except for the ruthenaphosphacycle and the allyl group) have been omitted for clarity. Non-hydrogen atoms are represented by their 10% probability ellipsoids. C* = centroid of the η^6-*p*-cymene ligand. Selected bond lengths (Å): Ru(1)−Cl(1) = 2.435(1), Ru(1)−P(4) = 2.323(1), Ru(1)−C(11) = 2.142(2), Ru(1)-C* = 1.735(1), C(11)−C(12) = 1.538(2), C(12)−C(13) = 1.526(2), C(13)−P(4) = 1.846(2), C(12)−P(2) = 1.834(2), P(2)−C(20) = 1.816(2), C(20)−C(21) = 1.498(3), C(21)−C(22) = 1.312(3). Selected bond angles (deg): C(11)−Ru(1)−Cl(1) = 85.59(6), C(11)−Ru(1)−P(4) = 82.37(5), P(4)−Ru(1)−Cl(1) = 87.18(2), C*−Ru(1)−C(11) = 124.60(5), C*−Ru(1)−Cl(1) = 125.18(1), C*−Ru(1)−P(4) = 135.77(1), C(13)−C(12)−C(11) = 111.62(14), C(13)−C(12)−P(2) = 111.14(12), C(11)−C(12)−P(2) = 113.14(12), C(22)−C(21)−C(20) = 122.48(19).

The formation of complex **1**$^+$ can be explained through the nucleophilic addition of 1 equiv of the allylphosphane to the coordinated ADIP ligand. In order to prove this hypothesis, although to our knowledge no nucleophilic attacks of neutral phosphanes at coordinated κ^3(*P*,*C*,*C*)-R$_2$PCH$_2$CH=CH$_2$ ligands have been described to date, the synthesis of the potential intermediate complex [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P*,*C*,*C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}]$^+$ was achieved.

Synthesis of [RuCl$_2$(η^6-$C_{10}H_{14}$){κ^1(*P*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}] (2) and [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P*,*C*,*C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}][BPh$_4$] (3-BPh$_4$). When the reaction of the complex [RuCl(μ-Cl)(η^6-$C_{10}H_{14}$)]$_2$ with a stoichiometric amount of ADIP was performed in dichloromethane, the complex [RuCl$_2$(η^6-$C_{10}H_{14}$){κ^1(*P*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}] (**2**) was isolated. Treatment with NaBPh$_4$ of a methanol suspension of complex **2** led to the cationic complex [RuCl(η^6-$C_{10}H_{14}$)-{κ^3(*P*,*C*,*C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}]$^+$ (**3**$^+$), which was isolated as its BPh$_4$ salt as an air-stable yellow solid (see Scheme 2). Both products have been characterized by elemental analysis and NMR data, which confirm the coordination mode of the allylphosphane as κ^1(*P*) for complex **2** and κ^3(*P*,*C*,*C*) for the salt **3-BPh$_4$**. In particular, the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of

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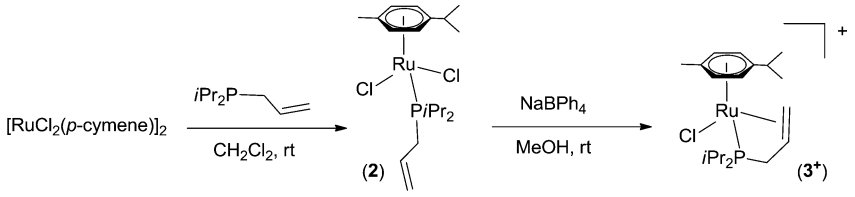
Scheme 2. Synthesis of the Complexes $[RuCl_2(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}iPr_2PCH_2CH{=}CH_2\}]$ (2) and $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}]^+$ (3^+)



3-BPh$_4$ show CH=CH$_2$ resonances which appear at higher field than those observed in complex **2** bearing the non-coordinated olefinic system $\kappa^1(P)$ (see the Experimental Section). $^{31}P\{^1H\}$ NMR spectra at room temperature also reveal the effect of the olefin coordination, showing the signal for the allylphosphane shifted toward higher field (δ −48.5 ppm for 3^+) with respect to that of the corresponding $\kappa^1(P)$ precursor (δ 33.6 ppm for **2**).

When the ADIP ligand is bound in a bidentate manner, the two faces of the alkene are diastereotopic.[18,19] The $^{31}P\{^1H\}$ NMR spectrum of complex 3^+ in CD_2Cl_2 shows one signal (δ −48.5 ppm for 3^+) and remains unchanged within a wide range of temperature (−60 to +25 °C). These NMR data agree either with the formation of only one isomer or with an equilibrium in which there is never a significant concentration (<0.01%) of the alternative-face isomer. Thus, the generation of the chelate ring $[Ru\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}]$ proceeds in a highly diastereoselective manner. This result agrees with those reported by us for the compounds $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)][PF_6]$[5b] and $[Ru(\eta^5\text{-}C_5H_5)\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)][PF_6]$[6b] and contrast with those reported for the analogous compound $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}\{\kappa^3(P,C,C)\text{-}Ph_2PCH_2CH{=}CH_2\}][PF_6]$,[19] for which a rapid fluxional equilibrium between the two diastereoisomers on the NMR time scale is observed.

In order to find out the coordination of the olefin, the structure of complex 3^+ was determined by single-crystal X-ray diffraction analysis. Suitable crystals were obtained by slow diffusion of diethyl ether into a solution of **3-BPh$_4$** in CH_2Cl_2. An ORTEP type representation of the complex is shown in Figure 2, and selected bond lengths and angles are presented in the caption.

The molecule exhibits a pseudooctahedral three-legged piano-stool geometry with the ruthenium atom bonded to the η^6-*p*-cymene ligand, to one chlorine atom, and to the ADIP ligand, which is bonded through the phosphorus atom and the η^2-coordinated olefin. Bond distances Ru−C(11) (2.261(4) Å) and Ru−C(12) (2.298(4) Å) indicate the symmetrical bonding of the olefin to the metal atom. Figure 2 shows the complex with relative configuration R_{Ru} and olefin coordination through the *si* enantioface, although both enantiomers are present in equal proportion in the crystal.

In order to prove our initial hypothesis, the reaction of free ADIP with **3-BPh$_4$** was achieved. From this reaction, we could isolate the compound $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(iPr_2PCH_2CH{=}CH_2)CH_2\}][BPh_4]$ (**1-BPh$_4$**), as expected (Scheme 3). **1-BPh$_4$** shows the same spectroscopic data as **1-Cl** except for those corresponding to the BPh_4 anion.

Reaction of $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}]^+$ (3^+) with P-Donor Nucleophiles: Synthesis of $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(PR_3)CH_2\}]^+$ (R = Ph ($4a^+$), Me ($4b^+$)) and $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}iPr_2PCH_2CH{=}CH_2\}\{P(OR)_3\}]^+$ (R = Ph ($5a^+$), Me ($5b^+$), Et ($5c^+$)). In order to generalize the behavior reported above, the reaction of complex 3^+ with different P-donor ligands was carried out.

Thus, the reaction of complex 3^+ with the phosphanes PPh_3 and PMe_3 in THF resulted in the isolation of the complexes $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(PR_3)CH_2\}]^+$ (R = Ph ($4a^+$), Me ($4b^+$)). However, when the same reaction was carried out using $P(OR)_3$ as nucleophiles, the substitution complexes $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}iPr_2PCH_2CH{=}CH_2\}\{P\text{-}$

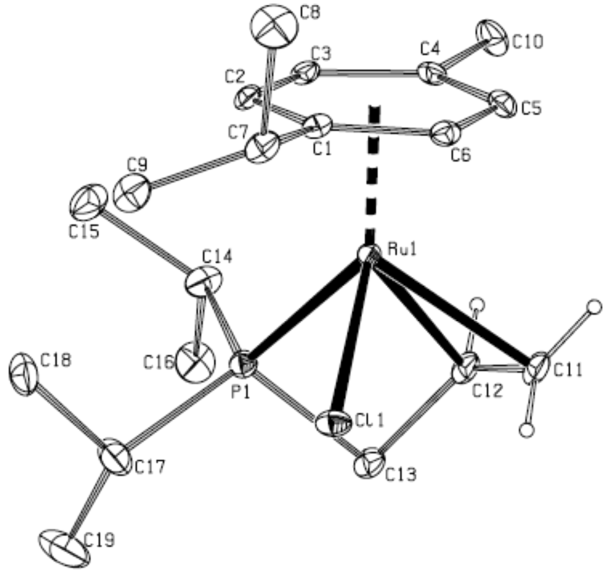
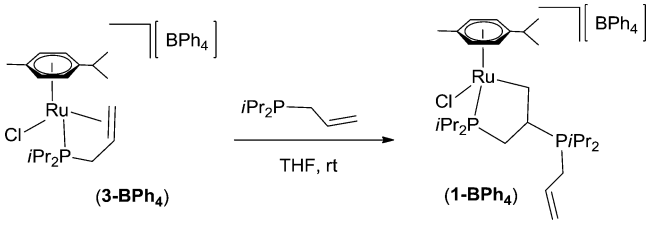


Figure 2. Molecular structure and atom-labeling scheme for the cationic complex $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}]^+$ (3^+). Hydrogen atoms, except those of the coordinated olefin, have been omitted for clarity. Non-hydrogen atoms are represented by their 10% probability ellipsoids. C* = centroid of the η^6-*p*-cymene ligand. Selected bond lengths (Å): Ru(1)−Cl(1) = 2.395(1), Ru(1)−P(1) = 2.337(1), Ru(1)−C(11) = 2.261(4), Ru(1)−C(12) = 2.298(4), Ru(1)−C* = 1.747(1), C(11)−C(12) = 1.363(7). Selected bond angles (deg): C*−Ru(1)−P(1) = 132.95(4), C*−Ru(1)−Cl(1) = 124.30(3), C*−Ru(1)−C(11) = 123.78(15), C*−Ru(1)−C(12) = 133.79(13), P(1)−Ru(1)−Cl(1) = 85.11(5), C(11)−C(12)−C(13) = 123.9(5).

Scheme 3. Synthesis of $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(iPr_2PCH_2CH{=}CH_2)CH_2\}][BPh_4]$ (1-BPh$_4$)



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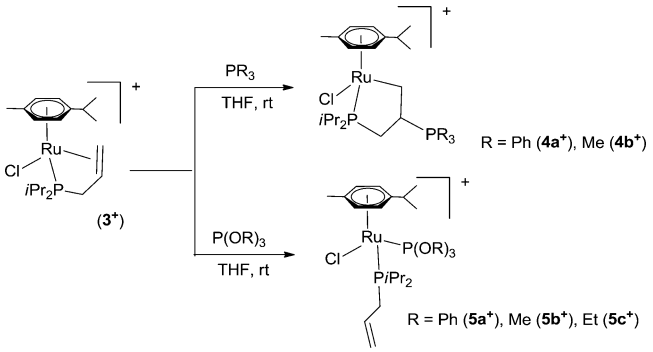
$(OR)_3\}]^+$ (R = Ph (**5a**$^+$), Me (**5b**$^+$), Et (**5c**$^+$)) were isolated as the result of an olefin−nucleophile exchange, showing the competition between the nuclephilic addition to the allylphosphane ligand and the substitution reaction on the ruthenium center (Scheme 4).

Scheme 4. Synthesis of the Complexes $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^2(P,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}(PR_3)\text{CH}_2\}]^+$ (R = Ph (4a**$^+$), Me (**4b**$^+$)) and $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}i\text{Pr}_2\text{PCH}_2\text{CHCH}_2\}\{P(OPh)_3\}]^+$ (R = Ph (**5a**$^+$), Me (**5b**$^+$), Et (**5c**$^+$))**

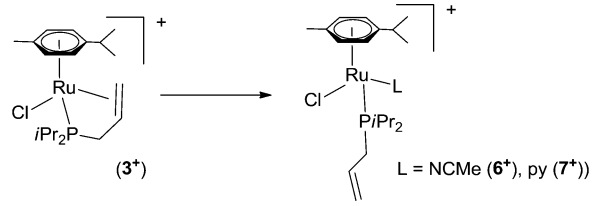


The complexes **4a**,**b**$^+$ and **5a**−**c**$^+$ were isolated as their tetraphenylborate salts in good yields as yellow stable solids which have been fully characterized by analytical and spectroscopic methods. In particular, $^{31}P\{^1H\}$ NMR spectra are indicative of the coordination mode of the allylphosphane. Thus, for complexes **4a**,**b**$^+$ two doublets appear for the phosphorus atoms bonded to ruthenium and carbon atoms, respectively, at δ 80.2 and 24.6 ppm ($^3J_{PP}$ = 65.6 Hz) for complex **4a**$^+$ and δ 86.8 and 28.7 ppm ($^3J_{PP}$ = 70.5 Hz) for complex **4b**$^+$. For complexes **5a**−**c**$^+$ the two doublets ($^2J_{PP}$ = 71.7 −75.3 Hz) appear at δ 45.9 (**5a**$^+$), 44.3 (**5b**$^+$), and 43.4 (**5c**$^+$) for the $\kappa^1(P)$-allylphosphane and 112.3 (**5a**$^+$), 117.4 (**5b**$^+$) and 112.1 (**5c**$^+$) for the $P(OR)_3$ ligand (see the Experimental Section). For all compounds, molar conductivity values in acetone are in the range expected for 1/1 electrolytes[20] and the analyses and electrospray mass spectra agree with the proposed stoichiometries.

Reaction of $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}]^+$ (3$^+$) with N-Donor Nucleophiles: Synthesis of $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(L)]^+$ (L = NCMe (6$^+$), py (7$^+$)). When the complex $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}]^+$ (**3**$^+$) was dissolved in acetonitrile, the complex $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(NCMe)]^+$ (**6**$^+$) was immediately formed. In the same way, the reaction of **3**$^+$ in THF with 1 equiv of pyridine led to the complex $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(py)]^+$ (**7**$^+$) (Scheme 5). The synthesis of these complexes agrees with the hemilabile character of the ADIP ligand in complex **3**$^+$.

Synthesis of $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(PPh_3)][BPh_4]$ (8-BPh$_4$) and Reaction of 8$^+$ with P- and N-Donor Nucleophiles To Give $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}\{P(OPh)_3\}][BPh_4]$ (9-BPh$_4$). We have previously described the indenyl complexes $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}Ph_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(PPh_3)]^+$ bearing the allyldiphenylphosphane ligand (ADPP) and their reactivity toward anionic nucleophiles (H^-, Me^-, $n\text{Bu}^-$), giving rise to ruthenaphosphacyclopentane complexes through regioselective

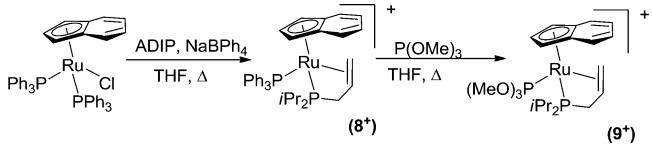
Scheme 5. Synthesis of the Complexes $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^1(P)\text{-}i\text{Pr}_2\text{PCH}_2\text{CHCH}_2\}(L)]$ (L = NCMe (6$^+$), py (7$^+$))



additions at the internal C_β atom of the coordinated allylic group.[5b] For comparative purposes, the synthesis of the indenyl complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(PPh_3)]^+$ (**8**$^+$) was achieved.

Reaction of the complex $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with ADIP in refluxing THF in the presence of $NaBPh_4$ led to the synthesis of the complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(PPh_3)]^+$ (**8**$^+$) (Scheme 6), which was

Scheme 6. Synthesis of the Complexes $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CHCH}_2\}(PPh_3)]^+$ (8$^+$) and $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}i\text{Pr}_2\text{PCH}_2\text{CHCH}_2\}\{P(OMe)_3\}]^+$ (9$^+$)



isolated as its tetraphenylborate salt in 85% yield. Attempts to obtain the complex $[RuCl(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}i\text{Pr}_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(PPh_3)]$ analogous to that reported with ADPP were unsuccessful.[5b]

Spectroscopic data agree with the proposed structure (see the Experimental Section). In particular, the $^{31}P\{^1H\}$ NMR spectrum at room temperature showed the expected doublets at δ 51.7 (PPh_3) and −51.6 ($\kappa^3(P,C,C)$-ADIP) ($^2J_{PP}$ = 32.3 Hz).

As reported for complex **3**$^+$, the formation of complex **8**$^+$ is an highly diastereoselective process, since NMR data agree with the formation of only one isomer.

The structure of complex **8**$^+$ was determined by single-crystal X-ray diffraction analysis. Suitable crystals were obtained by slow diffusion of diethyl ether into a solution of compound **8-BPh$_4$** in CH_2Cl_2. An ORTEP representation is shown in Figure 3, 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 interligand angles P(1)−Ru(1)−P(2) and those between the five-membered-ring centroid C* and the legs show values typical of a pseudooctahedron (see the caption to Figure 3). The Ru−C(1) and Ru−C(2) bond distances reflect the coordination of the olefin to the metal center and the C(1)−C(2) bond distance, 1.388(3) Å, is similar to those in complex **3**$^+$ (1.363(7) Å) and the complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}Ph_2\text{PCH}_2\text{CH}{=}\text{CH}_2\}(PPh_3)][PF_6]$ (1.391(8) Å).[5b] It is also interesting to note that the benzo ring of the indenyl ligand is oriented over the olefin ligand, slightly displaced toward the PPh_3 ligand. Figure 3 shows the complex with relative configuration R_{Ru} and olefin coordination through the *si* enantioface. However, both enantiomers are present in equal

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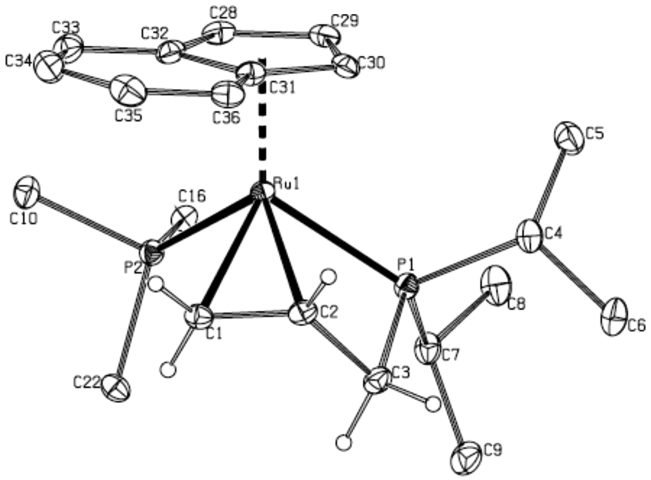


Figure 3. Molecular structure and atom-labeling scheme for the cationic complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}(PPh_3)]^+$ ($\mathbf{8}^+$). Phenyl rings, except C_{ipso}, and hydrogen atoms, except those of the coordinated olefin, have been omitted for clarity. Non-hydrogen atoms are represented by their 20% probability ellipsoids. C* = centroid of the η^5-indenyl ligand. Selected bond lengths (Å): Ru(1)−P(1) = 2.3295(7), Ru(1)−P(2) = 2.3396(9), Ru(1)−C(1) = 2.213(2), Ru(1)−C(2) = 2.222(2), Ru(1)-C* = 1.9155(6), C(1)−C(2) = 1.388(3). Selected bond angles (deg): C*−Ru(1)−P(1) = 125.33(2), C*−Ru(1)−P(2) = 120.67(2), C*−Ru(1)−C(1) = 123.86(7), C*−Ru(1)−C(2) = 120.42(7), P(1)−Ru(1)−P(2) = 98.89(3), C(1)−C(2)−C(3) = 121.8(2).

proportion in the crystal, which belongs to a centrosymmetric space group.

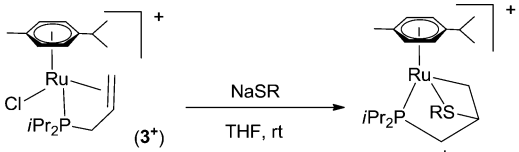
Reaction of complex $\mathbf{8}^+$ with neutral P-donor nucleophiles was tested. Thus, the reaction of $\mathbf{8}^+$ with $P(OMe)_3$ led to the PPh_3 substitution product $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}\{P(OMe)_3\}]^+$ ($\mathbf{9}^+$), which has been fully characterized (see the Experimental Section). No reaction was observed when PPh_3 was used.

The differences in reactivity between complexes $\mathbf{3}^+$ and $\mathbf{8}^+$ are also stated in the reactivity toward N-donor ligands. Thus, while complex $\mathbf{3}^+$ reacted with pyridine, leading to complex $\mathbf{7}^+$, complex $\mathbf{8}^+$ did not react with pyridine under the same reaction conditions. On the other hand, the complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}iPr_2PCH_2CHCH_2\}(PPh_3)(NCMe)]^+$ ($\mathbf{10}^+$) was inmediately formed when complex $\mathbf{8}^+$ was dissolved in NCMe. However, all attempts to isolate the salt **10-BPh$_4$** failed and complex **8-BPh$_4$** was recovered unchanged. Complex $\mathbf{10}^+$ has been spectroscopically characterized in NCMe-d_3 solution (see the Experimental Section).

The differences observed in the behaviors of the two metal fragments can be explained by electronic effect, since the arene−chloride−ruthenium fragment is electronically poorer than the indenyl−phosphane−ruthenium fragment, thus making the olefin more susceptible to nucleophilic attack.

Reaction of $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}]^+$ ($\mathbf{3}^+$) with Anionic S-Donor Nucleophiles: Synthesis of $[Ru\{\kappa^3(P,C,S)\text{-}iPr_2PCH_2CH(SR)CH_2\}(\eta^6\text{-}C_{10}H_{14})]^+$ (R = Me ($\mathbf{11a}^+$), *i*Pr ($\mathbf{11b}^+$), *t*Bu ($\mathbf{11c}^+$)) and $[Ru\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(SPhCH_3)CH_2\}(\eta^6\text{-}C_{10}H_{14})]$ (12). In order to determine the behavior of complex $\mathbf{3}^+$ with different donors, the reaction with the sulfur-donor salts NaSR were achieved. From this reaction, unexpected cationic complexes containing unprecedented tridentate $\kappa^3(P,C,S)$ ligands: $[Ru\{\kappa^3(P,C,S)\text{-}iPr_2PCH_2CH(SR)CH_2\}(\eta^6\text{-}C_{10}H_{14})]^+$ ($\mathbf{11a-c}^+$) were isolated as their BPh_4 salts (Scheme 7).

Scheme 7. Synthesis of the Complexes $[Ru\{\kappa^3(P,C,S)\text{-}iPr_2PCH_2CH(SR)CH_2\}(\eta^6\text{-}C_{10}H_{14})]^+$ (R = Me ($\mathbf{11a}^+$), *i*Pr ($\mathbf{11b}^+$), *t*Bu ($\mathbf{11c}^+$))



Complexes $\mathbf{11a-c}^+$ were spectroscopically characterized.[21] The most significant spectroscopic features are as follows. (i) The $^{31}P\{^1H\}$ NMR spectra exhibit a singlet at δ 75.7 ($\mathbf{11a}^+$), 76.0 ($\mathbf{11b}^+$), and 74.6 ($\mathbf{11c}^+$) ppm. (ii) For all complexes, the RSCH proton appears in the ^1H NMR spectra as a broad doublet centered at 4.89 ppm ($^3J_{HP}$ = 41.7 Hz) for $\mathbf{11a}^+$, 4.81 ppm ($^3J_{HP}$ = 43.2 Hz) for **11b**, and 4.84 ppm ($^3J_{HP}$ = 46.8 Hz) for $\mathbf{11c}^+$. These unusually large coupling constants[22] can be explained, since three routes are available for coupling between this proton and phosphorus atom in compounds $\mathbf{11a-c}^+$. An $^1H\{^{31}P\}$ NMR experiment allowed us to confirm this statement for complex $\mathbf{11a}^+$, since the two peaks of the doublet at 4.83 and 4.93 ppm collapse into one broad singlet at 4.89 ppm for that hydrogen. (iii) All other signals in the ^1H NMR spectra agree with the proposed structures (see the Experimental Section). (iv) $^{13}C\{^1H\}$ NMR spectra show the CH_2 bonded to ruthenium as a doublet at 3.0 ppm ($^3J_{CP}$ = 7.9 Hz) for **11a**, 5.2 ppm ($^3J_{CP}$ = 9.6 Hz) for $\mathbf{11b}^+$, and 5.7 ppm ($^3J_{CP}$ = 11.6 Hz) for $\mathbf{11c}^+$.

The structure of complex $\mathbf{11a}^+$ was determined by single-crystal X-ray diffraction analysis. For this complex, the asymmetric unit consists of two rotamers which present absolute configuration *S* for the ruthenium and *R* for the stereogenic carbon. However, for each rotamer both enantiomers ($S_{Ru}R_C$ and $R_{Ru}S_C$) are present in the crystal in equal proportion, as the crystal belongs to the centric space group $P\bar{1}$. Figure 4 shows an ORTEP type representation of the two rotamers of the complex, and selected bond lengths and angles for one of the two rotamers are presented in the caption.

As shown in Figure 4, both molecules are rotamers, the major difference being the orientation of the *i*Pr group of the *p*-cymene ring with respect to the ruthenabicycle ligand.

The Ru(1)−C(11) and Ru(2)−C(31) bond distances (2.147(4) and 2.162(4) Å, respectively) as well as the Ru(1)−S(1) and Ru(2)−S(2) distances (2.3701(11) and 2.3807(12) Å, respectively) agree with Ru−C and Ru−S single bonds. Also, the bond distances C(12)−S(1) (1.845(4) Å) and C(32)−S(2) (1.851(5) Å) are typical of a sulfur−carbon single bond (1.808(4) Å for C(14)−S(1) and 1.818(5) Å for C(34)−S(2)).

The formation of complexes $\mathbf{11a-c}^+$ can be formally explained through nucleophilic attack of the thiolate anion at both the olefin of the ADIP ligand and the ruthenium atom.

However, when this reaction was carried out using $NaSC_6H_4Me$ as a nucleophile, the neutral complex $[RuCl\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(SC_6H_4Me)CH_2\}(\eta^6\text{-}C_{10}H_{14})]$ (**12**) was obtained (Scheme 8).

Complex **12** has been spectroscopically[21] characterized. Thus, the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ 70.2

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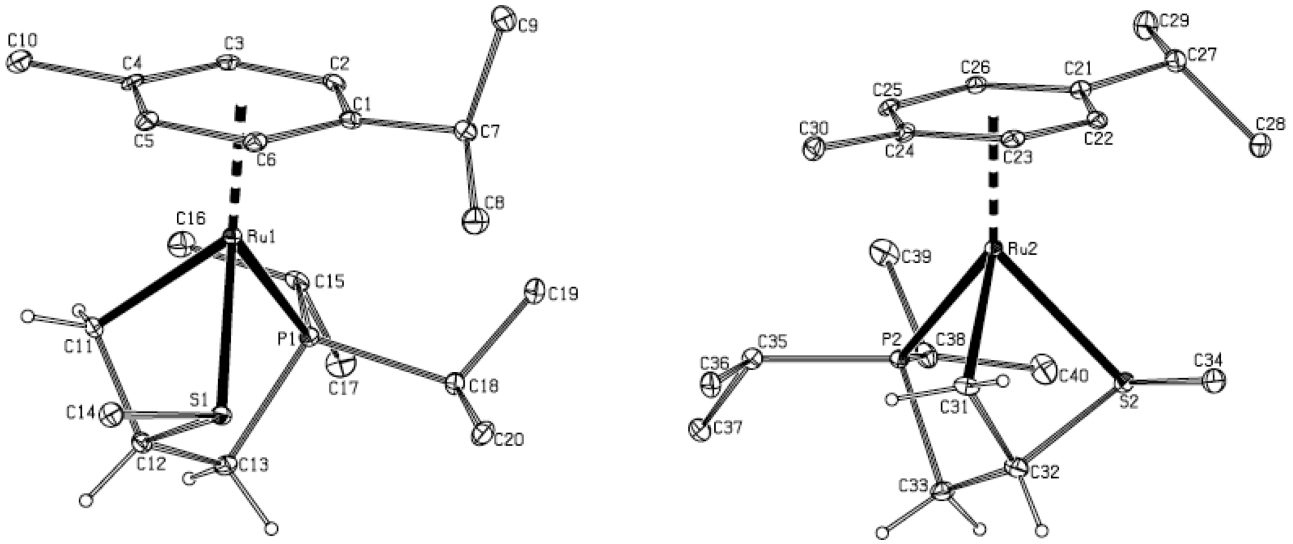
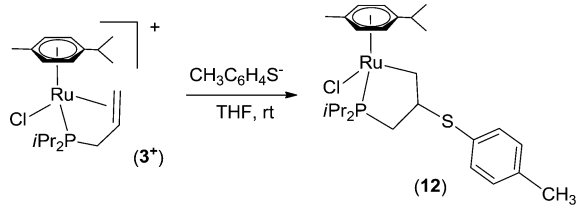


Figure 4. Molecular structure and atom-labeling scheme for the cation of the two rotamers found in the asymmetric unit for the compound $[Ru\{\kappa^3(P,C,S)\text{-}iPr_2PCH_2CH(SCH_3)CH_2\}(\eta^6\text{-}C_{10}H_{14})][BPh_4]$ (**11a-BPh$_4$**). Hydrogen atoms of arene and isopropyl groups (except for the ruthenaphosphacycle) have been omitted for clarity. Non-hydrogen atoms are represented by their 10% probability ellipsoids. C* = centroid of the η^6-*p*-cymene ligand. Selected bond lengths (Å): Ru(1)−S(1) = 2.3701(11), Ru(1)−P(1) = 2.3260(11), Ru(1)−C(11) = 2.147(4), Ru(1)−C* = 1.7363(6), S(1)−C(12) = 1.845(4), S(1)−C(14) = 1.808(4). Selected bond angles (deg): C*−Ru(1)−P(1) = 136.34(3), C*−Ru(1)−S(1) = 136.03(3), C*−Ru(1)−C(11) = 130.75(11), P(1)−Ru(1)−S(1) = 81.34(4), Ru(1)−S(1)−C(12) = 81.68(13), Ru(1)−S(1)−C(14) = 108.12(15), C(12)−S(1)−C(14) = 100.5(2), C(11)−C(12)−C(13) = 109.5(3).

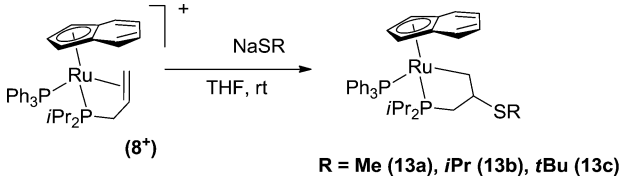
Scheme 8. Synthesis of the Complex $[RuCl\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(SC_6H_4Me)CH_2\}(\eta^6\text{-}C_{10}H_{14})]$ (12)



ppm and the ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra agree with the proposed structure (see the Experimental Section). In this complex the electron pair of the sulfur can be delocalized into the aromatic ring, which makes the sulfur a poorer nucleophile. In addition, probably the steric hindrance of the *p*-tolyl group prevents sulfur coordination to the metal.

Reaction of $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}(PPh_3)]^+$ (8$^+$) with Anionic S-Donor Nucleophiles: Synthesis of $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(SR)CH_2\}(PPh_3)]$ (R = Me (13a), *i*Pr (13b), *t*Bu (13c)). The complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}(PPh_3)]^+$ (8$^+$) reacts with S-donor anionic nucleophiles to yield the $\kappa^2(P,C)$ complexes $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(SR)CH_2\}(PPh_3)]$ (R = Me (**13a**), *i*Pr (**13b**), *t*Bu (**13c**)) (Scheme 9).

Scheme 9. Synthesis of the Complexes $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^2(P,C)\text{-}iPr_2PCH_2CH(SR)CH_2\}(PPh_3)]$ (R = Me (13a), *i*Pr (13b), *t*Bu (13c))



Complexes **13a−c** were spectroscopically characterized.[21] In particular, the $^{31}P\{^1H\}$ NMR spectra exhibit doublet signals in the range 75.2−77.3 ppm for the ADIP phosphane and 60.1−60.8 ppm for the PPh_3 ligand. All other signals in the ^{1}H NMR and $^{13}C\{^1H\}$ spectra agree with the proposed structures (see the Experimental Section).

All attempts to promote the intramolecular nucleophilic attack of the sulfur atom at the ruthenium center leading to complexes analogous to complexes **11a−c**$^+$ failed. Thus, heating THF solutions of complexes **13a−c** gives the precursor complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}(PPh_3)]^+$.

SUMMARY

In summary, nucleophilic attack at the coordinated ADIP ligand in the complex $[RuCl(\eta^6\text{-}C_{10}H_{14})\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}]$ (3$^+$) allows the synthesis of complexes with bidentate $\kappa^2(P,C)$ or unprecedented tridentate $\kappa^3(P,C,S)$ ligands. This nucleophilic addition to the $\kappa^3(P,C,C)$-alkenylphosphane ligand is competitive with the coordination of the nucleophile to the ruthenium and substitution of the coordinated π-olefin group as occurs for the $P(OR)_3$ ligands. The indenyl complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}iPr_2PCH_2CH{=}CH_2\}(PPh_3)]^+$ (8$^+$) has been synthesized for comparative purposes, showing great differences in its reactivity pattern toward nucleophiles.

EXPERIMENTAL SECTION

General Procedures. All manipulations were perfomed 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 complexes $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$[8] and $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[9] and the phosphane $^iPr_2P(C_3H_5)$[10] were prepared by previously reported procedures. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with Perkin-Elmer 240-B and LECO CHNS-TruSpec microanalyzers. Mass

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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 a Bruker AV400 spectrometer operating at 400.1 (^{1}H), 100.6 (^{13}C), and 162.1 MHz (^{31}P), an AV300 spectrometer operating at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 MHz (^{31}P), and an AV600 spectrometer operating at 600.1 (^{1}H) and 150.9 MHz (^{13}C). DEPT and bidimensional COSY HH, HSQC, and HMBC experiments were carried out for all of the compounds. Chemical shifts are reported in parts per million and referenced to TMS or 85% H_3PO_4 as standard. Coupling constants J are given in hertz. Abbreviations used: s, singlet; d, doublet; dd, double doublet; t, triplet; sept, septuplet; c, cuatriplet; m, multiplet; bd, broad doublet; br, broad.

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(*i*Pr$_2$PCH$_2$CH=CH$_2$)CH$_2$}][Cl] (1-Cl). To a solution of the complex [RuCl(μ-Cl)(η^6-$C_{10}H_{14}$)]$_2$ (0.1 g, 0.16 mmol) in methanol (10 mL) was added 5 equiv of diisopropylallylphosphane (122 μL, 0.8 mmol). The resulting suspension was stirred for 5 min at −20 °C. The solution was then evaporated and the yellow residue was washed with diethyl ether (3 × 20 mL) and dried under reduced pressure. Yield: 80%. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ 86.6 (d, $^3J_{PP}$ = 63.2 Hz, Ru−P^{i}Pr$_2$), 36.5 (d, $^3J_{PP}$ = 63.2 Hz, CH-P^{i}Pr$_2$). ^{1}H NMR (400.1 MHz, $CDCl_3$, −20 °C): δ 1.32 - 1.52 (m, 30H, CH*Me*$_2$, *Me*$_2$CH-P), 1.61 (m, 1H, Ru-PC*H*$_2$), 2.13 (s, 3H, Me), 2.24 (m, 1H, Ru-C*H*$_2$), 2.34 (m, 3H, Ru-PC*H*$_2$, C*H*P, Me$_2$C*H*-P), 2.62 (m, 1H, Me$_2$C*H*-P), 2.73 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C−C*H*Me$_2$), 2.96 (m, 2H, Me$_2$C*H*-P), 3.18 (m, 1H, Ru-C*H*$_2$), 3.50 (m, 2H, PC*H*$_2$CH=), 4.86, 4.97 (2d, $^3J_{HH}$ = 6.0 Hz, 2 × 1H, *p*-cym), 5.38 (d, $^3J_{HH}$ = 9.6 Hz, 1H, =CH$_2$), 5.61 (d, $^3J_{HH}$ = 17.4 Hz, 1H, =CH$_2$), 5.65, 5.70 (2d, $^3J_{HH}$ = 6.0 Hz, 2 × 1H, *p*-cym), 5.81 (m, 1H, C*H*=). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, −20 °C): δ 17.5−18.0 (m, *Me*$_2$CH-P), 18.2 (s, br, Ru-*C*H$_2$), 18.6 (s, Me), 19.2, 19.5, 20.1, 20.6 (4*s*, *Me*$_2$CH-P), 21.2, 21.5 (2d, $^1J_{CP}$ = 40.0 Hz, Me$_2$CH-P), 22.7, 22.8 (2s, CH*Me*$_2$), 22.9 (d, $^1J_{CP}$ = 41.7 Hz, PCH$_2$CH=), 25.6 (d, $^1J_{CP}$ = 24.2 Hz, Me$_2$CH-P), 28.5 (d, $^1J_{CP}$ = 20.0 Hz, Me$_2$CH-P), 29.3 (d, $^1J_{CP}$ = 24.7 Hz, Ru-PCH$_2$), 30.7 (s, *C*HMe$_2$), 34.1 (dd, $^1J_{CP}$ = 26.1 Hz, $^2J_{CP}$ = 19.6 Hz, CHP), 83.7, 84.3, 87.2, 91.3, 95.8, 111.3 (6s, *p*-cym), 124.4 (d, $^3J_{CP}$ = 10.4 Hz, =CH$_2$), 125.3 (d, $^2J_{CP}$ = 9.1 Hz, =CH). Conductivity (acetone, 20 °C): Λ = 103 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(C=C) 1635 (w). MS-ESI (*m*/*z*): 587 ([M]$^+$, 100%), 429 ([M − ADIP]$^+$, 81%). Anal. Calcd for $C_{28}H_{52}Cl_2P_2Ru$: C, 54.01; H, 8.42. Found: C, 53.93; H, 8.31.

Synthesis of [RuCl$_2$(η^6-$C_{10}H_{14}$){κ^1(*P*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}] (2). To a solution of the complex [RuCl(μ-Cl)(η^6-$C_{10}H_{14}$)]$_2$ (0.5 g, 0.81 mmol) in dichloromethane (15 mL) was added 2 equiv of diisopropylallylphosphane (255 μL, 16.2 mmol). The resulting dark red mixture was stirred at room temperature for 10 min. The solution was then evaporated, and the orange residue was washed with diethyl ether (3 × 10 mL) and dried under reduced pressure. Yield: 93%. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ 33.6 (s). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ 1.27 (dd, $^3J_{HP}$ = 12.9 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, *Me*$_2$CH-P), 1.30 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH*Me*$_2$), 1.33 (dd, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, *Me*$_2$CH-P), 2.10 (s, 3H, Me), 2.58 (m, 2H, Me$_2$C*H*-P), 2.82 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*Me$_2$), 3.37 (dd, $^2J_{HP}$ = $^3J_{HH}$ = 9.0 Hz, 2H, PC*H*$_2$), 5.04 (d, $^3J_{HH}$ = 10.2 Hz, 1H, =CH$_2$), 5.08 (d, $^3J_{HH}$ = 17.4 Hz, 1H, =CH$_2$), 5.62 (s, br, 4H, *p*-cym), 5.83 (m, 1H, =CH). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 20 °C): δ 18.1 (s, Me), 18.7, 19.3 (2s, *Me*$_2$CH-P), 22.4 (s, CH*Me*$_2$), 24.0 (d, $^1J_{CP}$ = 22.3 Hz, PCH$_2$), 27.8 (d, $^1J_{CP}$ = 22.5 Hz, Me$_2$CHP), 30.7 (s, *C*HMe$_2$), 83.0 (d, $^2J_{CP}$ = 4.8 Hz, 2C, *p*-cym), 88.5 (d, $^2J_{CP}$ = 2.7 Hz, 2C, *p*-cym), 94.1, 108.3 (2s, *p*-cym), 118.6 (d, $^3J_{CP}$ = 8.0 Hz, =CH$_2$), 132.5 (d, $^2J_{CP}$ = 11.6 Hz, =CH). IR (KBr, cm^{-1}): ν(C=C) 1630 (m). Anal. Calcd for $C_{19}H_{33}Cl_2PRu$: C, 49.14; H, 7.16. Found: C, 49.03; H, 7.15.

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P*,*C*,*C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}][BPh$_4$] (3-BPh$_4$). A suspension of the complex [RuCl$_2$(η^6-$C_{10}H_{14}$){κ^1(*P*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}] (**2**; 0.464 g, 1 mmol) was stirred with 3 equiv of NaBPh$_4$ (3 mmol, 1.03 g) in MeOH (20 mL) at room temperature for 2.5 h. Solvents were then decanted, the solid residue was extracted with dichloromethane, and the resultant solution was filtered through Kieselguhr and collected in hexane. Solvents were evaporated, and the yellow solid was washed with diethyl ether and dried under reduced pressure. Yield: 83%. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ −48.5 (s). ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ 1.13 − 1.30 (m, 12H, *Me*$_2$CH-P), 1.31−1.43 (m, 6H, CH*Me*$_2$), 1.54 (s, 3H, Me), 2.23 (m, 1H, PC*H*$_2$), 2.40 (m, 3H, Me$_2$C*H*-P, C*H*Me$_2$), 3.10 (m, 1H, PC*H*$_2$), 3.58 (m, 1H, =C*H*), 3.95 (d, $^3J_{HH}$ = 13.6 Hz, 1H, =CH$_2$), 4.34 (dd, $^2J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 8.0, 1H, =CH$_2$), 5.12, 5.40, 5.49, 5.68 (4*d*, $^3J_{HH}$ = 6.0 Hz, 4 × 1H, *p*-cym), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 7.05 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.42 (s, br, 8H, BPh$_4$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 20 °C): δ 17.6 (s, Me), 18.3, 18.7, 19.1, 19.5 (4s, *Me*$_2$CH-P), 21.6−22.3 (m, CH*Me*$_2$, Me$_2$CH−P), 25.5 (d, $^1J_{CP}$ = 31.4 Hz, PCH$_2$), 28.0 (d, $^1J_{CP}$ = 22.1 Hz, Me$_2$CH−P), 30.8 (s, CHMe$_2$), 65.5 (d, $^2J_{CP}$ = 18.9 Hz, =CH), 72.0 (s, =CH$_2$), 89.6, 90.9, 92.2, 95.3, 101.7, 115.3 (6*s*, *p*-cym), 122.0, 125.7, 136.3 (3*s*, BPh$_4$), 164.6 (c, $J_{C^{11}B}$ = 48.3 Hz, BPh$_4$). Conductivity (acetone, 20 °C): Λ = 134 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(C=C) 1477 (m), ν(BPh$_4$) 737, 707 (s). Anal. Calcd for $C_{49}H_{49}BClPRu$: C, 69.03; H, 7.14. Found: C, 69.15; H, 7.27.

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(*i*Pr$_2$PCH$_2$CH=CH$_2$)CH$_2$}][BPh$_4$] (1-BPh$_4$). To a solution of [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P*,*C*,*C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}][BPh$_4$] (**3-BPh$_4$**; 0.0374 g, 0.05 mmol) in THF (8 mL) was added ADIP (0.05 mmol, 8 μL), and the mixture was stirred at room temperature for 2 min. The solution was then concentrated under vacuum to a volume of approximately 1 mL. Addition of hexane (20 mL) afforded a yellow precipitate. Solvents were decanted, and the solid was washed with hexane (2 × 10 mL) and dried under reduced pressure. Spectroscopic data for complex **1-BPh$_4$** are the same as for complex **1-Cl** except for those signals due to the BPh$_4$ anion. Yield: 63%. IR (KBr, cm^{-1}): ν(C=C) 1580 (w), ν(BPh$_4$) 733, 705 (s). MS-ESI (*m*/*z*): 587 ([M]$^+$, 100%), 429 ([M − ADIP]$^+$, 15%). Anal. Calcd for $C_{52}H_{72}BClP_2Ru$: C, 68.90; H, 8.01. Found: C, 69.01; H, 8.02.

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(PR$_3$)CH$_2$}][BPh$_4$] (R = Ph (4a-BPh$_4$), Me (4b-BPh$_4$)). To a solution of [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P*,*C*,*C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}][BPh$_4$] (**3-BPh$_4$**; 0.0374 g, 0.05 mmol) in THF (8 mL) was added 1 equiv of the corresponding phosphane (0.05 mmol; 0.0131 mg for PPh$_3$ and 4.5 μL for PMe$_3$), and the mixture was stirred for 2 min at room temperature. The solution was then concentrated under vacuum to a volume of approximately 1 mL. Addition of diethyl ether (20 mL) afforded a yellow precipitate. Solvents were decanted, and the solid was washed with diethyl ether (2 × 10 mL) and dried under reduced pressure. R = Ph (**4a-BPh$_4$**): yield 57%; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C) δ 80.2 (d, $^3J_{PP}$ = 65.6 Hz, Ru-P*i*Pr$_2$), 24.6 (d, $^3J_{PP}$ = 65.6 Hz, PPh$_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C) δ 0.81 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 14.7 Hz, 3H, *Me*$_2$CH-P), 0.85 (m, 1H, Ru-PCH$_2$), 1.06 (m, 6H, *Me*$_2$CH-P, CH*Me*$_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH*Me*$_2$), 1.32 (m, 3H, *Me*$_2$CH-P), 1.46 (m, 1H, Ru-CH$_2$), 1.49 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 16.5 Hz, 3H *Me*$_2$CH-P), 1.89 (s, 3H, Me), 2.05 (m, 2H, Ru-PC*H*$_2$, Me$_2$C*H*-P), 2.48 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*Me$_2$), 2.57 (m, 1H, Me$_2$C*H*-P), 2.90 (m, 1H, Ru-C*H*$_2$), 4.16 (m, C*H*P), 4.76 (m, 2H, *p*-cym), 5.46, 5.61 (2d, $^3J_{HH}$ = 5.7 Hz, 2 × 1H, *p*-cym), 6.86 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 7.00 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.41 (m, 8H, BPh$_4$), 7.50−7.70 (PPh$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 20 °C) δ 15.9 (m, Ru-CH$_2$), 17.9 (s, Me), 18.0, 18.8, 19.1, 20.3 (4*s*, *Me*$_2$CH-P), 22.4, 22.7 (2s, CH*Me*$_2$), 25.1 (d, $^1J_{CP}$ = 20.7 Hz, Me$_2$CH−P), 26.5 (d, $^1J_{CP}$ = 25.7 Hz, Ru-PCH$_2$), 28.6 (d, $^1J_{CP}$ = 23.0 Hz, Me$_2$CH-P), 30.5 (s, CHMe$_2$), 31.9 (dd, $^1J_{CP}$ = 32.1 Hz, $^2J_{CP}$ = 16.0 Hz, CHP), 83.5, 86.3, 87.3, 89.2, 98.3, 110.1 (6*s*, *p*-cym), 118.6 (d, $^1J_{CP}$ = 81.0 Hz, PPh$_3$), 121.6, 125.4 (2s, BPh$_4$), 130.5 (d, $^2J_{CP}$ = 11.7 Hz, PPh$_3$), 133.2 (d, $^3J_{CP}$ = 8.7 Hz, PPh$_3$), 135.0 (s, PPh$_3$), 136.4 (s, BPh$_4$), 164.3 (c, $J_{C^{11}B}$ = 49.5 Hz, BPh$_4$); conductivity (acetone, 20 °C) Λ = 141 S cm^2 mol^{-1}; IR (KBr, cm^{-1}) ν(BPh$_4$) 731, 704 (s); MS-ESI (*m*/*z*) 691 ([M]$^+$, 100%), 429 ([M − PPh$_3$]$^+$, 18%). Anal. Calcd for $C_{61}H_{68}BClP_2Ru$: C, 72.51; H, 6.78. Found: C, 72.55; H, 6.47. R = Me (**4b-BPh$_4$**): yield 68%; ^{31}P{^{1}H} NMR (121.5 MHz, $(CD_3)_2CO$, 20 °C) δ 86.8 (δ, $^3J_{PP}$ = 70.5 Hz, Ru-P*i*Pr$_2$), 28.7 (δ, $^3J_{PP}$ = 70.5 Hz, CH-PMe$_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C) δ 0.86 (d, $^2J_{HP}$ = 13.2 Hz, 9H, PMe$_3$), 1.20−1.50 (m, 20H, *Me*$_2$CH-P, C-CH*Me*$_2$, Ru-PC*H*$_2$, Ru-CH$_2$C*H*), 1.61 (m, 1H, Ru-PC*H*$_2$), 1.89 (m, 1H, Ru-CH$_2$), 2.04 (s,

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3H, C-*Me*), 2.15 (m, 1H, Me_2CH-P), 2.65 (m, 3H, Ru-CH_2, Me_2CH-P, C-$CHMe_2$), 4.83, 5.72 (2d, $^3J_{HH}$ = 5.2 Hz, 2 × 1H, *p*-cym), 4.97, 5.62 (2d, $^3J_{HH}$ = 6.0 Hz, 2 × 1H, *p*-cym), 6.89 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh_4), 7.06 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh_4) 7.50 (bs, 8H, BPh_4); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C) δ 6.2 (d, $^1J_{CP}$ = 52.5 Hz, PMe_3), 15.3 (m, Ru-CH_2), 18.0 (s, C-*Me*), 18.9, 19.2, 19.8, 20.4 (4s, Me_2CH-P) 22.5, 22.8 (2s, C-$CHMe_2$), 25.5 (d, $^1J_{CP}$ = 26.2 Hz, Me_2CH-P), 27.8 (d, $^1J_{CP}$ = 24.4 Hz, Ru-PCH_2), 28.5 (d, $^1J_{CP}$ = 20.6 Hz, Me_2CH-P), 30.8 (s, C-$CHMe_2$), 35.9 (dd, $^1J_{HP}$ = 37.5 Hz, $^2J_{HP}$ = 18.7 Hz, $CHPMe_3$), 84.3, 84.5, 87.5, 91.7, 95.0, 110.9 (6s, *p*-cym), 121.8, 125.8, 136.3, (3s, BPh_4), 164.3 (c, $J_{C^{11}B}$ = 49.3 Hz, BPh_4); conductivity (acetone, 20 °C) Λ = 142 S cm^2 mol^{-1}; IR (KBr, cm^{-1}) $\nu(BPh_4)$ 731, 703 (s); MS-ESI (*m*/*z*) 505 ($[M]^+$, 100%), 429 ($[M - PMe_3]^+$, 24%). Anal. Calcd for $C_{46}H_{62}BClP_2Ru$: C, 67.03; H, 7.58. Found: C, 67.28; H, 7.21.

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^1(*P*)-*i*$Pr_2PCH_2CH{=}CH_2$}{P(OR)$_3$}][BPh_4] (R = Ph (5a-BPh_4), Me (5b-BPh_4), Et (5c-BPh_4)). To a solution of [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P,C,C*)-*i*$Pr_2PCH_2CH{=}CH_2$}][BPh_4] (**3-BPh_4**; 0.0374 mg, 0.05 mmol) in THF (8 mL) was added 1 equiv of P(OR)$_3$ (0.05 mmol; 13.1 μL for R = Ph, 5.9 μL for R = Me, and 8.6 μL for R = Et), and the mixture was stirred at room temperature for 2 min. The solution was then concentrated under vacuum to a volume of approximately 1 mL. Addition of hexane (20 mL) afforded a yellow precipitate. Solvents were decanted, and the solid was washed with hexane (2 × 10 mL) and dried under reduced pressure. The complex can be recrystallized from dichloromethane/diethyl ether if required. R = Ph (**5a-BPh_4**): yield 72%; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C) δ 45.9 (d, $^2J_{PP}$ = 71.7 Hz, ADIP), 112.3 (d, $^2J_{PP}$ = 71.7 Hz, P(OPh)$_3$); ^1H NMR (400.1 MHz, $CDCl_3$, 20 °C) δ 1.02, 1.18 (2d, $^3J_{HH}$ = 6.8 Hz, 2 × 3H, $CHMe_2$), 1.27 (m, 12H, Me_2CH-P), 1.61 (s, 3H, Me), 2.37 (m, 3H, Me_2CH-P, C-$CHMe_2$), 2.61 (m, 1H, PCH_2), 2.99 (m, 1H, PCH_2), 4.04, 5.30 (2d, J_{HP} = 6.0 Hz, 2 × 1H, *p*-cym), 4.78 (d, $^3J_{HH}$ = 17.2 Hz, 1H, $=CH_2$), 4.99 (d, $^3J_{HH}$ = 9.6 Hz, 1H, $=CH_2$), 5.47 (s, br, 1H, *p*-cym), 5.65 (m, 1H, =CH), 5.95 (s, br, 1H, *p*-cym), 6.86 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh_4), 7.00 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh_4), 7.10 (d, $^3J_{HH}$ = 8.0 Hz, 6H, P(OPh)$_3$), 7.27−7.38 (m, 17H, BPh_4, P(OPh)$_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C) δ 17.9 (s, Me), 18.3, 18.7, 19.0, 19.1 (4s, Me_2CH-P), 20.9, 21.8 (2s, $CHMe_2$), 24.5 (d, $^1J_{CP}$ = 24.1 Hz, PCH_2), 26.8 (d, $^1J_{CP}$ = 27.6 Hz, Me_2CH-P), 31.1 (d, $^1J_{CP}$ = 23.4 Hz, Me_2CH-P), 31.2 (s, $CHMe_2$), 84.7, 89.0, 95.0, 98.7, 108.5 (5s, *p*-cym), 120.2 (d, $^3J_{CP}$ = 8.8 Hz, $=CH_2$), 121.2 (s, P(OPh)$_3$), 121.7, 125.6 (2s, BPh_4), 126.2, 130.1 (2s, P(OPh)$_3$), 131.0 (d, $^2J_{CP}$ = 11.3 Hz, =CH), 132.5 (s, *p*-cym), 136.3 (s, BPh_4), 151.1 (d, $^2J_{CP}$ = 14.1 Hz, P(OPh)$_3$), 164.1 (c, $J_{C^{11}B}$ = 50.3 Hz, BPh_4); conductivity (acetone, 20 °C) Λ = 111 S cm^2 mol^{-1}; IR (KBr, cm^{-1}) ν(C=C) 1587 (m), $\nu(BPh_4)$ 733, 705 (s); MS-ESI (*m*/*z*) 739 ($[M]^+$, 100%). Anal. Calcd for $C_{61}H_{68}BClO_3P_2Ru{\cdot}^1/_2CH_2Cl_2$: C, 67.10; H, 6.31. Found: C, 67.34; H, 6.68. R = Me (**5b-BPh_4**): yield 72%; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C) δ 44.3 (d, $^2J_{PP}$ = 75.3 Hz, ADIP), 117.4 (d, $^2J_{PP}$ = 75.3 Hz, P(OMe)$_3$); ^1H NMR (400.1 MHz, $CDCl_3$, 20 °C) δ 1.09 (m, 6H, Me_2CH-P), 1.28 (m, 12H, Me_2CH-P, $CHMe_2$), 1.58 (s, 3H, Me), 2.35 (m, 2H, Me_2CH-P), 2.56 (m, 2H, PCH_2, $CHMe_2$), 3.00 (m, 1H, PCH_2), 3.76 (d, $^3J_{HP}$ = 10.8 Hz, 9H, P(OMe)$_3$), 5.13 (d, $^3J_{HH}$ = 19.2 Hz, 1H, $=CH_2$), 5.17 (d, $^3J_{HH}$ = 10.8 Hz, 1H, $=CH_2$), 5.47 (m, 3H, *p*-cym), 5.72 (m, 1H, *p*-cym), 5.77 (m, 1H, =CH), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh_4), 7.03 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh_4), 7.38 (m, 8H, BPh_4); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C) δ 18.0 (s, *Me*), 18.2, 19.2 (2s, Me_2CH-P), 21.1, 22.1 (2s, $CHMe_2$), 25.0 (d, $^1J_{CP}$ = 23.5 Hz, PCH_2), 26.2 (d, $^1J_{CP}$ = 26.9 Hz, Me_2CH-P), 31.0 (s, $CHMe_2$), 31.5 (d, $^1J_{CP}$ = 23.7 Hz, Me_2CH-P), 55.5 (d, $^2J_{CP}$ = 10.6 Hz, P(OMe)$_3$), 86.9 (d, $^2J_{CP}$ = 8.3 Hz, *p*-cym), 90.4 (d, $^2J_{CP}$ = 13.4 Hz, *p*-cym), 92.6, 99.0, 100.0 (3s, *p*-cym), 120.0 (d, $^3J_{CP}$ = 8.3 Hz, $=CH_2$), 121.7, 125.5 (2s, BPh_4), 128.3 (s, *p*-cym), 131.4 (d, $^2J_{CP}$ = 11.7 Hz, =CH), 136.3 (s, BPh_4), 164.1 (c, $J_{C^{11}B}$ = 48.3 Hz, BPh_4); conductivity (acetone, 20 °C) Λ = 107 S cm^2 mol^{-1}; IR (KBr, cm^{-1}) ν(C=C) 1580 (m), $\nu(BPh_4)$ 733, 705 (s); MS-ESI (*m*/*z*) 533 ($[M]^+$, 100%), 419 ($[M - p\text{-cym}]^+$, 19%). Anal. Calcd for $C_{46}H_{62}BClO_3P_2Ru$: C, 63.34; H, 7.16. Found: C, 63.18; H, 7.05. R = Et (**5c-BPh_4**): yield 68%; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C) δ 43.4 (d, $^2J_{PP}$ = 75.3 Hz, ADIP), 112.1 (d, $^2J_{PP}$ = 75.3 Hz, P(OEt)$_3$); ^1H NMR (400.1 MHz, $CDCl_3$, 20 °C) δ 1.11 (m, 6H, Me_2CH-P), 1.28 (m, 21H, Me_2CH-P, $CHMe_2$, CH_2CH_3), 1.61 (s, 3H, Me), 2.36 (m, 2H, Me_2CH-P), 2.58 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $CHMe_2$), 2.66, 3.02 (2m, 2 × 1H, PCH_2), 4.14 (m, 6H, CH_2CH_3), 5.12 (d, $^3J_{HH}$ = 18.4 Hz, 1H, $=CH_2$), 5.17 (d, $^3J_{HH}$ = 10.4 Hz, 1H, $=CH_2$), 5.44 (m, 3H, *p*-cym), 5.76 (m, 1H, *p*-cym), 5.78 (m, 1H, =CH), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh_4), 7.03 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh_4), 7.38 (m, 8H, BPh_4). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C) δ 16.0 (d, $^3J_{CP}$ = 6.3 Hz, CH_2CH_3), 17.8 (s, C-*Me*), 18.1, 18.3, 19.2, 19.3 (4s, Me_2CH-P), 21.1, 22.1 (2s, $CHMe_2$), 24.7 (d, $^1J_{CP}$ = 22.9 Hz, PCH_2), 26.4 (d, $^1J_{CP}$ = 27.1 Hz, Me_2CH-P), 31.1 (s, $CHMe_2$), 31.5 (d, $^1J_{CP}$ = 23.4 Hz, Me_2CH-P), 64.7 (d, $^2J_{CP}$ = 10.6 Hz, CH_2CH_3), 86.4 (d, $^2J_{CP}$ = 8.4 Hz, *p*-cym), 90.1 (d, $^2J_{CP}$ = 13.8 Hz, *p*-cym), 92.6, 97.9, 100.0 (3s, *p*-cym), 119.8 (d, $^3J_{CP}$ = 8.4 Hz, $=CH_2$), 121.7, 125.5 (2s, BPh_4), 128.3 (s, *p*-cym), 131.6 (d, $^2J_{CP}$ = 11.5 Hz, =CH), 136.3 (s, BPh_4), 164.2 (c, $J_{C^{11}B}$ = 49.3 Hz, BPh_4); conductivity (acetone, 20 °C) Λ = 117 S cm^2 mol^{-1}; IR (KBr, cm^{-1}) ν(C=C) 1573 (m), $\nu(BPh_4)$ 730, 704 (s); MS-ESI (*m*/*z*) 595 ($[M]^+$, 100%), 461 ($[M - p\text{-cym}]^+$, 23%). Anal. Calcd for $C_{49}H_{68}BClO_3P_2Ru{\cdot}1/4\ CH_2Cl_2$: C, 63.23; H, 7.38. Found: C, 63.55; H, 7.08.

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^1(*P*)-*i*$Pr_2PCH_2CH{=}CH_2$}(MeCN)][BPh_4] (6-BPh_4). The compound [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P,C,C*)-*i*$Pr_2PCH_2CH{=}CH_2$}][BPh_4] (**3-BPh_4**) was dissolved in the minimum volume of acetonitrile. The addition of diethyl ether (2 mL) and hexane (15 mL) afforded a yellow precipitate. Solvents were decanted, and the solid residue was dried in air, since vacuum drying results in reversibility of the reaction. Yield: 62%. IR (KBr, cm^{-1}): ν(C≡N) 2287 (m), ν(C=C) 1579 (m), $\nu(BPh_4)$ 734, 706 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN, 20 °C): δ 41.6 (s). ^1H NMR (400.1 MHz, CD_3CN, 20 °C): δ 1.23−1.36 (m, 18H, Me_2CH-P, C−$CHMe_2$), 2.08 (s, 3H, Me), 2.17 (s, 3H, CH_3CN), 2.55 (m, 1H, PCH_2), 2.67 (m, 3H, Me_2CH-P, C−$CHMe_2$), 2.99 (m, 1H, PCH_2), 5.20 (m, 2H, $=CH_2$), 5.86 (d, $^3J_{HH}$ = 6.0 Hz, 1H, *p*-cym), 5.89−5.98 (m, 4H, =CH, *p*-cym), 6.87 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh_4), 7.02 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh_4), 7.30 (bs, 8H, BPh_4). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN, 20 °C): δ 0.8 (s, CH_3CN), 17.4 (s, *Me*), 17.5, 17.7, 18.0, 18.1 (4s, Me_2CH-P), 21.3, 21.9 (2s, $CHMe_2$), 25.2 (d, $^1J_{CP}$ = 22.4 Hz, PCH_2), 27.1, 27.3 (2d, $^1J_{CP}$ = 24.1 Hz, Me_2CH-P), 31.1 (s, $CHMe_2$), 86.5 (d, $^2J_{CP}$ = 4.7 Hz, *p*-cym), 87.0 (d, $^2J_{CP}$ = 4.2 Hz, *p*-cym), 88.1, 91.9, 100.0, 110.3 (4s, *p*-cym), 119.0 (d, $^3J_{CP}$ = 8.5 Hz, $=CH_2$), 121.8, 125.6 (2s, BPh_4), 128.6 (s, CH_3CN), 131.8 (d, $^2J_{CP}$ = 10.4 Hz, =CH), 135.7 (s, BPh_4), 163.9 (c, $J_{C^{11}B}$ = 49.1 Hz, BPh_4). Conductivity (acetone, 20 °C): Λ = 142.4 S cm^2 mol^{-1}. The instability of this complex prevented us from obtaining any satisfactory analysis.

Synthesis of [RuCl(η^6-$C_{10}H_{14}$){κ^1(*P*)-*i*$Pr_2PCH_2CH{=}CH_2$}(py)][BPh_4] (7-BPh_4). To a solution of [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P,C,C*)-*i*$Pr_2PCH_2CH{=}CH_2$}][BPh_4] (0.0748 g, 0.1 mmol) in THF (10 mL) was added 1 equiv of pyridine (0.1 mmol, 8 μL). The mixture was stirred for 5 min at room temperature. The addition of hexane (50 mL) afforded a yellow precipitate, which was washed with hexane (3 × 10 mL) and dried under reduced pressure in the air, since vacuum drying results in reversibility of the reaction. Yield: 60%. $^{31}P\{^1H\}$ NMR (162.1 MHz, CD_2Cl_2, 20 °C): δ 32.0 (s). ^1H NMR (300.1 MHz, CD_2Cl_2, 20 °C): δ 1.07−1.33 (m, 18H, Me_2CH-P, C-$CHMe_2$), 1.98 (s, 3H, Me), 2.33 (sept, $^3J_{HH}$ = 7.2 Hz, 1H, $CHMe_2$), 2.50 (m, 1H, Me_2CH-P), 2.65 (m, 3H, PCH_2, Me_2CH-P), 5.13 (m, 2H, $=CH_2$), 5.30, 5.39 (2d, $^3J_{HH}$ = 6.0 Hz, 2 × 1H, *p*-cym) 5.55 (m, 1H, =CH), 5.65 5.76 (2d, $^3J_{HH}$ = 6.0 Hz, 2 × 1H, *p*-cym), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh_4), 7.06 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh_4), 7.36 (m, 10H, py, BPh_4), 7.87 (t, $^3J_{HH}$ = 7.8 Hz, 1H, py), 8.85 (d, $^3J_{HH}$ = 4.8 Hz, 2H, py). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 18.1 (s, Me), 18.2, 18.3, 18.9, 19.2 (4s, Me_2CH-P), 21.6, 22.4 (2s, $CHMe_2$), 26.2 (d, $^1J_{CP}$ = 24.1 Hz, Me_2CH-P), 26.5 (d, $^1J_{CP}$ = 21.1 Hz, Me_2CH-P), 26.8 (d, $^1J_{CP}$ = 22.1 Hz, PCH_2), 30.7 (s, $CHMe_2$), 83.0, 85.7, 90.0, 90.2, 97.5, 113.9 (6s, *p*-cym), 120.0 (d, $^3J_{CP}$ = 9.1 Hz, $=CH_2$), 122.0, 125.9 (2s, BPh_4) 126.3 (s, py), 129.9 (d, $^2J_{CP}$ = 7.0 Hz, =CH), 135.8 (s, BPh_4), 139.7, 156.2 (2s, py), 9 163.9 (c, $J_{C^{11}B}$ = 49.3 Hz, BPh_4). Conductivity (acetone, 20 °C): Λ = 139 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(C=C) 1601 (m), $\nu(BPh_4)$ 733, 703 (s). MS-ESI (*m*/*z*): 425 ($[M - py]^+$,

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100%), 395 ([M − py − Cl]$^+$, 62%). Anal. Calcd for $C_{48}H_{58}BClNPRu$: C, 69.69; H, 7.07; N, 1.31. Found: C, 69.74; H, 6.85; N, 1.64.

Synthesis of [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)][BPh$_4$] (8-BPh$_4$). To a solution of the complex [RuCl(η^5-C_9H_7)(PPh$_3$)$_2$] (0.388 g, 0.5 mmol) in THF (50 mL) were added 3 equiv of NaBPh$_4$ (1.5 mmol, 0.513 g) and allyldiisopropylphosphane (1.5 mmol, 224 μL). The mixture was refluxed for 30 min. Within this period of time, the initially red solution turned yellow. Once the reaction was complete, the solution was evaporated to dryness. The solid residue was extracted with dichloromethane and the resultant solution filtered through Kieselghur and concentrated. Addition of hexane (30 mL) afforded a yellow solid, which was washed with hexane (2 × 15 mL) and vacuum-dried. Yield: 85%. ^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2, 20 °C): δ 51.7 (d, $^2J_{PP}$ = 32.3 Hz, Ph_3P), −51.6 (d, $^2J_{PP}$ = 32.3 Hz, ADIP). ^{1}H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 0.75 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 14.0 Hz, 3H, *Me*$_2$CH-P), 1.10 (m, 3H, *Me*$_2$CH-P), 1.30 (m, 1H, =CH$_2$), 1.56 (m, 3H, *Me*$_2$CH-P), 1.78 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.6 Hz, 3H, *Me*$_2$CH-P), 1.86−1.95 (m, 2H, Me$_2$C*H*-P), 2.78 (m, 1H, PCH$_2$), 2.87 (m, 1H, =CH$_2$), 3.15 (m, 1H, =CH), 3.41 (m, 1H, PCH$_2$), 4.97, 5.41, 5.82 (3s, 3 × 1H, C_9H_7), 6.34 (d, $^3J_{HH}$ = 8.4 Hz, 1H, C_9H_7), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 7.07 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.48 (m, 8H, BPh$_4$), 6.90−7.57 (m, 18H, C_9H_7, PPh$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 17.7−20.2 (m, *Me*$_2$CH-P), 18.2 (d, $^1J_{CP}$ = 7.5 Hz, Me$_2$CH-P), 29.2 (s br, Me$_2$CH-P), 31.1 (d, $^1J_{CP}$ = 22.6 Hz, PCH$_2$), 46.4 (d, $^2J_{CP}$ = 19.2 Hz, =CH), 52.3 (s br, =CH$_2$), 73.9, 79.3, 85.8, 103.9, 105.4 (5s, C_9H_7), 121.7, 125.7, 135.8 (3s, BPh$_4$), 164.1 (c, $J_{C^{11}B}$ = 49.0 Hz, BPh$_4$), 121.6−133.8 (C_9H_7, PPh$_3$). Conductivity (acetone, 20 °C): Λ = 134 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(C=C) 1479 (m), ν (BPh$_4$) 732, 703 (s). MS-ESI (*m*/*z*): 637 ([M]+, 100%). Anal. Calcd for $C_{60}H_{61}BP_2Ru$: C, 75.38; H, 6.43. Found: C, 75.48; H, 6.66.

Synthesis of [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}(P(OMe)$_3$)][BPh$_4$] (9-BPh$_4$). To a suspension of the complex [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)][BPh$_4$] (0.05 mmol, 0.048 g) in a THF/toluene mixture (2/1, 15 mL) was added 3 equiv of P(OMe)$_3$ (0.15 mmol, 18 μL). The suspension was heated at 70 °C for 8 h. Once the reaction was completed and cooled, the yellow solution was concentrated and the adition of hexane (20 mL) afforded a yellow precipitate. Solvents were decanted, and the solid was washed with hexane (2 × 10 mL) and vacuum-dried. Yield: 65%. ^{31}P{^{1}H} NMR (162.1 MHz, $CDCl_3$, 20 °C): δ 154.9 (d, $^2J_{PP}$ = 52.0 Hz, P(OMe)$_3$), −39.6 (d, $^2J_{PP}$ = 52.0 Hz, ^{i}Pr$_2$P). ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ 0.98 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 14.8 Hz, 3H, *Me*$_2$CH-P), 1.05 (m, 1H, =CH$_2$), 1.09 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 17.6 Hz, 3H, *Me*$_2$CH-P), 1.37 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.2 Hz, 3H, *Me*$_2$CH-P), 1.51 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 14.8 Hz, 3H, *Me*$_2$CH-P), 1.59−1.71 (m, 2H, Me$_2$C*H*-P, PCH$_2$), 2.45−2.59 (m, 2H, Me$_2$C*H*-P, =CH), 2.76 (m, 1H, =CH$_2$), 3.10 (m, 1H, PCH$_2$), 3.55 (d, $^3J_{HP}$ = 11.2 Hz, 9H, P(OMe)$_3$), 5.42, 5.77 (2s, 2 × 1H, C_9H_7), 5.35 (t, $^3J_{HH}$ = 2.4 Hz, 1H, C_9H_7), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 7.06 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.44 (m, 8H, BPh$_4$), 7.00−7.72 (m, 4H, C_9H_7). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 20 °C): δ 18.3 (d, $^1J_{CP}$ = 7.0 Hz, Me$_2$CH−P), 18.4, 19.7 (2s br, *Me*$_2$CH-P), 27.5 (d, $^1J_{CP}$ = 22.5 Hz, Me$_2$CH−P), 29.7 (d, $^1J_{CP}$ = 33.8 Hz, PCH$_2$), 46.3 (d, $^2J_{CP}$ = 18.8 Hz, =CH), 50.4 (s br, =CH$_2$), 53.9 (d, $^2J_{CP}$ = 9.4 Hz, P(OMe)$_3$), 73.7, 74.0 (2s, C_9H_7), 84.3, 104.3, 105.2 (3s, C_9H_7), 121.6, 125.5, 136.4 (3s, BPh$_4$), 164.3 (c, $J_{C^{11}B}$ = 48.3 Hz, BPh$_4$), 122.3−132.2 (C_9H_7). Conductivity (acetone, 20 °C): Λ = 122 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(C=C) 1478 (m), ν(BPh$_4$) 733, 702 (s).

Synthesis of [Ru(η^5-C_9H_7){κ^1(*P*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)(NCMe)][BPh$_4$] (10-BPh$_4$). The compound [Ru(η^5-C_9H_7){κ^1(*P*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)(NCMe)][BPh$_4$] (**10-BPh$_4$**) was inmediatly formed when [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)][BPh$_4$] (**8-BPh$_4$**) was dissolved in the minimum volume of acetonitrile. This complex was spectroscopically characterized in acetonitrile solution. ^{31}P{^{1}H} NMR (121.5 MHz, CD_3CN, 20 °C): δ 50.2 (d, $^2J_{PP}$ = 30.3 Hz, Ph_3P), 47.4 (d, $^2J_{PP}$ = 30.3 Hz, ^{i}Pr$_2$P). ^{1}H NMR (300.1 MHz, CD_3CN, 20 °C): δ 1.12−1.30 (m, 12H, *Me*$_2$CH-P), 1.68 (m, 1H, Me$_2$C*H*-P), 1.83 (m, 1H, Me$_2$C*H*-P), 2.12 (s, 3H, MeCN), 2.39 (m, 2H, PCH$_2$), 4.75 (d, 1H, $^3J_{HH}$ = 16.8 Hz, =CH$_2$), 4.79 (d, 1H, $^3J_{HH}$ = 11.4 Hz, =CH$_2$), 4.05, 5.33, 5.38 (3s, 3 × 1H, C_9H_7), 5.67 (m, 1H, =CH), 6.39 (d, $^3J_{HH}$ = 8.7 Hz, 1H, C_9H_7), 6.86 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 7.02 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.30 (m, 8H, BPh$_4$), 6.84−7.60 (m, 18H, C_9H_7, PPh$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN, 20 °C): δ 2.0 (s, *Me*CN), 17.9−18.8 (m, *Me*$_2$CH-P), 28.8 (d, $^1J_{CP}$ = 17.0 Hz, PCH$_2$), 29.0 (d, $^1J_{CP}$ = 24.3 Hz, Me$_2$CH−P), 29.9 (d, $^1J_{CP}$ = 24.2 Hz, Me$_2$CH-P), 64.4 (d, $^2J_{CP}$ = 8.7 Hz, C_9H_7), 65.9, 88.4, 108.3, 110.1 (4s, C_9H_7), 117.9 (d, $^3J_{CP}$ = 9.8 Hz, =CH$_2$), 121.8, 125.6, 135.8 (3s, BPh$_4$), 163.8 (c, $J_{C^{11}B}$ = 48.8 Hz, BPh$_4$), 123.8−135.0 (=CH, C_9H_7, PPh$_3$). Conductivity (acetonitrile, 20 °C): Λ = 134 S cm^2 mol^{-1}.

Synthesis of [Ru{κ^3(*P,C,S*)-*i*Pr$_2$PCH$_2$CH(SCH$_3$)CH$_2$}(η^6-$C_{10}H_{14}$)][BPh$_4$] (11a-BPh$_4$). To a solution of the complex [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P,C,C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}][BPh$_4$] (**3-BPh$_4$**; 0.053 mmol, 0.040 g) in THF (10 mL) was added 2 equiv of NaSCH$_3$ (0.106 mmol, 0.007 g), and the mixture was stirred at room temperature for 1 h. The solution was then evaporated under reduced pressure, and the yellow residue was extracted with dichloromethane. The resulting solution was filtered through Kieselguhr and concentrated under vacuum to a volume of approximately 1 mL. The addition of hexane (20 mL) afforded a yellow precipitate. Solvents were decanted, and the solid residue was washed with hexane (2 × 15 mL) and vacuum-dried. Yield: 62%. ^{31}P{^{1}H} NMR (162.1 MHz, $CDCl_3$, 20 °C): δ 75.7 (s). ^{1}H NMR (400.1 MHz, CD_2Cl_2, 20 °C): δ 1.18−1.30 (m, 19H, *Me*$_2$CH-P, CH*Me*$_2$, Ru-CH$_2$), 1.88−1.92 (m, 2H, PCH$_2$), 2.13 (s, 3H, Me), 2.21 (m, 1H, Ru-CH$_2$), 2.29 (s, 3H, SCH$_3$), 2.31−2.41 (m, 2H, Me$_2$C*H*-P), 2.62 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*Me$_2$), 4.89 (bd, $^3J_{HP}$ = 41.7 Hz, 1H, S-CH), 5.00, 5.75 (2d, $^3J_{HH}$ = 6.0 Hz, 2 × 1H, *p*-cym), 5.38, 5.62 (2d, $^3J_{HH}$ = 6.4 Hz, 2 × 1H, *p*-cym), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 7.07 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.36 (m, 8H, BPh$_4$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ 3.0 (d, $^3J_{CP}$ = 7.9 Hz, Ru-CH$_2$), 18.6−18.8 (s, *Me*$_2$CH-P), 18.8 (s, *Me*), 21.7 (s, SCH$_3$), 22.2 (s, CH*Me*$_2$), 23.6 (d, $^1J_{CP}$ = 27.3 Hz, Ru-PCH$_2$), 24.1 (s, CH*Me*$_2$), 27.4 (d, $^1J_{CP}$ = 25.4 Hz, Me$_2$CH-P), 28.0 (d, $^1J_{CP}$ = 25.4 Hz, Me$_2$CH-P), 32.2 (s, CHMe$_2$), 67.2 (d, $^2J_{CP}$ = 4.8 Hz, S-CH), 81.5, 84.8, 86.4, 87.9, 102.3, 113.8 (6s, *p*-cym), 121.8, 125.7, 135.9 (3s, BPh$_4$), 164.1 (c, $J_{C^{11}B}$ = 49.3 Hz, BPh$_4$). Conductivity (acetone, 20 °C): Λ = 104 S cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(BPh$_4$) 736, 705 (s). MS-ESI (*m*/*z*): 441 ([M]$^+$, 100%).

Synthesis of [Ru{κ^3(*P,C,S*)-*i*Pr$_2$PCH$_2$CH(SR)CH$_2$}(η^6-$C_{10}H_{14}$)][BPh$_4$] (R = *i*Pr (11b-BPh$_4$), *t*Bu (11c-BPh$_4$)). The thiolate RS$^-$ was formed in situ by stirring NaOH (0.1 mmol, 4 mg) and the corresponding thiol (0.1 mmol) in THF (10 mL) for 30 min. Then, the complex [RuCl(η^6-$C_{10}H_{14}$){κ^3(*P,C,C*)-*i*Pr$_2$PCH$_2$CH=CH$_2$}][BPh$_4$] (**3-BPh$_4$**; 0.05 mmol, 0.04 g) was added and the mixture was stirred at room temperature for 45 min. Once the reaction was completed, the solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 and the extract filtered through Kieselghur. The resulting yellow solution was concentrated, and the addition of hexane (20 mL) afforded a brownish yellow solid precipitate. The solvent was decanted, and the solid was washed with hexane (2 × 15 mL) and vacuum-dried. R = *i*Pr (**11b-BPh$_4$**): yield 56%; ^{31}P{^{1}H} NMR (162.1 MHz, $CDCl_3$, 20 °C) δ 76.0 (s); ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C) δ 1.10−1.31 (m, 25H, *Me*$_2$CH-P, C-CH*Me*$_2$, *Me*$_2$CHS, Ru-CH$_2$), 1.68 (m, 2H, PCH$_2$), 1.93 (m, 1H, Ru-CH$_2$), 1.99 (s, 3H, C-Me), 2.25 (m, 2H, Me$_2$C*H*-P), 2.55 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C−C*H*Me$_2$), 2.81 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, Me$_2$C*H*-S), 4.71 (d, $^3J_{HH}$ = 5.6 Hz, 1H, *p*-cym), 4.81 (bd, 1H, J_{HP} = 43.2 Hz, S-C*H*CH$_2$), 5.32, 5.36, 5.59 (3d, $^3J_{HH}$ = 5.6 Hz, 3 × 1H, *p*-cym), 6.91 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 7.05 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.43 (m, 8H, BPh$_4$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 20 °C) δ 5.2 (d, $^3J_{CP}$ = 9.6 Hz, Ru-CH$_2$), 18.4, 18.8, 19.0, 19.1, 21.6, 21.9, 22.1 (7s, *Me*$_2$CH-P, *Me*$_2$CH-S, C-*Me*), 23.5 (d, $^1J_{CP}$ = 29.2 Hz, Ru-PCH$_2$), 24.9 (s, C-CH*Me*$_2$), 27.4, 28.0 (2d, $^1J_{CP}$ = 25.3 Hz, Me$_2$CH-P), 32.1 (s, C-CHMe$_2$), 42.2 (s, Me$_2$CH-S), 63.9 (d, $^2J_{CP}$ = 5.8 Hz, S-CHCH$_2$), 79.9, 85.0, 85.7, 104.4, 113.7 (5s, *p*-cym), 121.6, 125.5, 136.3 (3s, BPh$_4$), 164.3 (c, $J_{C^{11}B}$ = 50.3 Hz, BPh$_4$); conductivity (acetone, 20 °C): Λ = 102 S cm^2 mol^{-1}; IR (KBr, cm^{-1}) ν(BPh$_4$) 733, 705 (s); MS-ESI (*m*/*z*) 469 ([M]$^+$, 100%). R = *t*Bu (**11c-BPh$_4$**): yield 42%; ^{31}P{^{1}H} NMR (162.1 MHz, $CDCl_3$, 20 °C) δ 74.6 (s); ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C δ 0.89 (m, 1H,

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$RuCH_2$), 1.08−1.28 (m, 18H, Me_2CH-P, C-CHMe_2), 1.33 (s, 9H, Me_3C), 1.69 (m, 2H, PCH_2), 1.98 (s, 3H, C-Me), 2.19 (m, 2H, Ru-CH_2, Me_2CH-P), 2.29 (m, 1H, Me_2CH-P), 2.53 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C-CHMe$_2$), 4.77 (d, $^3J_{HH}$ = 5.2 Hz, 1H, *p*-cym), 4.84 (bd, 1H, J_{HP} = 46.8 Hz, S−CHCH$_2$), 5.42, 5.60 (2d, $^3J_{HH}$ = 5.6 Hz, 2 × 1H, *p*-cym), 5.72 (d, $^3J_{HH}$ = 5.2 Hz, 1H, *p*-cym), 6.91 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh_4), 7.05 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh_4), 7.41 (m, 8H, BPh_4); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C) δ 5.7 (d, $^3J_{CP}$ = 11.6 Hz, Ru-CH_2), 18.6, 18.8, 19.0, 19.1, 19.2 (5s, Me_2CH-P, C-*Me*), 22.4, 24.8 (2s, C-CHMe_2), 24.9 (d, $^1J_{CP}$ = 31.0 Hz, Ru-PCH_2), 27.9, 28.2 (2d, $^1J_{CP}$ = 25.4 Hz, Me_2CH−P), 29.1 (s, Me_3C), 32.1 (s, C-CHMe$_2$), 49.4 (s, Me_3C-S), 64.7 (d, $^2J_{CP}$ = 5.5 Hz, S-CHCH$_2$), 80.0, 85.0, 86.2, 103.8, 113.5 (5s, *p*-cym), 121.7, 125.6, 136.4 (3s, BPh_4), 164.3 (c, $J_{C^{11}B}$ = 49.3 Hz, BPh_4); Conductivity (acetone, 20 °C) Λ = 100 S cm^2 mol^{-1}; IR (KBr, cm^{-1}) ν(BPh_4) 731, 702 (s); MS-ESI (*m*/*z*) 483 ([M]$^+$, 100%).

Synthesis of [RuCl{κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(SC$_6$H$_4$Me)CH$_2$}(η^6-C$_{10}$H$_{14}$)] (12). The thiolate $C_7H_7S^-$ was formed in situ by stirring NaOH (0.1 mmol, 0.004 g) and *p*-toluenethiol (0.1 mmol, 0.0124 g) in THF (10 mL) for 30 min. Then, the complex [RuCl{κ^3(*P*,*C*,*C*)-*i*Pr$_2$PCH$_2$CH═CH$_2$}(η^6-$C_{10}H_{14}$)][BPh_4] (**3-BPh$_4$**; 0.05 mmol, 0.04 g) was added and the mixture was stirred at room temperature for 45 min. Once the reaction was completed, the solution was evaporated to dryness under reduced pressure and the solid residue was extracted with hexane. The resulting yellow solution was filtered through Kieselguhr and evaporated to dryness, affording a brownish solid. Yield: 65%. $^{31}P\{^1H\}$ NMR (162.1 MHz, $CDCl_3$, 20 °C): δ 70.2 (s). ^1H NMR (400.1 MHz, $CDCl_3$, −30 °C): δ 1.09−1.40 (m, 18H, Me_2CH-P, C-CHMe_2), 1.45 (m, 1H, PCH_2), 1.99 (s, 3H, C-Me), 2.09 (m, 1H, PCH_2), 2.20 (m, 2H, Me_2CH-P, $RuCH_2$), 2.37 (s, 3H, C_6H_4Me), 2.60 (m, 1H, Me_2CH-P), 2.71 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C-CHMe$_2$), 2.96 (m, 1H, $RuCH_2CH$), 3.43 (m, 1H, $RuCH_2$), 4.63, 5.76 (2d, $^3J_{HH}$ = 5.6 Hz, 2 × 1H, *p*-cym), 4.87, 5.67 (2d, $^3J_{HH}$ = 6.0 Hz, 2 × 1H, *p*-cym), 7.07, 7.29 (2d, $^3J_{HH}$ = 9.2 Hz, 2 × 2H, *p*-tol). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, −30 °C): δ 17.8 (s, C-*Me*), 18.5, 19.5, 19.9, 20.4 (4s, Me_2CH-P), 21.4 (s, C_6H_4Me), 21.7, 23.6 (2s, C-CHMe_2), 25.2 (d, $^1J_{CP}$ = 22.5 Hz, Me_2CH-P), 27.8 (d, $^1J_{CP}$ = 20.3 Hz, Me_2CH-P), 28.4 (d, $^2J_{CP}$ = 11.3 Hz, $RuCH_2$), 30.2 (s, C-CHMe$_2$), 34.1 (d, $^1J_{CP}$ = 22.4 Hz, PCH_2), 53.5 (d, $^2J_{CP}$ = 22.5 Hz, $RuCH_2CH$), 80.6, 85.8, 87.1, 93.3, 111.6, 116.4 (6s, *p*-cym), 129.6, 130.0, 132.6, 133.4 (4s, C_6H_4Me). Conductivity (acetone, 20 °C): Λ = 16 S cm^2 mol^{-1}. MS- ESI (*m*/*z*): 517 ([M − Cl]$^+$, 100%).

Synthesis of [Ru(η^5-C$_9$H$_7$){κ^2(*P*,*C*)-*i*Pr$_2$PCH$_2$CH(SR)CH$_2$}(PPh$_3$)] (R = Me (13a), *i*Pr (13b), *t*Bu (13c)). When NaOH (0.1 mmol, 0.004 g) and the thiol (0.1 mmol, 0.0124 g) were stirred in THF (10 mL) for 30 min, the corresponding thiolate was formed. Then, [Ru(η^5-C_9H_7){κ^3(*P*,*C*,*C*)-*i*PrPCH$_2$CH═CH$_2$}(PPh_3)][BPh_4] (0.05 mmol, 0.048 g) was added. The mixture was stirred at room temperature for 30 min. Once the reaction was completed, the orange 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 = Me (**13a**): yield 72%; $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 20 °C) δ 75.2 (d, $^2J_{PP}$ = 27.5 Hz, ^{i}Pr$_2$P), 60.8 (d, $^2J_{PP}$ = 27.5 Hz, PPh_3); ^1H NMR (400.1 MHz, C_6D_6, 20 °C) δ 0.79 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 10.4 Hz, 3H, Me_2CH-P), 0.98 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 14.2 Hz, 3H, Me_2CH-P), 1.14 (m, 1H, PCH_2), 1.24 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 11.6 Hz, 3H, Me_2CH-P), 1.29 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 12.7 Hz, 3H, Me_2CH-P), 1.61 (m, 1H, Me_2CH-P), 1.75 (m, 1H, $RuCH_2$), 2.11 (s, MeS), 2.25 (m, 2H, Me_2CH-P, PCH_2), 2.84 (m, 1H, $RuCH_2$), 2.92 (m, 1H, $RuCH_2CH$), 4.73, 5.04 (2s, 2 × 1H, C_9H_7), 5.10 (t, $^3J_{HH}$ = 2.3 Hz, C_9H_7), 6.33 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C_9H_7), 6.87−7.87 (m, 18H, C_9H_7, PPh_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 20 °C) δ 13.1 (m, Ru-CH_2), 14.4 (s, MeS), 18.2, 18.7, 20.5, 21.5, (4s, Me_2CH-P), 29.3 (d, $^1J_{CP}$ = 19.5 Hz, Me_2CH-P), 32.8 (d, $^1J_{CP}$ = 20.9 Hz, Me_2CH-P), 34.5 (d, $^1J_{CP}$ = 21.2 Hz, Ru-PCH_2), 52.3 (d, $^2J_{CP}$ = 23.2 Hz, Ru-CH_2CH), 71.1, 71.4 (2d, $^2J_{CP}$ = 7.3 Hz, C_9H_7), 92.4, 105.5, 108.3 (3s, C_9H_7), 122.1−138.8 (C_9H_7, PPh_3); conductivity (acetone, 20 °C) Λ = 27 S cm^2 mol^{-1}; MS-ESI (*m*/*z*) 637 ([M − SMe]$^+$, 100%). R = *i*Pr (**13b**): yield 77%; $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 20 °C) δ 77.3 (d, $^2J_{PP}$ = 27.9 Hz, ^{i}Pr$_2$P), 60.3 (d, $^2J_{PP}$ = 27.9 Hz, PPh_3); ^1H NMR (400.1 MHz, C_6D_6, 20 °C) δ 0.77 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 10.4 Hz, 3H, Me_2CH-P), 1.00 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 14.4 Hz, 3H, Me_2CH-P), 1.24 (m, 4H, Me_2CH-P, PCH_2), 1.34 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 12.8 Hz, 3H, Me_2CH-P), 1.41, 1.43 (2d, $^3J_{HH}$ = 6.8 Hz, 2 × 3H, Me_2CH-S), 1.62 (m, 1H, Me_2CH-P), 1.81 (m, 1H, $RuCH_2$), 2.28 (m, 2H, Me_2CH-P, PCH_2), 2.87 (m, 1H, $RuCH_2$), 3.12 (m, 1H, $RuCH_2CH$), 3.19 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, Me_2CH-S), 4.82, 5.03 (2s, 2 × 1H, C_9H_7), 5.14 (t, $^3J_{HH}$ = 2.4 Hz, C_9H_7), 6.37 (d, $^3J_{HH}$ = 8.4 Hz, 1H, C_9H_7), 6.89−7.87 (m, 18H, C_9H_7, PPh_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 20 °C) δ 14.4 (m, Ru-CH_2), 18.2, 18.6, 20.5, 21.6, (4s, Me_2CH-P), 24.3 (s, Me_2CH-S), 29.1 (d, $^1J_{CP}$ = 19.6 Hz, Me_2CH-P), 32.6 (d, $^1J_{CP}$ = 22.8 Hz, Me_2CH-P), 34.8 (s, Me_2CH-S), 35.1 (d, $^1J_{CP}$ = 19.5 Hz, Ru-PCH_2), 49.6 (d, $^2J_{CP}$ = 26.2 Hz, $RuCH_2CH$), 71.0 (d, $^2J_{CP}$ = 6.0 Hz, C_9H_7), 71.5 (d, $^2J_{CP}$ = 8.0 Hz, C_9H_7), 91.8, 105.9, 107.7 (3s, C_9H_7), 122.5−139.4 (C_9H_7, PPh_3); conductivity (acetone, 20 °C): Λ = 16 S cm^2 mol^{-1}; MS-ESI (*m*/*z*) 637 ([M − S*i*Pr]$^+$, 100%). R = *t*Bu (**13c**): yield 66%; $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 20 °C) δ 76.1 (d, $^2J_{PP}$ = 27.4 Hz, ^{i}Pr$_2$P), 60.1 (d, $^2J_{PP}$ = 27.4 Hz, PPh_3); ^1H NMR (400.1 MHz, C_6D_6, 20 °C) δ 0.77 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 10.4 Hz, 3H, Me_2CH-P), 0.98 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 14.4 Hz, 3H, Me_2CH-P), 1.16 (m, 1H, PCH_2), 1.28 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 10.4 Hz, 3H, Me_2CH-P), 1.40 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 13.1 Hz, 3H, Me_2CH-P), 1.54 (s, 9H, Me_3C-S), 1.66 (m, 1H, Me_2CH-P), 1.98 (m, 1H, $RuCH_2$), 2.33 (m, 2H, Me_2CH-P, PCH_2), 3.00 (m, 1H, $RuCH_2$), 3.12 (m, 1H, $RuCH_2CH$), 4.80, 5.08, 5.21 (3s, 3 × 1H, C_9H_7), 6.32 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C_9H_7), 6.87−7.87 (m, 18H, C_9H_7, PPh_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 20 °C) δ 17.6 (m, Ru-CH_2), 18.2, 18.3, 20.5, 21.8, (4s, Me_2CH-P), 28.8 (d, $^1J_{CP}$ = 19.4 Hz, Me_2CH-P), 29.8 (d, $^1J_{CP}$ = 18.7 Hz, Me_2CH-P), 32.2 (s, Me_3CH-S), 36.3 (d, $^1J_{CP}$ = 22.7 Hz, Ru-PCH_2), 42.6 (s, Me_3C-S), 49.2 (d, $^2J_{CP}$ = 23.5 Hz, $RuCH_2CH$), 70.7 (d, $^2J_{CP}$ = 8.7 Hz, C_9H_7), 71.7 (d, $^2J_{CP}$ = 11.8 Hz, C_9H_7), 92.1, 104.7, 106.2 (3s, C_9H_7), 122.5−139.2 (C_9H_7, PPh_3); conductivity (acetone, 20 °C) Λ = 24 S cm^2 mol^{-1}; MS-ESI (*m*/*z*) 637 ([M − S*t*Bu]$^+$, 100%).

X-ray Crystal Structure Determination of 1-Cl, 3-BPh$_4$, 8-BPh$_4$·CH$_2$Cl$_2$, and 11a-BPh$_4$. Crystals suitable for X-ray diffraction analysis were obtained from a dichloromethane/hexane solvent system. The most relevant crystal and refinement data are collected in Table 1 (Supporting Information).

In all cases, diffraction data were recorded on a 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 times per image: 16−50, 6−26, 3.5−12, and 5−30 s, respectively. The data collection strategy was calculated with the program CrysAlis Pro CCD.[11] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[11] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[11]

The software package WINGX[12] was used for space group determination, structure solution, and refinement. The structure of complex **1-Cl** was solved by Patterson interpretation and phase expansion using DIRDIF.[13] For **3-BPh$_4$**, **8-BPh$_4$**, and **11a-BPh$_4$**, structures were solved by direct methods using SIR2004.[14]

In the crystal of **8-BPh$_4$** a CH_2Cl_2 solvent molecule per unit formula of the complex is present. For **11a-BPh$_4$** electron density peaks could not be sensibly modeled as solvent and the SQUEEZE/PLATON algorithm[15] was applied.

Isotropic least-squares refinement on F^2 using SHELXL97[16] 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 and the H atoms were geometrically located and their coordinates were refined riding on their parent atoms. For **3**, the crystal studied was a racemic twin, the ratio of the twin components being 0.499(10)/0.511(10).

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 Table 1) from counting statistics and $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

Atomic scattering factors were taken from ref 17. The crystallographic plots were made with PLATON.[15]

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■ ASSOCIATED CONTENT

Supporting Information

^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra for complexes **6**$^{+}$, **9**$^{+}$, **10**$^{+}$, **11a−c**$^{+}$, **12**, and **13a−c** and CIF files and a table giving X-ray crystallographic data of **1-Cl**, **3-BPh$_4$**, **8-BPh$_4$** and **11a-BPh$_4$** (CCDC: 916383, **1-Cl**; 941935, **3-BPh$_4$**; 941936, **8-BPh$_4$**; 916384, **11a-BPh$_4$**). 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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