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C–H versus O–H Bond Activation in Phosphino-alcohol Ligands: Synthesis of the α-Hydroxy-alkyl Ruthenium(II) Derivatives [RuCl{κ^2(*P*,*C*)-$Ph_2PC_6H_4C(R)OH$}(η^6-arene)]

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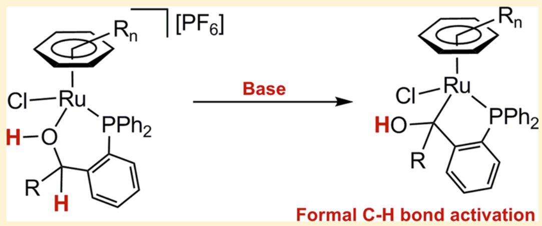
Supporting Information

ABSTRACT: The coordination of the phosphino-alcohol ligands 2-$Ph_2PC_6H_4CH(R)OH$ (R = H, Me) onto an arene-ruthenium(II) fragment gave rise to the formation of complexes of general formula [$RuCl_2${2-$Ph_2PC_6H_4CH(R)OH$}(η^6-arene)] (R = H, arene = C_6H_6 (**3a**), *p*-cymene (**3b**), mesitylene (**3c**), C_6Me_6 (**3d**); R = Me, arene = *p*-cymene (**5b**)). In solution, different isomers were observed depending on the solvent polarity. They arise from the different coordination modes adopted by the phosphino-alcohol: (i) the classical κ^1-P mode through the selective coordination of the phosphorus atom, (ii) the establishment of both Ru–P and Cl···H–O interactions, and (iii) the *P*,*O*-chelate formation. Treatment of these species with $NaPF_6$ led to the selective formation of the corresponding cationic species [RuCl{κ^2-(*P*,*O*)-2-$Ph_2PC_6H_4CH(R)OH$}(η^6-arene)][PF_6] **6a–d** and **7b**, respectively. Unexpectedly, under basic conditions these cationic compounds evolved into the neutral α-hydroxy-alkyl derivatives [RuCl{κ^2-(*P*,*C*)-$Ph_2PC_6H_4C(R)OH$}(η^6-arene)] through a formal C–H bond activation process.



■ INTRODUCTION

The design of new functionalized ligands is a field of constant ongoing research activity. In this context, heteroditopic ligands, combining a soft P-donor fragment with hard-donor atoms, such as oxygen or nitrogen, have attracted particular interest due to their potential hemilabile properties.[1,2] As far as the P,O-donor ligands are concerned, most of the synthetic endeavors and reactivity studies were focused on phosphines containing an ether,[1a,3] ester,[1a,4] aldehyde,[1a,5] ketone,[1a,6] or phosphine-oxide[1a,7] functionality. In contrast, the synthesis and coordination chemistry of phosphino-alcohols have been comparatively much less explored.[1a,8] This is probably due to the usual instability of alcohols coordinated onto a metal center. Indeed, the complexation of the OH moiety increases the acidity of the hydrogen atom,[8h,9] thus favoring the generation of alkoxide derivatives.[10] In general, the alkoxo complexes derived from a tertiary alcohol or a phenol function can be isolated,[11] but analogous species generated from secondary and primary alcohols turned out to be rather unstable due to their high tendency to undergo β-elimination.[8g,12] However, the incorporation of the alcohol function in the structure of a P-donor ligand, strongly coordinated to the metal through the phosphorus atom, could help in the stabilization of the alcohol unit, making it possible to study in detail the different modes of activation of this functional group by a metallic center.

In the present paper, we report on the coordination of the 2-$Ph_2PC_6H_4CH(R)OH$ (R = H, Me) ligands to arene-ruthenium(II) fragments, giving evidence that, in solution, the type of interactions between the phosphino-alcohol and the organometallic fragment strongly depends on the polarity of the solvent. Moreover, by deprotonation of the resulting complexes, we could obtain selectively unexpected α-hydroxy-alkyl ruthenium derivatives, through a formal C–H bond activation of the functionalized phosphine ligand.

■ RESULTS AND DISCUSSION

Synthesis of Neutral Complexes [$RuCl_2${2-$Ph_2PC_6H_4$-$CH(R)OH$}(η^6-arene)] (arene = Benzene, *p*-Cymene, Mesitylene, Hexamethylbenzene) and Study of Their Behavior in Solution. The treatment of the ruthenium(II) dimeric precursors [{RuCl(μ-Cl)(η^6-arene)}$_2$] (**2a–d**) with a slight excess of the phosphino-alcohol ligand 2-$Ph_2PC_6H_4CH_2OH$ (**1**) led to the formation of the mononuclear derivatives [$RuCl_2$(2-$Ph_2PC_6H_4CH_2OH$)(η^6-arene)] (arene = benzene (**3a**), *p*-cymene (**3b**), mesitylene (**3c**), hexamethylbenzene (**3d**)). These compounds were isolated in 80–95% yield as brownish-orange air-stable solids and characterized by means of standard spectroscopic techniques (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR), elemental analyses, and conductance measurements, the data obtained being in complete accord with the proposed stoichiometry (details are

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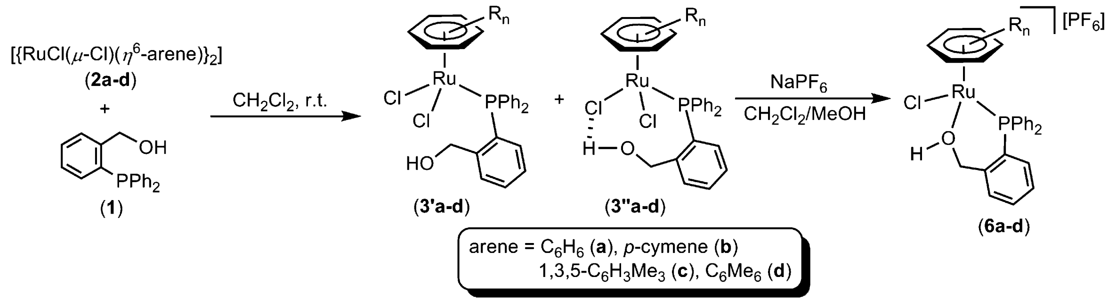
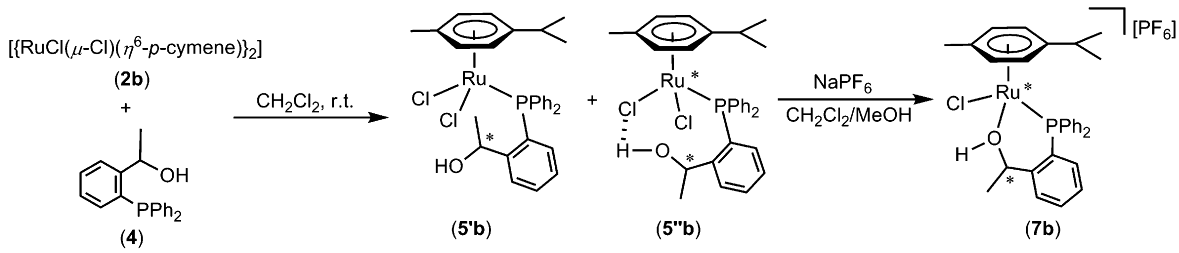
Scheme 1. Synthesis of Arene-ruthenium(II) Complexes Derived from the Phosphino-alcohol Ligand 1



Scheme 2. Synthesis of Arene-ruthenium(II) Complexes Derived from the Phosphino-alcohol Ligand 4



given in the Experimental Section). Remarkably, in $CDCl_3$ solution, these derivatives exist as a mixture of two isomeric forms, **3′a–d** and **3″a–d** (Scheme 1). In the former, the phosphino-alcohol ligand adopts a classical κ^1-P coordination mode, while for the latter, both Ru–P and Cl···H–O interactions[13] are established between the ligand **1** and the organometallic fragment (Scheme 1). The neutral nature of both isomers is clearly evidenced by the extremely low molar conductivity values of the corresponding solutions ($\Lambda < 0.7$ $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$).[14] The most significant spectroscopic features for isomers **3′a–d** are the following: (i) In the $^{31}P\{^1H\}$ NMR spectra, the phosphorus nucleus gives rise to a resonance at 29.3 (**3′a**), 28.3 (**3′b**), 30.9 (**3′c**), or 29.9 (**3′d**) ppm, in full agreement with its coordination to the metal.[15] (ii) Regarding the ^1H NMR spectra, the singlet signal observed at 4.56 (**3′a**), 4.45 (**3′b**), 4.37 (**3′c**), or 4.40 (**3′d**) ppm, which corresponds to the two equivalent methylenic CH_2OH hydrogen atoms, is consistent with the C_s-symmetry of the molecule.[16] In contrast, isomers **3″a–d** exhibit two broad doublets at ca. 4.7 and 5.2 ppm attributable to the diastereotopic protons of the CH_2OH unit.[17] In addition, the low-field resonance observed for the OH hydrogen at δ = 10.36 (**3″a**), 10.43 (**3″b**), 10.31 (**3″c**), or 9.36 (**3″d**) ppm evidences the existence of an OH···Cl interaction.[18,19] Isomers **3″** are the major species present in $CDCl_3$ solution, their relative proportion being dependent on the nature of the arene ligand (72% (C_6H_6, **3″a**), 88% (*p*-cymene, **3″b**), 90% (1,3,5-$C_6H_3Me_3$, **3″c**), 54% (C_6Me_6, **3″d**)). Apparently, the OH···Cl interaction is somewhat less favored for the electronically poorest (C_6H_6) and the more sterically hindered (C_6Me_6) organometallic centers. The molar ratio between **3′**and **3″** was found to be also strongly dependent on the polarity of the medium. As an example, while **3″b** is the major isomer in $CDCl_3$ (88%), the **3′b** form becomes predominant in acetone-d_6 (71%; see the Supporting Information). In the latter medium, the OH hydrogen atom seems to interact preferably with the solvent molecules rather than with the neighboring chlorido ligand. Finally, in highly polar solvents, such as methanol, these derivatives evolve selectively into the cationic species [RuCl{κ^2(*P*,*O*)-2-$Ph_2PC_6H_4CH_2OH$}(η^6-arene)][Cl], as the result of the cleavage of one of the Ru–Cl bonds and subsequent coordination of the oxygen atom onto the metal (see spectroscopic characterization in the Supporting Information). According to their ionic nature, the molar conductivity values measured from methanol solutions range from Λ = 53 (arene = benzene) to 73 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (arene = *p*-cymene). The relative proportion of isomers **3′** and **3″** also depends on the temperature, the formation of the latter being favored by decreasing the temperature. Thus, the **3′b**/**3″b** ratios in CD_2Cl_2 solutions are 16/84, 11/89, and 6/94 at 25, 0, and −20 °C, respectively.

The coordination of 2-$Ph_2PC_6H_4CH(Me)OH$ (**4**), featuring a secondary alcohol function, has also been explored. This ligand, which possesses a stereogenic center at the CMe carbon, was employed as the corresponding racemic mixture. The treatment of the dimeric precursor [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (**2b**) with 2.4 equiv of ligand **4** gave rise to the expected mononuclear complex [$RuCl_2${2-$Ph_2PC_6H_4CH(Me)$-OH}(η^6-*p*-cymene)] (**5b**) (Scheme 2). Like its counterpart **3b**, compound **5b** exists in $CDCl_3$ solution as two isomeric forms, **5′b** and **5″b**. Moreover, due to the presence of two stereogenic centers, i.e., the CMe carbon and the ruthenium atom, the species **5″b** appears as a mixture of diastereoisomers.[20]

Synthesis of the Cationic Complexes [RuCl{κ^2(*P*,*O*)-2-$Ph_2PC_6H_4CH(R)OH$}(η^6-arene)][PF_6]. As expected, the cationic species [RuCl{κ^2(*P*,*O*)-2-$Ph_2PC_6H_4CH_2OH$}(η^6-arene)]$^+$, previously observed dissolving **3a–d** in alcoholic media (see above), could be isolated as the corresponding hexafluorophosphate salts. Thus, complexes [RuCl{κ^2(*P*,*O*)-$Ph_2PC_6H_4$-CH_2OH}(η^6-arene)][PF_6] (arene = benzene (**6a**), *p*-cymene (**6b**), mesitylene (**6c**), hexamethylbenzene (**6d**)) were cleanly obtained in good yield by treatment of **3a–d** with a slight excess of $NaPF_6$ in a 1:1 mixture of dichloromethane/methanol and subsequent workup (Scheme 1). In their $^{31}P\{^1H\}$ NMR spectra, these derivatives exhibit a unique singlet resonance at ca. 30 ppm, while in the ^1H NMR spectra, the most characteristic features are two signals at ca. 5.1 and 4.4 ppm attributable to the diastereotopic CH_2OH protons. The

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analogous complex [RuCl{κ^2(P,O)-Ph$_2$PC$_6$H$_4$CH(Me)OH}(η^6-p-cymene)][PF$_6$] (**7b**), containing a methyl substituent in α-position with respect to the OH group, was prepared from **5b** following a similar protocol, and it was obtained as a 90:10 mixture of diastereomers (Scheme 2). The configuration of the predominant species was assigned as $S_{Ru}R_C/R_{Ru}S_C$ on the basis of DFT calculations.[21] This diastereomer, in which the methyl group is oriented in opposite direction with respect to the diphenylphosphino fragment to minimize steric repulsions, was 2.3 kcal/mol more stable than the $R_{Ru}R_C/S_{Ru}S_C$ one (details are given in the Supporting Information).

On the other hand, the structure of the cationic complex [RuCl{κ^2(P,O)-Ph$_2$PC$_6$H$_4$CH$_2$OH}(η^6-p-cymene)][PF$_6$] (**6b**) could be unequivocally confirmed by means of a single-crystal X-ray diffraction study. An ORTEP drawing is depicted in Figure 1, and selected bond distances and angles are listed in the caption. The cation exhibits a classical pseudo-octahedral three-legged piano-stool geometry around the ruthenium atom with values of the interligand angles Cl(1)−Ru−P(1) (88.23(8)°), P(1)−Ru−O(1) (87.5(2)°), and O(1)−Ru−Cl(1) (83.3(2)°) and those between the centroid of the p-cymene ring and the legs (124.8(2)°, 131.62(6)°, and 126.45(6)°) being typical for this compound class.[22] The Ru(1)−O(1) bond length of 2.151(6) Å is consistent with the coordination of the OH unit to the metal center.[23] Worthy of note, the hydrogen atom of the alcohol points to the same side as the chlorido ligand. Moreover, the short H(1)···Cl(1) distance of 2.645 Å, shorter than the sum of the van der Waals radii (2.95 Å), could be ascribed to the existence of a weak intramolecular interaction between these two atoms.[24,25]

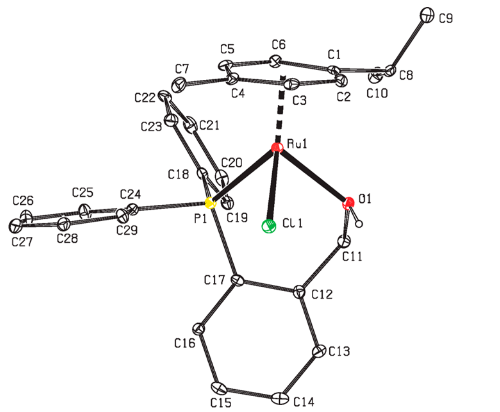
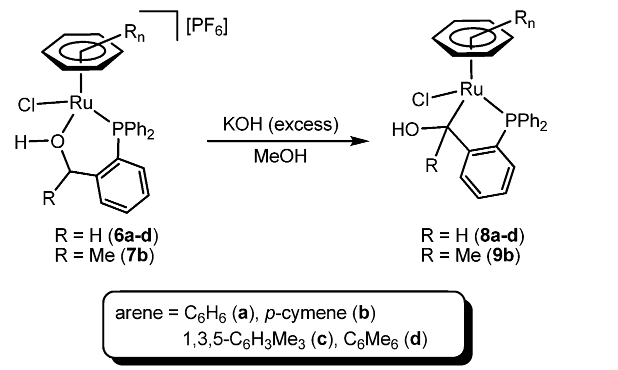


Figure 1. ORTEP-type view of the cation [RuCl{κ^2(P,O)-2-Ph$_2$PC$_6$H$_4$CH$_2$OH}(η^6-p-cymene)]$^+$ (**6b**) showing the crystallographic labeling scheme. Hydrogen atoms, except the OH one, and the PF$_6^-$ anion have been omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level. Selected bond distances (Å) and angles (deg): Ru(1)−Cl(1) = 2.380(2); Ru(1)−P(1) = 2.351(2); Ru(1)−O(1) = 2.151(6); O(1)−H(1) = 1.00(3); Cl(1)···H(1) = 2.645; C*−Ru(1)−O(1) = 124.8(2); C*−Ru(1)−P(1) = 131.62(6); C*−Ru(1)−Cl(1) = 126.45(6); O(1)−Ru(1)−P(1) = 87.5(2); O(1)−Ru(1)−Cl(1) = 83.3(2); P(1)−Ru(1)−Cl(1) = 88.23(8); C* denotes the centroid of the p-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

Synthesis of the α-Hydroxy-alkyl Complexes [RuCl{κ^2(P,C)-2-Ph$_2$PC$_6$H$_4$C(R)OH}(η^6-arene)]. Interestingly, methanolic solutions of the cationic derivatives [RuCl{κ^2(P,O)-2-Ph$_2$PC$_6$H$_4$CH(R)OH}(η^6-arene)][PF$_6$] (R = H, arene = C$_6$H$_6$ (**6a**), p-cymene (**6b**), 1,3,5-C$_6$H$_3$Me$_3$ (**6c**), C$_6$Me$_6$ (**6d**); R = Me, arene = p-cymene (**7b**)) readily react with an excess of KOH to generate the α-hydroxy-alkyl compounds [RuCl{κ^2(P,C)-2-Ph$_2$PC$_6$H$_4$C(R)OH}(η^6-arene)] (R = H, arene = C$_6$H$_6$ (**8a**), p-cymene (**8b**), 1,3,5-C$_6$H$_3$Me$_3$ (**8c**), C$_6$Me$_6$ (**8d**); R = Me, arene = p-cymene (**9b**)), through a formal C−H activation of the alcohol −CH(R)OH unit (Scheme 3). In the case of the benzene derivative [RuCl{κ^2(P,C)-2-Ph$_2$PC$_6$H$_4$-CHOH}(η^6-C$_6$H$_6$)] (**8a**), the reaction was not completely clean, and other unidentified and inseparable species were also formed (**8a** accounted for approximately 60% of the mixture). In the other cases, the reactions were more selective and the corresponding α-hydroxy-alkyl compounds **8b−d** and **9b** could be isolated in analytically pure form. Alternatively, the α-hydroxy-alkyl derivatives **8−9b** have been obtained directly from the neutral complexes [RuCl$_2${2-Ph$_2$PC$_6$H$_4$CH(R)OH}(η^6-p-cymene)] (R = H (**3b**), Me (**5b**)), by reaction with KOH in methanol.[26]

Scheme 3. Synthesis of the α-Hydroxy-alkyl Complexes 8a−d and 9b



The most relevant spectroscopic features of these compounds are the following: (i) in the ^{31}P{^{1}H} NMR spectra, a singlet resonance at lower fields (ca. 53 ppm) in comparison to those observed for their precursors **6a−d** and **7b** (ca. 30 ppm), which is in accord with the formation of a five-membered metallacycle;[27] (ii) in the ^{1}H NMR spectra of **8a−d**, a singlet resonance in the range 5.1−6.1 ppm attributable to the methinic C*H*OH proton;[28] (iii) in the ^{13}C{^{1}H} NMR spectra, a characteristic signal at ca. 84 ppm corresponding to the COH carbon atom,[28,29] which appears as a singlet (**8a**, **8d**) or a doublet (**8b**,**c**, **9b**) due to its coupling with the phosphorus nuclei. Remarkably, despite the existence of two stereogenic centers in the molecule (the metal and COH carbon), all the spectroscopic data obtained were consistent with the formation of a single diastereomer. Unfortunately, the relative configuration of the two chiral centers could not be unequivocally determined, since all attempts to obtain single crystals of these compounds suitable for X-ray diffraction studies failed.[30]

Although complexes **8a−d** and **9b** formally result from the C−H activation of the CH(R)OH unit, it is expected that the first step of the process is the deprotonation of the more acidic hydrogen, i.e., the OH one.[31] Subsequently, β-elimination leading to the ruthenium(II) hydride intermediate (**B**), containing a pendant aldehyde (or ketone) group, followed by the insertion of the C═O moiety into the Ru−H bond, would provide the final product (Scheme 4). We must note here that, in agreement with this proposal, the structurally related phosphino-alcohol derivative [RuCl(η^6-p-cymene){κ^2-P,O-Ph$_2$P-X-CH(Me)OH}][BPh$_4$] (X = 1,2-ferrocenediyl)

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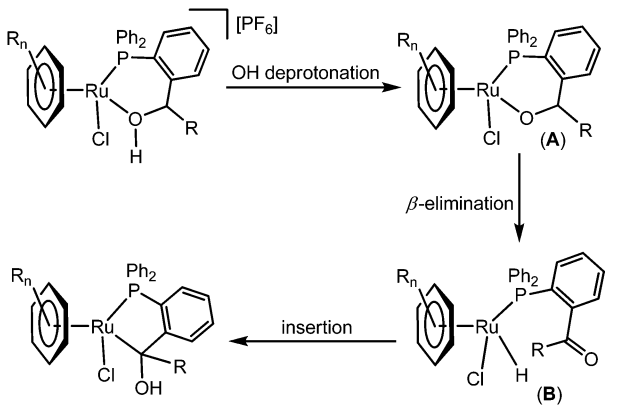
Scheme 4. Proposed Mechanism for the Formation of the α-Hydroxy-alkyl Derivatives



described previously by Manzano and co-workers, was found to evolve by deprotonation into the hydride species [RuH(η^6-*p*-cymene){κ^2-*P*,*O*-Ph_2P-X-C(Me)═O}][BPh_4], featuring a keto-phosphine ligand.[8g] On the other hand, the insertion of aldehydes into a metal−hydride bond has shown to be a reliable route to synthesize α-hydroxyalkyl complexes.[28,32] However, as far as we are aware, this is the first time that an α-hydroxyalkyl compound is formed directly from an alcohol precursor.

Finally, also relevant in this context is the fact that, when the reaction of [RuCl{κ^2(*P*,*O*)-2-$Ph_2PC_6H_4CH_2OH$}(η^6-*p*-cymene)][PF_6] (**6b**) was carried out with K_2CO_3, instead of KOH, a small amount (ca. 5%) of the ruthenium hydride species [RuHCl{κ^1-(*P*)-$Ph_2PC_6H_4$CH(═O)}(η^6-*p*-cymene)] of type **B** (see Scheme 4) could be detected, along with the α-hydroxy-alkyl derivative **8b**.[33,34] This observation strongly supports the proposed mechanism.

At this stage, we would like to stress the difference in reactivity observed between the complexes [RuCl{κ^2(*P*,*O*)-$Ph_2PC_6H_4$CH(R)OH}(η^6-arene)][X] (X = Cl, PF_6) described herein and the closely related derivatives [RuCl(η^6-arene){κ^2-*P*,*O*-Ph_2P-X-CH(R)OH}][Cl] (X = 1,2-ferrocenediyl; arene = *p*-cymene, benzene; R = H, Me) previously reported by Manzano and co-workers.[8g] The latter are prone to suffer β-elimination when dissolved in methanol, giving rise to the formation, in variable quantities, of the corresponding hydride species [RuH(η^6-arene){κ^2-*P*,*O*-Ph_2P-X-C(═O)R}][Cl] with a phosphino-aldehyde or -ketone ligand. This process turned out to be favored with secondary alcohols (i.e., when R = Me) and could be drastically accelerated by adding $NaBPh_4$ salt to the medium. Moreover, the transformation could be promoted by a base, such as NEt_3. In contrast, [RuCl{κ^2(*P*,*O*)-$Ph_2PC_6H_4$CH(R)OH}(η^6-arene)][X] (X = Cl, PF_6) proved to be stable in methanol solutions, at least for 24 h, hydride derivatives not being detected under these conditions. This difference in reactivity could probably be ascribed to the different electronic properties of the ligands, the higher electron density of the ferrocenediyl fragment (vs the phenylene group) facilitating the oxidation of the alcohol function. On the other hand, a different chemical behavior toward base was observed, since the treatment of complexes [RuCl{κ^2-(*P*,*O*)-$Ph_2PC_6H_4$CH(R)OH}(η^6-arene)][PF_6] (**6a−d**, **7b**) with KOH leads to the α-hydroxy-alkyl derivatives [RuCl{κ^2-(*P*,*C*)-$Ph_2PC_6H_4$C(R)OH}(η^6-arene)] (**8a−d**, **9b**), instead of the corresponding hydride species. This is possibly due to steric concerns. Effectively, the formation of α-hydroxy-alkyl compounds requires the generation of a five-membered metallacycle, which would be particularly congested when the sterically demanding ferrocenediyl group is present in the structure.

■ CONCLUSION

The phosphino-alcohols $Ph_2PC_6H_4CH_2OH$ (**1**) and $Ph_2PC_6H_4$CH(Me)OH (**4**) have demonstrated to be versatile ligands able to adopt different coordination modes as a function of the experimental conditions, i.e., (i) the classical κ^1-(*P*) mode through the selective coordination of the phosphorus atom; (ii) the establishment of both Ru−P and Cl···H−O interactions; (iii) the κ^2-(*P*,*O*)-chelate formation. In basic medium, they are also unexpected precursors of α-hydroxy-alkyl derivatives. Indeed, we evidenced that complexes [RuCl{κ^2-(*P*,*O*)-$Ph_2PC_6H_4$CH(R)OH}(η^6-arene)][PF_6] (**6a−d**, **7b**; arene = C_6H_6, *p*-cymene, 1,3,5-$C_6H_3Me_3$, C_6Me_6, R = H, Me) react with KOH in MeOH to generate the α-hydroxy-alkyl species [RuCl{κ^2-(*P*,*C*)-$Ph_2PC_6H_4$C(R)OH}(η^6-arene)] (**8a−d**, **9b**; arene = C_6H_6, *p*-cymene, 1,3,5-$C_6H_3Me_3$, C_6Me_6, R = H, Me). Although this type of compound has been previously prepared with other organometallic fragments through the insertion of an aldehyde into a metal−hydride bond, as far as we know, their formation from an alcohol precursor is unprecedented. Although complexes **8a−d** and **9b** formally result from a C−H bond activation of the ligand, they are most likely generated through an O−H deprotonation/β-elimination/insertion sequence.

■ EXPERIMENTAL SECTION

General Considerations. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers with the exception of compounds 2-$Ph_2PC_6H_4CH_2OH$ (**1**),[35] [{RuCl(μ-Cl)(η^6-arene)}$_2$] (arene = C_6H_6 (**2a**), *p*-cymene (**2b**), 1,3,5-$C_6H_3Me_3$ (**2c**), C_6Me_6 (**2d**)),[36] and 2-$Ph_2PC_6H_4$CH(Me)OH (**4**),[37] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a PerkinElmer 1720-XFT spectrometer in Nujol, and absorption frequencies are given in cm^{-1}. The C and H analyses were carried out with a PerkinElmer 2400 microanalyzer. Conductivities are given in $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ and were measured at room temperature, in ca. 10^{-3} $mol\cdot dm^{-3}$ solutions, with a Jenway PCM3 conductimeter. NMR spectra were recorded on a Bruker AC300 or 300DPX instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C), using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the complexes. Coupling constants *J* are given in hertz.

Synthesis of [$RuCl_2$(2-$Ph_2PC_6H_4CH_2OH$)(η^6-C_6H_6)], ***3a′/3a″***. A solution of **2a** (0.230 g, 0.46 mmol) and ligand **1** (0.333 g, 1.13 mmol) in 20 mL of dichloromethane was stirred overnight at room temperature. The reaction mixture was then filtered through Kieselguhr, and the filtrate evaporated to dryness. The resulting residue was washed three times with 10 mL of a mixture of hexane/diethyl ether (1:1) and vacuum-dried to afford a brown solid. Yield: 0.398 g (80%). Anal. Found (calcd for $C_{25}H_{23}Cl_2OPRu$): C, 55.47 (55.36); H, 4.11 (4.27). Conductivity: 0.2 (in CH_2Cl_2), 53 (in MeOH). In $CDCl_3$, **3′a** (28%), ^{31}P{^{1}H} NMR, δ: 29.3 (s). ^{1}H NMR, δ: 7.83−6.94 (m, 14 H, ArH), 5.47 (s, 6 H, C_6H_6), 4.56 (s, 2 H, CH_2), OH not observed. ^{13}C{^{1}H} NMR, δ: 134.8−127.4 (m, $C_{aromatic}$), 88.3 (s, C_6H_6), 62.9 (d, $^3J_{PC}$ = 6.6, CH_2); **3″a** (72%), ^{31}P{^{1}H} NMR, δ: 27.5 (s). ^{1}H NMR, δ: 10.36 (s, 1 H, OH), 7.83−6.94 (m, 14 H, ArH), 5.71 (s, 6 H, C_6H_6), 5.16 and 4.57 (both d, 1 H each, $^2J_{HH}$ = 14.3, CH_2). ^{13}C{^{1}H} NMR, δ: 134.8−127.4 (m, $C_{aromatic}$), 89.4 (d, $^2J_{PC}$ = 3.3, C_6H_6), 60.8 (s, CH_2). IR, ν_{OH}: 3382.

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*Synthesis of [RuCl$_2$(2-Ph$_2$PC$_6$H$_4$CH$_2$OH)(η^6-p-cymene)], **3′b/3″b**.* Following a similar procedure, [RuCl$_2$(2-Ph$_2$PC$_6$H$_4$CH$_2$OH)(η^6-*p*-cymene)] was prepared as an orange solid using **2b** (0.360 g, 0.59 mmol) and ligand **1** (0.424 g, 1.45 mmol). Yield: 0.667 g (95%). Anal. Found (calcd for $C_{29}H_{31}Cl_2OPRu$): C, 58.12 (58.00); H, 5.18 (5.22). Conductivity: 0.5 (in CH_2Cl_2); 4 (in acetone); 73 (in MeOH). In $CDCl_3$, **3′b** (12%), $^{31}P\{^1H\}$ NMR, δ: 28.3 (s). ^1H NMR, δ: 7.86−7.09 (m, 14 H, ArH), ∼5.4 (2 H, CH of cym, overlapped by major isomer), 4.83 (m, 2 H, CH of cym), 4.45 (s, 2 H, CH_2), 3.47 (m, 1 H, C*H*Me$_2$), 1.72 (s, 3 H, ArMe), 1.30 (d, 6 H, $^3J_{HH}$ = 6.6, CH*Me*), OH not observed. $^{13}C\{^1H\}$ NMR, δ: 146.2−123.7 (m, C_{arom}), 113.8 (d, $^2J_{PC}$ = 6.8, C of cym), 99.3 (s, C of cym), 89.0 (d, $^2J_{PC}$ = 4.5, CH of cym), 86.6 (d, $^2J_{PC}$ = 1.5, CH of cym), 63.2 (d, $^3J_{PC}$ = 5.3, CH_2), 31.0 (s, *C*HMe$_2$), 24.3 (s, CH*Me*$_2$), 18.0 (s, ArMe); **3″b** (88%), $^{31}P\{^1H\}$ NMR, δ: 26.2 (s). ^1H NMR, δ: 10.43 (s, 1 H, OH), 7.86−7.09 (m, 14 H, ArH), 5.90 and 5.86 (both d, 1 H each, $^3J_{HH}$ = 5.4, CH of cym), 5.46 and 5.30 (both d, 1 H each, $^3J_{HH}$ = 5.4, CH of cym), 5.21 and 4.70 (both d, 1 H each, $^2J_{HH}$ = 14.7, CH_2), 3.03 (m, 1 H, C*H*Me$_2$), 1.87 (s, 3 H, ArMe), 1.06 (d, 3 H, $^3J_{HH}$ = 7.1, CH*Me*), 1.03 (d, 3 H, $^3J_{HH}$ = 7.4, CH*Me*). $^{13}C\{^1H\}$ NMR, δ: 146.2−123.7 (m, C_{arom}), 111.5 (d, $^2J_{PC}$ = 2.3, C of cym), 96.2 (s, C of cym), 90.0 (d, $^2J_{PC}$ = 3.8, CH of cym), 87.2 (d, $^2J_{PC}$ = 5.3, CH of cym), 86.7 (d, $^2J_{PC}$ = 2.3, CH of cym), 85.2 (d, $^2J_{PC}$ = 4.5, CH of cym), 61.9 (s, CH_2), 30.8 (s, *C*HMe$_2$), 22.2 and 21.6 (both s, CH*Me*$_2$), 18.1 (s, ArMe). IR, ν_{OH}: 3414.

*Synthesis of [RuCl$_2$(2-Ph$_2$PC$_6$H$_4$CH$_2$OH)(η^6-1,3,5-C$_6$H$_3$Me$_3$)], **3′c/3″c**.* Following a similar procedure, [RuCl$_2$(2-Ph$_2$PC$_6$H$_4$CH$_2$OH)(η^6-1,3,5-C$_6$H$_3$Me$_3$)] was prepared as a brownish solid using **2c** (0.190 g, 0.32 mmol) and ligand **1** (0.230 g, 0.79 mmol). Yield: 0.339 g (90%). Anal. Found (calcd for $C_{28}H_{29}Cl_2OPRu$): C, 57.49 (57.54); H, 4.87 (5.00). Conductivity: 0.3 (in CH_2Cl_2), 68 (in MeOH). In $CDCl_3$, **3′c** (10%), $^{31}P\{^1H\}$ NMR, δ: 30.9 (s). ^1H NMR, δ: 7.94−7.07 (m, 14 H, ArH), 4.74 (s, 3 H, C$_6$*H*$_3$Me$_3$), 4.37 (s, 2 H, CH_2), 2.02 (s, 9 H, Me), OH not observed. $^{13}C\{^1H\}$ NMR, δ: 145.5−123.5 (m, $C_{aromatic}$), 104.2 (d, $^2J_{PC}$ = 2.3, C of $C_6H_3Me_3$), 85.5 (d, $^2J_{PC}$ = 4.5, CH of $C_6H_3Me_3$), 63.2 (d, $^3J_{PC}$ = 5.3, CH_2), 15.2 (s, Me); **3″c** (90%), $^{31}P\{^1H\}$ NMR, δ: 26.7 (s). ^1H NMR, δ: 10.31 (br s, 1 H, OH), 7.94−7.07 (m, 14 H, ArH), 5.49 (s, 3 H, C$_6$*H*$_3$Me$_3$), 5.26 and 4.76 (both br d, 1 H each, $^2J_{HH}$ = 15.7, CH_2), 1.93 (s, 9 H, C$_6$H$_3$*Me*$_3$). $^{13}C\{^1H\}$ NMR, δ: 143.9−123.5 (m, $C_{aromatic}$), 100.4 (d, $^2J_{PC}$ = 3.0, C of $C_6H_3Me_3$), 87.1 (d, $^2J_{PC}$ = 3.0, CH of $C_6H_3Me_3$), 60.9 (d, $^3J_{PC}$ = 1.5, CH_2), 18.3 (s, Me). IR, ν_{OH}: 3432.

*Synthesis of [RuCl$_2$(2-Ph$_2$PC$_6$H$_4$CH$_2$OH)(η^6-C$_6$Me$_6$)], **3′d/3″d**.* Following a similar procedure, [RuCl$_2$(2-Ph$_2$PC$_6$H$_4$CH$_2$OH)(η^6-C$_6$Me$_6$)] was prepared as an orange solid using **2d** (0.437 g, 0.65 mmol) and ligand **1** (0.460 g, 1.57 mmol). Yield: 0.759 g (93%). Anal. Found (calcd for $C_{31}H_{35}Cl_2OPRu$): C, 59.48 (59.43); H, 5.58 (5.63). Conductivity: 0.7 (in CH_2Cl_2), 64 (in MeOH). In $CDCl_3$, **3′d** (44%), $^{31}P\{^1H\}$ NMR, δ: 29.9 (s). ^1H NMR, δ: 7.95−6.90 (m, 14 H, ArH), 4.40 (br s, 2 H, CH_2), 1.78 (s, 18 H, C_6Me_6), OH not observed. $^{13}C\{^1H\}$ NMR, δ: 146.5−126.8 (m, $C_{aromatic}$), 96.8 (d, $^2J_{PC}$ = 3.0, *C*$_6$Me$_6$), 61.8 (s, CH_2), 16.3 (s, C$_6$*Me*$_6$); **3″d** (56%), $^{31}P\{^1H\}$ NMR, δ: 28.2 (s). ^1H NMR, δ: 9.36 (br s, 1 H, OH), 7.95−6.90 (m, 14 H, ArH), 5.06 and 4.75 (both d, 1 H each, $^2J_{HH}$ = 15.7, CH_2), 1.96 (s, 18 H, C_6Me_6). $^{13}C\{^1H\}$ NMR, δ: 146.5−126.8 (m, $C_{aromatic}$), 97.2 (d, $^2J_{PC}$ = 3.0, *C*$_6$Me$_6$), 63.4 (d, $^3J_{PC}$ = 4.5, CH_2), 15.1 (s, C$_6$*Me*$_6$). IR, ν_{OH}: 3421.

*Synthesis of [RuCl$_2${2-Ph$_2$PC$_6$H$_4$CH(Me)OH}(η^6-p-cymene)], **5b**.* Following a similar procedure, [RuCl$_2${2-Ph$_2$PC$_6$H$_4$CH(Me)OH}(η^6-*p*-cymene)] was prepared as an orangish-brown solid using **2b** (0.104 g, 0.17 mmol) and ligand **4** (0.126 g, 0.41 mmol). Yield: 0.194 g (93%). Anal. Found (calcd for $C_{30}H_{33}Cl_2OPRu$): C, 58.99 (58.83); H, 5.40 (5.43). Conductivity: 0.8 (CH_2Cl_2), 76 (MeOH). Only characterized in CD_3OD as [RuCl{κ^2(*P,O*)-2-Ph$_2$PC$_6$H$_4$CH(Me)-OH}(η^6-*p*-cymene)][Cl].[20,38] $^{31}P\{^1H\}$ NMR, CD_3OD, δ: 28.2 (s, *minor diastereoisomer*, 10%), 26.2 (s, *major diastereoisomer*, 90%). ^1H NMR, CD_3OD, δ: *major diastereoisomer*: 8.18−6.78 (m, 14 H, ArH), 6.24 (d, 1 H, $^3J_{HH}$ = 6.4, CH of cym), 6.11 (d, 1 H, $^3J_{HH}$ = 6.4, CH of cym), 5.81 (d, 1 H, $^3J_{HH}$ = 5.2, CH of cym), 5.69 (d, 1 H, $^3J_{HH}$ = 5.2, CH of cym), 4.40 (q, 1 H, $^3J_{HH}$ = 6.5, C*H*Me), 2.50 (m, 1 H, C*H*Me$_2$), 2.01 (s, 3 H, ArMe), 1.76 (d, 3 H, $^3J_{HH}$ = 6.5, CH*Me*), 1.24 (d, 3 H, $^3J_{HH}$ = 7.1, CH*Me*$_2$), 0.81 (d, 3 H, $^3J_{HH}$ = 7.0, CH*Me*$_2$), OH not observed; *minor diastereoisomer*: 8.18−6.78 (m, 14 H, ArH), 5.98 (d, 1 H, $^3J_{HH}$ = 6.5, CH of cym), 5.90 (d, 1 H, $^3J_{HH}$ = 5.6, CH of cym), 5.43 (d, 1 H, $^3J_{HH}$ = 6.5, CH cym), 5.34 (d, 1 H, $^3J_{HH}$ = 5.6, CH of cym), 5.00 (q, 1 H, $^3J_{HH}$ = 6.5, C*H*Me), 1.91 (s, 3 H, ArMe), 1.50 (d, 3 H, $^3J_{HH}$ = 6.5, CH*Me*), 1.09 (d, 3 H, $^3J_{HH}$ = 6.9, CHMe$_2$), the other signals are overlapped. $^{13}C\{^1H\}$ NMR, CD_3OD, δ: *major diastereomer*: 147.5−124.8 (m, $C_{aromatic}$), 107.8 (s, C of cym), 98.5 (d, $^2J_{PC}$ = 7.0, CH of cym), 95.4 (s, C of cym), 91.8 (d, $^2J_{PC}$ = 7.0, CH of cym), 86.9 (s, CH of cym), 82.6 (s, CH of cym), 75.5 (d, $^3J_{PC}$ = 10.9, CHMe), 31.4 (s, *C*HMe$_2$), 23.8, 20.0, 19.5, and 18.3 (all s, Me); *minor diastereomer*: 147.5−124.8 (m, $C_{aromatic}$), 110.4 (d, $^2J_{PC}$ = 2.3, C of cym), 96.9 (s, C of cym), 91.4 (d, $^2J_{PC}$ = 6.3, CH of cym), 91.3 (s, CH of cym), 87.3 (d, $^2J_{PC}$ = 8.6, CHMe), 70.7 (d, $^2J_{PC}$ = 5.5, CH of cym), 67.8 (d, $^2J_{PC}$ = 4.7, CH of cym), 22.5, 22.1, 21.6, and 18.2 (all s, Me).

*Synthesis of [RuCl{κ^2(P,O)-2-Ph$_2$PC$_6$H$_4$CH$_2$OH}(η^6-C$_6$H$_6$)][PF$_6$], **6a**.* A solution of **3a** (0.206 g, 0.38 mmol) and $NaPF_6$ (0.120 g, 0.71 mmol) in 20 mL of a mixture of methanol and CH_2Cl_2 (1:1) was stirred at room temperature for 3 h. After evaporation, the residue was extracted with 20 mL of dichloromethane. The resultant solution was evaporated to dryness, and the solid washed with diethyl ether (3 × 10 mL), affording a brownish solid. Yield: 0.179 g (72%). Anal. Found (calcd for $C_{25}H_{23}ClF_6OP_2Ru$): C, 45.95 (46.06); H, 3.58 (3.56). Conductivity: 88 (in acetone). $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 29.3 (s), −143.6 (sept, $^1J_{FP}$ = 708, PF_6^-). ^1H NMR, acetone-d_6, δ: 7.81−7.10 (m, 14 H, ArH), 6.01 (s, 6 H, C_6H_6), 5.20 and 4.50 (both d, 1 H each, $^2J_{HH}$ = 13.9, CH_2), 3.30 (vbr s, 1 H, OH). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 142.9−124.6 (m, $C_{aromatic}$), 89.3 (d, $^2J_{PC}$ = 3.0, C_6H_6), 65.4 (d, $^3J_{PC}$ = 5.4, CH_2). IR, ν_{OH}: 3447, ν_{PF}: 843.

*Synthesis of [RuCl{κ^2(P,O)-2-Ph$_2$PC$_6$H$_4$CH$_2$OH}(η^6-p-cymene)]-[PF$_6$], **6b**.* Following a similar procedure, **6b** was prepared as an orange solid using **3b** (0.610 g, 1.02 mmol) and $NaPF_6$ (0.233 g, 1.39 mmol). Yield: 0.722 g (87%). Anal. Found (calcd for $C_{29}H_{31}ClF_6OP_2Ru$): C, 49.07 (49.20); H, 4.52 (4.41). Conductivity: 130 (in acetone). $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 27.3 (s), −143.4 (sept, $^1J_{FP}$ = 707, PF_6^-). ^1H NMR, acetone-d_6, δ: 7.91−6.97 (m, 14 H, ArH), 6.29 and 6.13 (both d, 1 H each, $^3J_{HH}$ = 6.5, CH of cym), 5.89 and 5.78 (both d, 1 H each, $^3J_{HH}$ = 5.1, CH of cym), 5.12 and 4.42 (both d, 1 H each, $^2J_{HH}$ = 13.7, CH_2), 2.98 (vbr s, 1 H, OH), 2.57 (m, 1 H, C*H*Me$_2$), 2.03 (s, 3 H, ArMe), 1.20 (d, 3 H, $^3J_{HH}$ = 6.9, CH*Me*), 0.89 (d, 3 H, $^3J_{HH}$ = 6.8, CH*Me*). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 141.4−126.3 (m, $C_{aromatic}$), 107.4 (s, C of cym), 96.7 (d, $^2J_{PC}$ = 5.8, CH of cym), 95.9 (s, C of cym), 90.1 (d, $^2J_{PC}$ = 6.4, CH of cym), 88.0 (s, CH of cym), 83.4 (d, $^2J_{PC}$ = 1.6, CH of cym), 68.7 (d, $^3J_{PC}$ = 6.8, CH_2), 31.0 (s, CHMe), 23.2 and 20.0 (both s, CH*Me*), 18.1 (s, ArMe). IR, ν_{OH}: 3403, ν_{PF}: 842.

*Synthesis of [RuCl{κ^2(P,O)-2-Ph$_2$PC$_6$H$_4$CH$_2$OH}(η^6-1,3,5-C$_6$H$_3$Me$_3$)][PF$_6$], **6c**.* Following a similar procedure, **6c** was prepared as an orange solid using **3c** (0.432 g, 0.74 mmol) and $NaPF_6$ (0.190 g, 1.13 mmol). Yield: 0.349 g (68%). Anal. Found (calcd for $C_{28}H_{29}ClF_6OP_2Ru$): C, 48.37 (48.43); H, 4.28 (4.21). Conductivity: 103 (in acetone). $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 31.0 (s), −143.8 (sept, $^1J_{FP}$ = 707, PF_6^-). ^1H NMR, acetone-d_6, δ: 7.90−7.00 (m, 14 H, ArH), 5.59 (s, 3 H, C$_6$*H*$_3$Me$_3$), 5.06 and 4.25 (both d, 1 H each, $^2J_{HH}$ = 13.9, CH_2), 1.98 (s, 9 H, C$_6$H$_3$*Me*$_3$), OH not observed. $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 141.5−128.5 (m, $C_{aromatic}$), 105.1 (d, $^2J_{PC}$ = 2.1, C of $C_6H_3Me_3$), 85.1 (d, $^2J_{PC}$ = 2.9, CH of $C_6H_3Me_3$), 66.1 (d, $^3J_{PC}$ = 6.5, CH_2), 18.6 (s, Me). IR, ν_{OH}: 3470, ν_{PF}: 842.

*Synthesis of [RuCl{κ^2(P,O)-2-Ph$_2$PC$_6$H$_4$CH$_2$OH}(η^6-C$_6$Me$_6$)][PF$_6$], **6d**.* Following a similar procedure, **6d** was prepared as a brownish solid using **3d** (0.300 g, 0.48 mmol) and $NaPF_6$ (0.120 g, 0.71 mmol). Yield: 0.282 g (80%). Anal. Found (calcd for $C_{31}H_{35}ClF_6OP_2Ru$): C, 50.49 (50.58); H, 4.87 (4.79). Conductivity: 118 (in acetone). $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 32.1 (s), −143.8 (sept, $^1J_{FP}$ = 709, PF_6^-). ^1H NMR, acetone-d_6, δ: 7.73−7.16 (m, 14 H, ArH), 6.36 (d, 1 H, $^3J_{HH}$ = 8.2, OH), 5.02 (d, 1 H, $^2J_{HH}$ = 14.0, CH_2), 4.43 (m, 1 H, CH_2), 1.96 (s, 18 H, C_6Me_6). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 140.0−127.6 (m, $C_{aromatic}$), 98.2 (d, $^2J_{PC}$ = 2.5, *C*$_6$Me$_6$), 69.4 (m, CH_2), 15.9 (s, C$_6$*Me*$_6$). IR, ν_{OH}: 3417, ν_{PF}: 842.

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*Synthesis of RuCl{κ^2(P,O)-2-Ph_2PC_6H_4CH(Me)OH}(η^6-p-cymene)]-[PF_6], **7b**.* Following a similar procedure, **7b** was prepared as an orange solid using **5b** (0.300 g, 0.49 mmol) and $NaPF_6$ (0.121 g, 0.72 mmol). Yield: 0.294 g (83%). Anal. Found (calcd for $C_{30}H_{33}ClF_6OP_2Ru$): C, 49.68 (49.90); H, 4.88 (4.61). Conductivity: 122 (in acetone). $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 28.1 (s, *minor diastereoisomer*, 12%), 26.0 (s, *major diastereoisomer*, 88%), −143.6 (sept, $^1J_{FP}$ = 709, PF_6^-). ^1H NMR, acetone-d_6, δ: *major diastereoisomer*: 8.20−6.70 (m, 14 H, ArH), 6.05 (d, 1 H, $^3J_{HH}$ = 6.3, CH of cym), 6.13 (d, 1 H, $^3J_{HH}$ = 6.3, CH of cym), 5.99 (d, 1 H, $^3J_{HH}$ = 5.5, CH of cym), 5.48 (d, 1 H, $^3J_{HH}$ = 5.5, CH of cym), 4.22 (q, 1 H, $^3J_{HH}$ = 6.7, C*H*Me), 2.95 (vbr s, 1 H, OH), 2.39 (m, 1 H, C*H*Me_2), 1.97 (s, 3 H, ArMe), 1.73 (d, 3 H, $^3J_{HH}$ = 6.5, CH*Me*), 1.18 (d, 3 H, $^3J_{HH}$ = 6.9, CH*Me*$_2$), 0.80 (d, 3 H, $^3J_{HH}$ = 7.0, CH*Me*$_2$); *minor diastereoisomer*: 8.20−6.70 (m, 14 H, ArH), 5.80 (d, 1 H, $^3J_{HH}$ = 6.6, CH of cym), 5.92 (d, 1 H, $^3J_{HH}$ = 5.8, CH of cym), 5.63 (d, 1 H, $^3J_{HH}$ = 6.6, CH cym), 5.44 (d, 1 H, $^3J_{HH}$ = 5.8, CH of cym), 4.79 (q, 1 H, $^3J_{HH}$ = 6.5, C*H*Me), 1.86 (s, 3 H, ArMe), 1.46 (d, 3 H, $^3J_{HH}$ = 6.6, CH*Me*), 1.00 (d, 3 H, $^3J_{HH}$ = 6.8, CHMe_2), the rest of the signals are overlapped.

*Detection of [RuCl{κ^2(P,C)-2-Ph_2PC_6H_4CHOH}(η^6-C_6H_6)], **8a**.* To a solution of **6a** (0.100 g, 0.16 mmol) in 20 mL of methanol was added an excess of KOH (0.230 g, 4.10 mmol). After stirring 10 min at room temperature, the reaction mixture was evaporated to dryness. The residue was extracted with diethyl ether (30 mL), evaporated to dryness, and washed with 3 mL of hexane. The yellow solid obtained contains ∼60% of **8a** along with unidentified products. $^{31}P\{^1H\}$ NMR, C_6D_6, δ: 53.0 (s). ^1H NMR, C_6D_6, δ: 8.19−6.77 (m, 14 H, ArH), 6.06 (s, 1 H, C*H*OH), 4.88 (s, 6 H, C_6H_6), OH not observed. $^{13}C\{^1H\}$ NMR, C_6D_6, δ: 159.4−124.9 (m, $C_{aromatic}$), 82.5 (d, $^2J_{PC}$ = 3.6, C_6H_6), 80.0 (s, CHOH).

*Synthesis of [RuCl{κ^2(P,C)-2-Ph_2PC_6H_4CHOH}(η^6-p-cymene)], **8b**.* Following a similar procedure, **8b** was prepared as a yellow solid using **6b** (0.150 g, 0.22 mmol). Yield: 0.087 g (70%). Anal. Found (calcd for $C_{29}H_{30}ClOPRu$): C, 61.88 (61.97); H, 5.47 (5.38). $^{31}P\{^1H\}$ NMR, C_6D_6, δ: 52.8 (s). ^1H NMR, C_6D_6, δ: 8.22−6.78 (m, 14 H, ArH), 5.84 (s, 1 H, C*H*OH), 4.89 (d, 1 H, $^3J_{HH}$ = 5.5, CH of cym), 5.80 and 4.77 (both d, 1 H each, $^3J_{HH}$ = 6.1, CH of cym), 4.68 (d, 1 H, $^3J_{HH}$ = 5.5, CH of cym), 2.31 (m, 1 H, C*H*Me_2), 1.80 (s, 3 H, ArMe), 1.15 (d, 3 H, $^3J_{HH}$ = 6.7, CH*Me*), 1.12 (d, 3 H, $^3J_{HH}$ = 7.1, CH*Me*), OH not observed. $^{13}C\{^1H\}$ NMR, C_6D_6, δ: 161.0−125.9 (m, $C_{aromatic}$), 109.9 (d, $^2J_{PC}$ = 3.0, C of cym), 97.7 (d, $^2J_{PC}$ = 1.5, C of cym), 84.1 (d, $^2J_{PC}$ = 3.0, CH of cym), 84.0 (d, $^2J_{PC}$ = 3.8, CH of cym), 82.5 (d, $^2J_{PC}$ = 2.4, CHOH), 81.8 (d, $^2J_{PC}$ = 4.5, CH of cym), 80.3 (d, $^2J_{PC}$ = 3.8, CH of cym), 32.3 (s, CHMe_2), 24.3 and 23.7 (both s, CH*Me*), 19.5 (s, ArMe). Assignments confirmed by HSQC-^1H,^{13}C correlation. IR, ν_{OH}: 3447.

*Synthesis of [RuCl{κ^2(P,C)-2-Ph_2PC_6H_4CHOH}(η^6-1,3,5-C_6H_3Me_3)], **8c**.* Following a similar procedure, **8c** was prepared as a yellow solid using **6c** (0.150 g, 0.22 mmol). Yield: 0.083 g (69%). Anal. Found (calcd for $C_{28}H_{28}ClOPRu$): C, 61.29 (61.37); H, 5.20 (5.15). $^{31}P\{^1H\}$ NMR, C_6D_6, δ: 54.1 (s). ^1H NMR, C_6D_6, δ: 8.40−6.83 (m, 14 H, ArH), 5.78 (s, 1 H, C*H*OH), 4.81 (s, 1 H, $C_6H_3Me_3$), 1.94 (s, 9 H, Me), OH not observed. $^{13}C\{^1H\}$ NMR, C_6D_6, δ: 161.2−125.8 (m, $C_{aromatic}$), 97.2 (d, $^2J_{PC}$ = 2.9, C of $C_6H_3Me_3$), 84.9 (d, $^2J_{PC}$ = 3.4, CH of $C_6H_3Me_3$), 83.1 (d, $^2J_{PC}$ = 2.2, CHOH), 20.0 (s, Me).

*Synthesis of [RuCl{κ^2(P,C)-2-Ph_2PC_6H_4CHOH}(η^6-C_6Me_6)], **8d**.* Following a similar procedure, **8d** was prepared as a yellow solid using **6d** (0.150 g, 0.20 mmol). Yield: 0.092 g (78%). Anal. Found (calcd for $C_{31}H_{34}ClOPRu$): C, 63.46 (63.10); H, 6.09 (5.81). $^{31}P\{^1H\}$ NMR, C_6D_6, δ: 52.9 (s). ^1H NMR, C_6D_6, δ: 8.32−6.86 (m, 14 H, ArH), 5.10 (s, 1 H, C*H*OH), 1.94 (s, 18 H, C_6Me_6), OH not observed. $^{13}C\{^1H\}$ NMR, C_6D_6, δ: 162.2−125.9 (m, $C_{aromatic}$), 94.8 (d, $^2J_{PC}$ = 3.9, C_6Me_6), 87.2 (s, CHOH), 17.1 (s, C_6Me_6).

*Synthesis of [RuCl{κ^2(P,C)-2-Ph_2PC_6H_4C(Me)OH}(η^6-p-cymene)], **9b**.* Following a similar procedure, **9b** was prepared as a yellow solid using **7b** (0.150 g, 0.21 mmol). Yield: 0.078 g (65%). Anal. Found (calcd for $C_{30}H_{32}ClOPRu$): C, 62.82 (62.55); H, 5.23 (5.60). $^{31}P\{^1H\}$ NMR, C_6D_6, δ: 52.0 (s). ^1H NMR, C_6D_6, δ: 8.37−6.91 (m, 14 H, ArH), 5.32 and 5.30 (both d, 1 H each, $^3J_{HH}$ = 4.7, CH of cym), 4.33 and 4.21 (both d, 1 H each, $^3J_{HH}$ = 5.7, CH of cym), 2.51 (s, 3 H, Me), 2.25 (m, 1 H, C*H*Me_2), 1.91 (s, 3 H, ArMe), 1.31 and 1.24 (both d, 3 H each, $^3J_{HH}$ = 6.9, CH*Me*$_2$), OH not observed. $^{13}C\{^1H\}$ NMR, C_6D_6, δ: 163.8−124.7 (m, $C_{aromatic}$), 109.5 and 97.3 (both s, C of cym), 87.7 (d, $^2J_{PC}$ = 3.1, CH of cym), 87.6 (d, $^2J_{PC}$ = 2.3, *C*MeOH), 85.3 (d, $^2J_{PC}$ = 1.6, CH of cym), 83.8 (d, $^2J_{PC}$ = 5.5, CH of cym), 81.6 (d, $^2J_{PC}$ = 5.5, CH of cym), 32.7 (s, CHMe_2), 28.1 (s, C*Me*OH), 25.0 24.6 and 19.8 (all s, Me).

■ ASSOCIATED CONTENT

Supporting Information

CIF file and table giving crystallographic data for compound **6b**. Details on NMR spectroscopic data and DFT calculations. A text file of all computed molecule Cartesian coordinates in a format for convenient visualization. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00074.

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Notes

The authors declare no competing financial interest.

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(15) Chemical shift of the free phosphino-alcohol ligand **1** in $CDCl_3$ is $\delta = -15.6$ ppm ($\Delta\delta = 43.9$−46.5 ppm upon coordination).

(16) For the *p*-cymene complex (**3′b**), the presence of only two signals for the four CH hydrogen nuclei of the arene ring also supports the C_s-symmetry of the molecule.

(17) The diastereotopicity of these hydrogen nuclei is due to the generation of a stereogenic center on the ruthenium atom. In the case of **3″b**, the inequivalence of all four aromatic CH protons of the *p*-cymene ring also evidences the absence of symmetry.

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(20) The complexity of the ^{1}H and ^{13}C NMR spectra of [$RuCl_2${2-$Ph_2PC_6H_4CH$(Me)OH}(η^6-*p*-cymene)] recorded in $CDCl_3$, due to the presence of the three isomers mentioned, does not allow the assignment of all the signals. For this reason, its spectroscopic characterization is given exclusively in CD_3OD, in which it appears as [RuCl{κ^2(*P*,*O*)-2-$Ph_2PC_6H_4C$(Me)OH}(η^6-*p*-cymene)][Cl] as a 89:11 mixture of two diastereoisomers.

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(33) Key NMR data for [RuHCl{κ^1-(*P*)-$Ph_2PC_6H_4CH$(=O)}(η^6-*p*-cymene)] are the following: ^{31}P{^{1}H} NMR, δ: 49.3 (s). ^{1}H NMR (CD_2Cl_2), δ: −7.21 (d, 1 H, $^2J_{PH} = 54.4$ Hz, Ru-H), 10.7 (s, 1 H, HC(=O)), other signals overlapped by the resonances of **8b**. These NMR data compare well with those described in the literature for related [RuHCl(η^6-arene)(PR_3)] complexes. See for example: Chaplin, A. B.; Dyson, P. J. *Organometallics* **2007**, *26*, 4357−4360. Moreover, the multiplicity (i.e., singlet) and the chemical shift of the *H*C=O resonance support the presence of a phosphino-aldehyde ligand coordinated in a monodentate κ^1-(*P*) mode (see ref 5a).

(34) Approximately 5% of the dihydride complex [RuH_2{κ^1-(*P*)-$Ph_2PC_6H_4CH_2OH$}(η^6-*p*-cymene)] was also observed in the reaction mixture. The identity of this compound has been confirmed by preparing [RuH_2{κ^1-(*P*)-$Ph_2PC_6H_4CH_2OH$}(η^6-*p*-cymene)] through an alternative pathway in quantitative yield (see the Supporting Information). In addition, its NMR data compare well with those reported for other [$RuH_2(\eta^6$-arene)(PR_3)] species. See for example: Espino, G.; Caballero, A.; Manzano, B. R.; Santos, L.; Pérez-Manrique, M.; Moreno, M.; Jalón, F. A. *Organometallics* **2012**, *31*, 3087−3100.

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Organometallics 2015, 34, 3670–3677