ORGANOMETALLICS

Solvent-Dependent Hemilability of (2-Diphenylphosphino)Phenol in a Ru(II) para-Cymene System

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S Supporting Information

ABSTRACT: The addition of $Ph_2P(2-C_6H_4OH)$ to $[(\eta^6-p$ cymene)RuCl(μ -Cl)]₂ led to the formation of three distinct products, depending on the experimental conditions. The previously reported $[(\eta^6 - p - cymene) \text{RuCl} \{\kappa^2 P, O - \text{PPh}_2(2 - \rho - cymene)\}$ C_6H_4O]], 1, was obtained in 90% yield using MeOH as the solvent, in the presence of a base (Et₃N). Conversely, $[(\eta^6-p$ cymene)RuCl{ $\kappa^2 P, O$ -PPh₂(2-C₆H₄OH)}]Cl, [2]Cl, was afforded (88% yield) in MeOH without using the base. However, $[(\eta^6 \text{-}p\text{-}cymene)\text{RuCl}_2\{\kappa P\text{-}PPh_2(2\text{-}C_6H_4OH)\}], 3,$



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was the major species in chlorinated solvents. Compounds 1, [2]Cl, and 3 were characterized by analytical and spectroscopic (IR, NMR) methods. The X-ray structures of $[2]^+$ and 3 were determined, with the latter forming hydrogen bond dimeric units in the solid state. The dissolution of [2]Cl into a series of deuterated solvents, except methanol, led to rapid equilibration between [2]Cl and 3, revealing the hemilabile behavior of the phosphino-phenol ligand. According to Pulsed-Field Gradient Spin Echo (PGSE)-NMR and DFT studies, the dimeric nature of 3 persists in solution; thus, the hydrogen-bonding properties of MeOH are crucial to stabilize [2]Cl with respect to 3, with the latter being 3.4 kcal mol⁻¹ more stable than the former in the gas phase. Compound 1 underwent electrophilic additions by HCl, HBF4, and MeCOCl to give, respectively, [2]Cl (the reverse process being viable with Et₃N), [2]BF₄, and the ester $[(\eta^6-p-cymene)RuCl_2{\kappa P-PPh_2(2-C_6H_4OCOMe)}]$, 5. The reaction of 1 with AgNO₃ afforded the nitrate complex $[(\eta^6-p\text{-cymene})\text{Ru}(\text{NO}_3)\{\kappa^2 P, O\text{-PPh}_2(2\text{-}C_6\text{H}_4\text{O})\}]$, 4. Compounds [2]BF₄, 4, and 5 were isolated in the solid state in good to high yields and characterized by elemental analysis and IR and NMR spectroscopy.

INTRODUCTION

Hemilabile ligands play a prominent role in coordination chemistry, since their reversible binding to one metal site is crucial to the effectiveness of many metal mediated processes.¹ In this regard, a number of heteroditopic P,O-donors have been reported to behave as hemilabile ligands,² most of the examples being referred to phosphines containing an additional ether,³ carbonyl,^{2c-e,4} or phosphine-oxide functionality.^{2b,5} However, the hemilability properties of phosphino-alcohols have been much less developed, as a consequence of the increased acidity of the OH unit when approaching the metal center, thus facilitating the formation of stable metal-alkoxide derivatives via deprotonation.⁶ This process is even more favorable when dealing with phosphino-phenols, due to the superior acidity of the phenolic group.⁷ As a matter of fact, (2diphenylphosphino)phenol (Figure 1), i.e., a typical phosphino-phenol widely employed in coordination chemistry, is usually found in related complexes as its conjugate base, i.e., (2diphenylphosphino)phenolate. The presence in the latter of both soft (P) and hard (O) donor atoms enables firm binding of the anion to a variety of metal centers in different oxidation states,^{8,9} including main group elements¹⁰ and early late



Figure 1. Structure of (2-diphenylphosphino)phenol.

combination in heterobimetallic compounds.¹¹ It is noteworthy that complexes of various metals containing the $\kappa^2 P_{,O}$ -(2diphenylphosphino)phenolate ligand have been studied as catalysts for alkene oligomerization and polymerization,^{8a,c,12} hydroformylation,¹³ and hydrogenation reactions.^{9a,b} In this setting, examples of structurally characterized metal adducts containing non-deprotonated (2-diphenylphosphino)phenol,¹⁴ and more generally, a non-deprotonated phosphino-phenol, 6a,15 are exceedingly rare. These systems may show some hemilabile character of the P,O-ligand in solution, via reversible binding to the metal of the hydroxyl pendant.

Received: February 5, 2018

In the framework of our investigation on (η^{6} -arene)Ru(II)phosphine compounds as possible anticancer agents,¹⁶ herein we report on the synthesis and structural characterization of three compounds exhibiting distinct coordination modes of (2diphenylphosphino)phenol(ate). The uncommon hemilabile character of this ligand will be discussed with reference to variable experimental conditions, with the assistance of PGSE-NMR and DFT studies.

RESULTS AND DISCUSSION

Coordination of Ph₂P(4-C₆H₄OH) to $[(\eta^6-p-Cymene)-$ RuCl(μ -Cl)]₂. The reaction between (2-diphenylphosphino)-phenol and $[(\eta^6-p-cymene)RuCl(\mu-Cl)]_2$ resulted in the formation of three different products, depending on the experimental conditions (Scheme 1). The previously reported

Scheme 1. Different Modes of Incorporation and Bidentate P,O Coordination^{*a*}



^{*a*}(a-c) Different modes of incorporation of (2-diphenylphosphino)phenol within (η^{6} -*p*-cymene)Ru(II) compounds. (d) Bidentate *P*,*O* coordination of (2-diphenylphosphino)benzoic acid with release of HCl.

 $[(\eta^6\text{-}p\text{-}cymene)\text{RuCl}\{\kappa^2 P, O\text{-}PPh_2(2\text{-}C_6H_4O)\}], 1$, comprising the *P*,*O*-chelating phosphino-phenolate ligand, can be obtained in ca. 80% yield upon addition of the organic reactant to a suspension of $[(\eta^6\text{-}p\text{-}cymene)\text{RuCl}(\mu\text{-}Cl)]_2$ in MeOH in the presence of a base (Et₃N in the present work, Scheme 1a; Cs₂CO₃ according to the literature procedure).^{9a}

Performing the same reaction in the absence of a base, the unprecedented cationic derivative $[(\eta^6\text{-}p\text{-}cymene)\text{RuCl}\{\kappa^2P,O-\text{PPh}_2(2\text{-}C_6\text{H}_4\text{OH})\}]^+$, $[\mathbf{2}]^+$, featuring a *P*,*O*-chelating phosphino-phenol ligand, was isolated in 88% yield as its chloride salt, $[\mathbf{2}]\text{Cl}$ (Scheme 1b). For comparison, under analogous conditions, the more Brönsted acidic (2-diphenylphosphino)-benzoic acid coordinated as a bidentate phosphino-carboxylate ligand, with concomitant release of HCl (Scheme 1d).^{16d}

Furthermore, the neutral adduct with a κP -monodentate phosphine ligand, i.e., $[(\eta^6-p\text{-cymene})\text{RuCl}_2\{\kappa P\text{-PPh}_2(2\text{-})\}$

 $C_6H_4OH)$], **3**, was detected via NMR in solution upon reaction of $Ph_2P(2-C_6H_4OH)$ with $[(\eta^6-p-cymene)RuCl(\mu-Cl)]_2$ in chlorinated solvents, together with minor amounts of [**2**]Cl (Scheme 1c).

Compounds 1 and [2]Cl were isolated as orange-brown airstable solids and characterized by analytical and spectroscopic techniques. IR, NMR, and conductivity data are given in the Supporting Information; selected data are compiled in Table 1. The ³¹P resonance of the phosphine ligand within [2]Cl was found at ca. 45 ppm, slightly shifted with respect to 1 (50.2 ppm), whereas compound 3 displayed a signal at ca. 24 ppm; all these $\delta_{\rm P}$ values are considerably deshielded with respect to that of uncoordinated (2-diphenylphosphino)phenol ($\delta_{\rm P}$ = -27.8 ppm). Analogous ³¹P chemical shift separation ($\Delta \delta_P \approx 20-30$ ppm) between bidentate and monodentate coordination of (2diphenylphosphino)phenol(ate) to a given metal system can be found in the literature,^{8e,13,14b,17} the absolute δ_p values depending on the chemical environment. Compound 2[Cl], as well as 1, manifested distinct resonances for all ¹H and ¹³C nuclei belonging to the p-cymene ligand and for the two diastereotopic phenyl rings. Moving from 1 to its protonated counterpart, [2]Cl, the ¹H resonances related to the aromatic protons¹⁸ and the 1,2-disubstituted phenyl ring¹⁹ experienced deshielding ($\Delta \delta_{\rm H}$ = +0.2–0.3 ppm). Concerning ¹³C{¹H} spectra, the resonance belonging to the C-O atom moved upfield from 177.5 (1, phenoxide) to 165.3 ppm ($[2]^+$, phenol) while the corresponding ${}^{13}C - {}^{31}P$ coupling constant (${}^{1}J_{CP} =$ 50-55 Hz) became smaller with protonation. Such trends (including the ³¹P data discussed above) were previously observed for $(\eta^3$ -allyl)M (M = Ni, Pd) derivatives.^{14a} The ionic nature of [2]Cl in methanol was consistent with the observed high molar conductivity, approaching that of HCl in the same solvent (140-150 S·cm²·mol⁻¹), and the ³⁵Cl NMR spectrum, displaying a signal at -30 ppm accounting for the chloride anion.

The structures of $[2]^+$ and 3 were determined by X-ray diffraction studies on single crystals of $3 \cdot CH_3COCH_3$ and $3 \cdot [2]Cl$, the latter being a cocrystal of the two complexes. In particular, $3 \cdot [2]Cl$ contains neutral complex 3, which shows the same structure and bonding parameters as those found in $3 \cdot CH_3COCH_3$, and the cationic complex $[2]^+$, with Cl^- as counterion. Views of the structures are shown in Figures 2 and 3, while relevant bonding parameters are reported in Table 2. Hydrogen bonding parameters are summarized in Table 3.

Complexes $[2]^+$ and 3 adopt a typical three-leg piano-stool geometry,²⁰ and the bonding parameters around the Ru(II) center are similar to those previously reported for $[(\eta^6-p-cymene)RuCl_2(\kappa P-PR_3)]$ and related compounds.^{6,16a-d,21} The structure of the neutral complex 3, as found in both 3·CH₃COCH₃ and 3·[2]Cl, is closely related to those of the already reported $[(\eta^6-p-cymene)RuCl_2{\kappa P-PPh_3}]^{22}$ and $[(\eta^6-p-cymene)RuCl_2{\kappa P-PPh_3}]^{22}$ and $[(\eta^6-p-cymene)RuCl_2{\kappa P-PPh_2(4-C_6H_4CO_2H)}].^{23}$ Cation $[2]^+$ within 3·[2]Cl represents a rare example of $(\eta^6-arene)Ru$ complex with a $\kappa^2 P$,O-coordinated phosphino-alcohol;^{6b,24} by a different point of view, the chelating $\kappa^2 P$,O coordination exhibited here by (2-diphenylphosphino)phenol is rather uncommon (see the Introduction).^{14,25}

The presence of the OH group in the structures of both $[2]^+$ and 3 is confirmed by the occurrence of H-bonds involving the alcohol and chloride anions/ligands within the crystals of 3· CH₃COCH₃ and 3·[2]Cl (Table 3). In particular, in the solidstate structure of 3·CH₃COCH₃, dimers of 3 are present, generated by 2 equivalent intermolecular H-bonds involving the Table 1. Selected IR, NMR, and Conductivity Data for PPh₂(2-C₆H₄OH) and Ru Compounds 1, [2]X (X = Cl, BF₄), and 3-5

		IR		NMR ^b			
compound	coord. mode	$\tilde{v} \; (\mathrm{cm}^{-1})^{a}$	1 H(Ru-CH) δ (ppm)	¹³ C(C–O) δ (ppm)	$^{13}C(C-P)^{-1}J_{CP}^{-1}J_{CP}^{-1}$	³¹ P δ (ppm)	$\Lambda_{\rm m} \; ({\rm S}{\cdot}{\rm cm}^2{\cdot}{ m mol}^{-1})^{a}$
$PPh_2(2-C_6H_4OH)$		ν (OH): 3518w, 3232m-br	5 94 5 50 5 26 4 91	159.4	n.d.	-27.8	2 (CH CL)
1	к ² Р,О		(5.64, 5.40, 5.08, 4.81) $(4.74)^e$	177.5	55	50.7	2 (CH ₂ Cl ₂) 34 (MeOH)
[2]Cl	$\kappa^2 P, O(H)$	ν(OH): 3500–3400w-br	6.08, 5.81, 5.64, 5.13	165.3	51	44.6	154 (MeOH)
[2]BF ₄	$\kappa^2 P, O(H)$	ν (OH): 3500–3450w-br ν (BF ₄): 1056s-br	6.05, 5.80, 5.63, 5.12	166.1	51	45.0	25 (CH ₂ Cl ₂) 86 (MeOH)
3	κР		5.48, 4.85			23.9	
4	к ² Р,О	ν(NO ₃): ³⁶ 1471m, 1262s, 984m	5.68, 5.53, 5.04 (×2)	178.1	55	53.6	3 (CH ₂ Cl ₂) 91 (MeOH)
5	кР	ν(C=O): 1764s, 1750s. 1769 (CH ₂ Cl ₂)	5.22, 4.97	151.4 (C ^{Ar} –O) 168.2 (CO ₂)	41	21.8	

^{*a*}Solid-state IR data, unless otherwise specified. ^{*b*}Compounds 3–5 and PPh₂(2-C₆H₄OH) in CDCl₃ solutions; 1 and [2]X (X = Cl, BF₄) in CD₃OD solutions, except where otherwise noted. ^{*c*}Related to the 1,2-disubstituted aryl ring (C12 on Charts 1–5). ^{*d*}Measured on ca. 1 × 10⁻³ mol·L⁻¹ solutions. ^{*e*}CDCl₃ solution.

С



Figure 2. View of the structure of **3**. Displacement ellipsoids are at the 30% probability level. H atoms, except H(1), have been omitted for clarity.



Figure 3. View of the structure of the cation $[2]^+$ with the chloride anion Cl(2) as found in $3 \cdot [2]$ Cl. Displacement ellipsoids are at the 30% probability level. H atoms, except H(1), have been omitted for clarity. Since the cation $[2]^+$ cocrystallizes with 3, $[2]^+$ has been relabeled in Figure 3 respect to the corresponding cif file, in order to facilitate the comparison between $[2]^+$ and 3. The O(1)–H(1)···Cl(2) H-bond between the cation and anion is represented as a dashed line.

Table 2. Selected Bond	l Distances	(Å) and	Angles (deg) for 3
and [2] ⁺				

	3 ^{<i>a</i>}	3 ^b	[2] ⁺ ^b
$\operatorname{Ru}(1) - (\eta^6 - p - \text{cymene})_{av}$	2.21(2)	2.22(5)	2.21(5)
Ru(1)-P(1)	2.365(2)	2.361(7)	2.313(7)
Ru(1)-Cl(1)	2.405(2)	2.414(6)	2.399(6)
Ru(1)-Cl(2)	2.414(2)	2.403(6)	
Ru(1) - O(1)			2.071(17)
P(1)-C(11)	1.844(8)	1.85(2)	1.82(2)
P(1)-C(17)	1.846(8)	1.85(2)	1.84(3)
P(1)-C(23)	1.832(8)	1.81(2)	1.83(3)
C(12) - O(1)	1.375(10)	1.37(3)	1.36(3)
Cl(1)-Ru(1)-Cl(2)	85.10(7)	89.3(2)	
Cl(1)-Ru(1)-O(1)			84.7(5)
Cl(1)-Ru(1)-P(1)	88.72(8)	88.9(2)	87.6(2)
Cl(2)-Ru(1)-P(1)	87.37(7)	88.1(2)	
O(1)-Ru(1)-P(1)			80.4(5)
Ru(1)-P(1)-C(11)	113.7(3)	111.7(8)	100.3(8)
P(1)-C(11)-C(12)	119.8(6)	125.4(18)	114.5(17)
C(11)-C(12)-O(1)	117.1(7)	118(2)	119(2)
C(12) - O(1) - Ru(1)			121.4(15)
^a As found in 3·CH ₃ COCH	3. ^b As found i	n 3·[2]Cl.	

Table 3. Hydrogen Bonds for $[2]^+$ and 3: Distances (Å) and Angles (deg)

	3 ^{<i>a</i>}	3 ^b	[2] ^{+b}
O(1)-H(1)	0.84	0.83	0.84(2)
$H(1)\cdots Cl(2)$	2.19	1.89, 2.72	1.81(2), 2.55(12)
O(1)···Cl(2)	3.017(6)	2.71(2), 3.49(4)	2.62(3), 3.22(4)
$O(1)-H(1)\cdots Cl(2)$	167.3	172.7, 157.2	161(11), 137(15)

^{*a*}As found in $3 \cdot CH_3COCH_3$. Symmetry transformations used to generate equivalent atom Cl(2)#1: -x, -y + 1, -z + 1. ^{*b*}As found in $3 \cdot [2]Cl. Cl(2)$ is disordered over two positions.

OH groups and Cl(2) ligands of the two symmetry related (by an inversion center) molecules (Figure 4). Conversely, in the solid-state structure of $3 \cdot [2]$ Cl, both the OH groups of 3 and $[2]^+$ form H-bonds with the same chloride anion (Figure 5).

Equilibrium between [2]Cl and 3 in Solution: PGSE-NMR and DFT Studies. It is apparent from the previous section that the solvent plays a key role in the interaction



Figure 4. View of the hydrogen-bonded dimer of **3** as found in the crystal structure of $3 \cdot CH_3COCH_3$. Displacement ellipsoids are at the 30% probability level. H atoms, except H(1), have been omitted for clarity. The second molecule of the dimer is generated by an inversion center (symmetry transformation -x, -y + 1, -z + 1).



Figure 5. View of the hydrogen-bonds involving the OH groups of **3** and $[2]^+$ and the chloride anion, as found in the crystal structure of **3**·[2]Cl. Displacement ellipsoids are at the 30% probability level. H atoms, except those bonded to O atoms, have been omitted for clarity.

between (2-diphenylphosphino)phenol and $[(\eta^6-p\text{-cymene})-\text{RuCl}(\mu\text{-Cl})]_2$ (see Scheme 1 for details). In order to shed light on this point, [2]Cl was dissolved in a series of deuterated solvents (CD₃OD, CD₂Cl₂, CDCl₃, (CD₃)₂CO, CD₃CN) and the resulting solutions ($c_{\text{Ru,total}} = 17 \text{ mM}$) were analyzed by ¹H and ³¹P NMR (see the Experimental Section and Supporting Information). A rapid equilibration (t < 15 min)²⁶ between [2] Cl and **3** took place in all the solvents with the exception of CD₃OD and CD₃OD:D₂O 4:1 v/v,²⁷ where only [2]Cl was present (Scheme 2a/b). Compound 3 was the major species detected in (CD₃)₂CO (0.75 molar fraction), CDCl₃ (0.70), CD₂Cl₂ (0.65), and CD₃CN (0.40). A third species was identified in CD₃CN, featured by a chiral Ru atom and a monodentate phosphine ligand ($\delta_{\rm P}$ = 28.3 ppm), being presumably the CD₃CN monosolvate complex $[(\eta^6-p-cymene) \operatorname{RuCl}{\kappa P-PPh_2(2-C_6H_4OH)}(MeCN)]^+$ ([3-MeCN]⁺; Scheme 2c). Acetonitrile displacement of the coordinated oxygen donor belonging to $\kappa^2 P_1 O_2$ (2-diphenylphosphino)phenol was previously observed in $[Rh(CO)(PPh_3) \{\kappa^2 P, O-Ph_2 P(2 C_6H_4OH)$]⁺.^{14b} Our findings suggest that the hydrogenbonding properties of MeOH are crucial to stabilize the ionic species $[2]\hat{C}l$; otherwise, the Cl^- ion may substitute the phenolic group to give 3, thus determining a change in the coordination mode of the hemilabile phosphino-phenol ligand.

Additional NMR experiments and DFT calculations were performed, aiming to rationalize the factors affecting the equilibrium between [2]Cl and 3. On considering that 3 exists in the solid state as a hydrogen-bonded dimer (Figure 4), the presence of analogous adducts in solution was investigated. It should be mentioned here that self-aggregation of both neutral²⁸ and cationic Ru(II) *p*-cymene complexes²⁹ in solution was previously documented. Therefore, Pulsed-Field Gradient Spin Echo (PGSE) NMR³⁰ measurements were performed on mixtures of [2]Cl and 3 in CDCl₃, obtained by dissolution of pure [2]Cl at two different total concentrations ($c_{Ru,total} = 17$ and 77 mM, respectively, Table 4). At the lower concentration,

Table 4. Diffusion Coefficients ($10^{10} D_t$, $m^2 s^{-1}$), Average Hydrodynamic Radii ($r_{\rm H}$, Å), Volumes ($V_{\rm H}$, Å³), Aggregation Numbers (N), and Concentration (C, mM) for Compounds [2]Cl and 3 (in Equilibrium) in CDCl₃

compound	D_{t}	$r_{\rm H}$	$V_{\rm H}$	Ν	С
3 ^{<i>a</i>}	10.3	5.08	549	1.31	12
[2]Cl ^a	n.d.	n.d.	n.d.	n.d.	5
3 ^b	8.91	5.73	788	1.89	61
[2]Cl ^b	8.89	5.74	792	1.89	16

^aSpecies in equilibrium in the same solution; overall Ru concentration = 17 mM. ^bSpecies in equilibrium in the same solution; overall Ru concentration = 77 mM. n.d. = not determined.

the molar ratio between [2]Cl and 3 is 5:12, whereas at the higher concentration it is 16:61. The hydrodynamic volume $(V_{\rm H})$ of 3 was 549 Å³ at 12 mM, i.e., slightly larger than the

Scheme 2. Behaviour of [2]X (X = Cl, BF₄) in Different Solvents^{*a*}



 $a^{c}_{c_{Rutotal}}$ = ca. 16–17 mM. Equilibrium between [2]Cl and 3 (a), presence of [2]⁺ only (b), and formation of [3-MeCN]⁺ (c).



Figure 6. Optimized geometries of 3_{intr} [2]Cl, and 3_{ext} and corresponding energies (in kcal mol⁻¹) in gas phase and in different solvents. H…Cl hydrogen bond distances are in Å.

Scheme 3. Reactivity of 1 towards HX (X = F, Cl, BF₄), NH₄Y (Y = Cl, HF₂), CH₃Z (Z = COCl, I), and AgNO₃



corresponding van der Waals volume (418 Å³). Possible explanations for this discrepancy may be the presence of a small amount of dimer or the fact that in some cases the vdW volume underestimates the $V_{\rm H}$ of the isolated monomer $(V_{\rm H}^{\ 0})^{.31}$ At the higher concentration ($c_{Ru,total} = 77 \text{ mM}$; 61 mM for 3), V_H (3) increases up to 788 Å³, thus confirming the presence of a monomer-dimer equilibrium in solution. If 418 Å³ is taken as $V_{\rm H}^{\ 0}$, then the aggregation number values, i.e., the ratio N between $V_{\rm H}$ and $V_{\rm H}^{0}$, are 1.3 and 1.9 at the low and high concentrations, respectively. The measurement of $V_{\rm H}([2]{\rm Cl})$ was not possible in the more diluted solution ($c_{Ru,total} = 17 \text{ mM}$; 5 mM for [2]Cl because of the broadness of the corresponding signals. At a higher concentration ($c_{Ru,total} = 77$ mM; 16 mM for [2]Cl), it exhibited the same $V_{\rm H}$ value as 3, as expected when considering that [2]Cl and 3 are in rapid equilibrium and the PGSE NMR technique only provides average information. It must be considered that hydrodynamic radii of $\lfloor 2 \rfloor^+$ and 3 cannot be measured independently. In fact,

addition of $[R_4N]X$ (R = hexyl, X = Cl; R = Me, X = F) to solutions of [2]Cl in CDCl₃ did not increase the amount of 3 (see the Supporting Information for details). However, in $[2]BF_4$ (see onward) the anion is presumably weakly bound to the -OH moiety, thus allowing the formation of hydrogenbonded dimers and leaving the hydrodynamic ratio of the monomer $[2]^+$ undetermined.

DFT calculations were performed in order to evaluate the relative stability of [2]Cl and 3; DFT-optimized structures and ΔG values are reported in Figure 6. The geometry of 3 was optimized starting from the solid-state structure, leading to a local energy minimum in which the proton of the phosphine OH group points to the opposite direction with respect to ruthenium (3_{ext}). However, 3_{ext} is the most stable conformation only if a hydrogen-bonded dimer is formed (see X-ray and PGSE NMR results). In the isolated monomer, the OH can establish an intramolecular hydrogen bond with one of the chloride ligands, 3_{intr} leading to a conformation that is 10.0 kcal

mol⁻¹ more stable than 3_{ext} in terms of free energy in the gas phase. When the solvent is taken into account using a conductor-like polarizable continuum model (CPCM,³² see the Computational Details section), the ΔG between the two conformers decreases to 5.0, 4.4, 4.2, and 4.1 kcal mol⁻¹ in dichloromethane, acetone, methanol, and acetonitrile, respectively. For this reason, and since at the studied concentration the monomer is the most abundant species (see Diffusion NMR section), only 3_{int} will be considered in the following discussion.

Also, the geometry of [2]Cl was optimized, comprising a covalent Ru–O bond (2.14 Å) and a hydrogen bond between the anion and the OH group of the cation (1.73 Å). In [2]Cl, the hydrogen bond is shorter than in 3_{int} , since there are no geometrical constraints. Thus, the chloride can assume the most favorable position.

The free energy difference between 3_{int} and [2]Cl is 3.4 kcal mol⁻¹ in the gas phase, the former being more stable than the latter; nevertheless, such a value decreases in the presence of the solvent to 0.1, -0.2, -0.3, and -0.3 kcal mol⁻¹, in chloroform, dichloromethane, acetonitrile, and methanol, respectively (Figure 6). Considering the simplicity of our solvation model, these ΔG values can be considered within the computational error, but from the qualitative point of view our results justify the simultaneous presence in solution of 3_{int} and [2]Cl.³³

Reactivity of 1 toward Brönsted and Lewis Acids. In order to test the reactivity of the chelating (2-diphenylphosphino)phenolate ligand coordinated to the (η^{6} -*p*-cymene)Ru(II) unit, compound **1** was treated with a selection of Brönsted (HX, X = F, Cl, BF₄; NH₄Y; Y = Cl, HF₂) and Lewis (CH₃I, CH₃COCl) acids. The reaction with AgNO₃ as a chloride-abstracting agent was also considered (Scheme 3).

Compound 1 easily underwent protonation by aqueous HCl in MeOH affording [2]Cl (Scheme 3a); the process can be reversed at room temperature by treatment with Et₃N. Protonation of 1 with aqueous HBF_4 in MeOH gave [2] BF_4 (Scheme 3b), which was isolated in 77% yield as an orange solid. The main spectroscopic features of $[2]BF_4$ resemble those of [2]Cl (see the Supporting Information and Table 1). The $[BF_4]^-$ anion manifested itself with a strong IR absorption at 1056 cm⁻¹ in the solid state and by signals at -154.86 and -157.71 ppm in the ¹⁹F spectrum (for ¹¹B¹⁹F₄⁻ and ¹⁰B¹⁹F₄⁻, respectively). In the light of the dynamics found in solution for [2]Cl, the behavior of [2]BF₄ in a selection of deuterated solvents was studied by ¹H and ³¹P NMR. Unlike the chloride salt, $[2]BF_4$ was not modified in CD₂Cl₂, CDCl₃, (CD₃)₂CO, and CD₃OD (Scheme 2b), as expected upon replacement of the chloride with the less coordinating $[BF_4]^-$ anion.^{34,35} Accordingly, the molar conductivity of $[2]BF_4$ was high in both CH₂Cl₂ and MeOH and comparable to that of NaBF₄ in the latter solvent ($\Lambda_m \approx 90 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$). The ³¹P NMR spectrum displayed a singlet at ca. 45 ppm in all solvents except CD₃CN $(\delta_{\rm p} = 28.3 \text{ ppm})$, due to the presumable formation of $[(\eta^6 - p - \eta^6 - p - \eta^6)]$ cymene)RuCl{ κP -PPh₂(2-C₆H₄OH)}(MeCN)]BF₄, [3-MeCN BF_4 (Scheme 2c).

However, protonation of 1 by weaker Brönsted acids, such as $[NH_4]^+$ (as Cl⁻ or $[HF_2]^-$ salt) or aqueous HF in MeOH did not work, leading to quantitative recovery of the starting material 1 (Scheme 3c). Therefore, based on a simple acid–base model in aqueous solutions with HF as a reference Brønsted acid, the pK_a of 1 is expected to be lower than 3.2.³⁶

The reaction of $AgNO_3$ (as chloride acceptor) with 1 in methanol afforded the nitrato complex $[(\eta^6-p-cymene)Ru (NO_3){\kappa^2 P, O-PPh_2(2-C_6H_4O)}], 4$ (Scheme 3d and Table 1), isolated as a yellow-brown solid in 94% yield. Conversely, the former treatment of 1 with AgPF₆ in acetone yielded the solvato-complex, $[(\eta^6-p-cymene)Ru\{\kappa^2P,O-PPh_2(2-C_6H_4O)\}$ - $(\kappa O-Me_2CO)$]PF₆.^{9b} By comparison to precursor 1, the IR spectrum of 4 in the solid state showed additional medium to strong bands at 1471, 1262, and 984 cm⁻¹. These absorptions are typical of a coordinated nitrate ligand³⁷ and were already reported for other $Ru(\eta^6-arene)(\kappa O-NO_3)$ complexes.³⁸ Conductivity data suggest that 4 preserves its coordination sphere in CH_2Cl_2 solution, whereas $[NO_3]^-$ /solvent exchange occurs in MeOH ($\Lambda_m = 91$ S·cm²·mol⁻¹). The ¹⁴N NMR spectrum of 4 displayed one resonance at -3.2 ppm ($\Delta \nu_{1/2}$ = 18 Hz) in methanol and -10.2 ppm ($\Delta \nu_{1/2}$ = 69 Hz) in dichloromethane; the former value is comparable to that generated by NaNO₃ ($\delta_{\rm N}$ = -2.7 ppm; $\Delta \nu_{1/2}$ = 14 Hz) in the same solvent. On going from the chlorido (1) to the nitrato complex (4), both the ³¹P resonance ($\delta_P \approx 54$ ppm for 4) and ¹H signals belonging to the *p*-cymene ligand experience lowfield shifting (CD₃OD or CDCl₃ solutions).

Remarkably, compound 1 underwent straightforward addition of acetyl chloride in CH2Cl2 at room temperature, affording $[(\eta^6 - p - cymene) \operatorname{RuCl}_2 \{\kappa P - \operatorname{PPh}_2(2 - C_6 H_4 OCOMe)\}],$ 5 (Scheme 3e). The formation of 5 entails the activation of the Ru-phenolate bond,³⁹ the phenolate being converted into its acetyl ester. Compound 5 was isolated as an orange solid in 66% yield after purification with silica chromatography and then characterized by IR and NMR spectroscopy (CDCl₂) (see Table 1). A signal at 21.8 ppm was observed in the ${}^{31}P{}^{1}H$ NMR spectrum, in agreement with the change of the coordination mode of the phosphine ligand from bi- to monodentate ($\delta_{\rm P}$ = 50.7 ppm in 1). The ester moiety in 5 gave rise to new ¹³C resonances at 168.2 and 21.0 ppm due to the carbonyl and methyl carbons, respectively, as well as to a strong IR absorption at 1769 cm⁻¹ (CH₂Cl₂ solution). The ${}^{1}H$ spectrum of 5 showed two doublets at 5.22 and 4.98 for the aromatic CH of the *p*-cymene and a single set of signals for the two phenyl groups, due to the loss of chirality of the Ru center (with respect to the precursor 1).

In the light of the clean addition of acetyl chloride to 1, the reaction with another carbon electrophilic reagent, namely, methyl iodide, was attempted (Scheme 3f). Nevertheless, compound 1 was inert toward addition of MeI in MeOH or acetone. This seems consistent with the fact that the reverse reaction, i.e., demethoxylation of an *ortho*-phosphine-ether coordinated to a metal chloride, may be a favorable process, affording the corresponding $\kappa^2 P$,O chelate complex and CH₃Cl.^{8b,17a,25c,40}

CONCLUSIONS

Phosphino-phenols bearing two sites for metal binding in suitable positions are potential hemilabile ligands. Notwithstanding, this feature has been substantially undeveloped in coordination chemistry heretofore. However, ruthenium(II) arene compounds have been intensively investigated for their catalytic and medicinal applications, and in this light, hemilabile ligands may play important roles to activate specific synthetic and biological pathways.⁴¹

In the present manuscript, we have described the coordination of (2-diphenylphosphino)phenol to the $[(\eta^6-p-cymene)RuCl_2]$ frame, exhibiting unusual hemilabile character

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in a range of solvents, consisting in the competition for one metal site between the hydroxyl pendant and one chloride anion. The hemilability is quenched by introducing a non-coordinating counterion $([BF_4]^-)$ or by reaction with a base, resulting in a robust, bidentate binding to the metal of the phosphino-phenolate anion. Nevertheless, the phenolate moiety displays significant nucleophilic character, and thus appears to be easily derivatized via Ru–O bond cleavage, including the regeneration of the neutral phosphino-phenol unit. It must be remarked that the occurrence of hemilability for phosphino-phenol ligands under modulated conditions may open new perspectives in the chemistry and applications of Ru(II) arene compounds.

EXPERIMENTAL SECTION

General Experimental Details. RuCl₃·3H₂O (99.9%) was purchased from Strem, while all the other reactants were obtained from Alfa Aesar, Sigma-Aldrich, or TCI Europe, and were of the highest purity available. (2-diphenylphosphino)phenol (see the next section for the spectral characterization of the commercial compound) and acetyl chloride were stored under nitrogen as received. Compound $[(\eta^{6}\text{-}p\text{-}cymene)\text{RuCl}(\mu\text{-}Cl)]_{2}$ was prepared according to the literature.⁴² The syntheses of 1, 2[Cl], and 3 from (2-diphenylphosphino)phenol were carried out under a nitrogen atmosphere using standard Schlenk techniques and deareated solvents. The synthesis of 5 was performed under a nitrogen atmosphere using standard Schlenk techniques and CH₂Cl₂ distilled over CaH₂. All other operations were carried out in air with common laboratory glassware. Once isolated, the Ru compounds were air-stable in the solid state; [2]X (X = Cl, BF_4) and 5 were stored under nitrogen for precaution. Silica gel (Merck, 70-230 mesh) was used for column chromatography. NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. Chemical shifts (expressed in parts per million) are referenced to the residual solvent peaks⁴³ (¹H, ¹³C) or to external standard (¹⁴N to CH₃NO₂, ¹⁹F to CFCl₃, ³¹P to 85% H₃PO₄; ³⁵Cl to 1 M NaCl in D₂O).⁴⁴ Spectra were assigned with the assistance of ${}^{1}H{}^{31}P$, DEPT-135 spectra and ${}^{1}H{-}^{1}H$ (COSY), ${}^{1}H{-}^{13}C$ (gs-HSQC and gs-HMBC) correlation experiments.⁴⁵ CDCl₃ stabilized either with Ag foil (Carlo Erba) or Na₂CO₃ was used for NMR samples. Infrared spectra of solid samples were recorded on a PerkinElmer Spectrum One FT-IR spectrometer, equipped with a UATR sampling accessory. Infrared spectra of solutions were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer with a CaF₂ liquid transmission cell (4000-1000 cm⁻ range). IR spectra were processed with Spectragryph software.46 Carbon, hydrogen, and nitrogen analysis was performed on a Vario MICRO cube instrument (Elementar). Conductivity measurements were carried out at 21 °C using an XS COND 8 instrument (cell constant = 1.0 cm^{-1}). Molar conductivity of reference 1:1 electrolytes: NaBF₄, $\Lambda_{\rm m}$ (MeOH, $c = 4 \times 10^{-3}$ mol·L⁻¹) = 93 S·cm²·mol⁻¹; NaCl, $\Lambda_{\rm m}$ (MeOH, $c = 3 \times 10^{-3}$ mol·L⁻¹) = 85 S·cm²·mol⁻¹; HCl, $\Lambda_{\rm m}$ (MeOH, $c = 2 \times 10^{-3}$ mol·L⁻¹) = 140 S·cm²·mol⁻¹.

Synthesis and Characterization of Ruthenium Compounds. $[(\eta^{6}-p-Cymene)RuCl[\kappa^{2}P,O-PPh_{2}(2-C_{6}H_{4}O)]]$, **1** (Chart 1). The title compound was prepared according to a modified literature

Chart 1. Structure of 1^a



^aNumbering refers to carbon atoms.

procedure.^{9a} In a 25 mL Schlenk tube, PPh₂(2-C₆H₄OH) (328 mg, 1.18 mmol) and $[(\eta^6$ -*p*-cymene)RuCl₂]₂ (334 mg, 0.545 mmol) were suspended in MeOH (6 mL). Addition of Et₃N (0.20 mL, 1.43 mmol) afforded a dark red solution which was stirred for 1 h at room temperature. The progress of reaction was checked by TLC and ³¹P NMR, and volatiles were removed under vacuum. The residue was dissolved in CH₂Cl₂ (10 mL) and extracted with H₂O (3 × 20 mL). The organic phase was taken to dryness under vacuum, and the resulting solid was suspended in Et₂O. The blue-green Et₂O solution was separated by filtration, and the resulting orange solid was washed with Et₂O then dried under vacuum (40 °C). Yield: 480 mg, 80%. Alternatively, the compound was purified by silica chromatography; impurities were eluted with CH₂Cl₂ and a red band containing 1 was eluted with CH₂Cl₂:acetone 7:1 v/v.

Alternative Preparation. A solution of compound [2]Cl (50 mg, 0.086 mmol) in MeOH (4 mL) was treated with Et₃N (15 μ L, 0.11 mmol). The resulting dark red solution was stirred at room temperature for 1 h and the progress of reaction checked by ³¹P NMR. Compound 1 was isolated in 90% yield following the same workup procedure.

Compound 1 is soluble in MeOH, acetone, and chlorinated solvents and is insoluble in Et_2O and hexane. Anal. Calcd for $C_{28}H_{28}ClOPRu:$ C, 61.37; H, 5.15. Found: C, 61.7; H, 5.2. Spectroscopic (IR/NMR) and conductivity data are given in the Supporting Information.

 $[(\eta^6-p-Cymene)RuCl[\kappa^2P,O-PPh_2(2-C_6H_4OH)]]CI, [2]Cl (Chart 2).$ In a 25 mL Schlenk tube, PPh_2(2-C_6H_4OH) (209 mg, 0.751 mmol) and

Chart 2. Structure of [2]Cl^a



^aNumbering refers to carbon atoms.

 $[(\eta^{6}\text{-}p\text{-}\text{cymene})\text{RuCl}_{2}]_{2}$ (192 mg, 0.314 mmol) were suspended in MeOH (6 mL). The reaction mixture was stirred at room temperature for 1 h, affording an orange solution. The progress of reaction was checked by TLC and ³¹P NMR, and volatiles were removed under vacuum. The residue was suspended in Et₂O and then filtered, discarding the green Et₂O solution. The resulting orange-green/brown solid was washed with Et₂O, dried under vacuum (room temperature) and stored in N₂. Yield: 322 mg, 88%.

Alternative Preparation. A solution of compound 1 (55 mg, 0.10 mmol) in MeOH (3 mL) was treated with HCl (0.2 mol·L⁻¹ in H₂O; 0.50 mL, 0.10 mmol). The resulting dark red solution was stirred at room temperature for 1 h and the progress of reaction was checked by ³¹P NMR. Therefore, [2]Cl was isolated in 85% yield following the same workup procedure.

Compound [2]Cl is soluble in MeOH and is insoluble in Et₂O and hydrocarbons. Dissolution of [2]Cl in other solvents (e.g., acetone, dichloromethane, THF, chloroform) caused partial conversion to 3 (vide infra). Orange-brown solutions of [2]Cl in MeOH turned to green when kept for several days at room temperature with partial degradation of the starting material; X-ray quality crystals of $3 \cdot [2]Cl$ were obtained by slow evaporation of this solution. Anal. Calcd for $C_{28}H_{29}Cl_2OPRu: C, 57.54$; H, 5.00. Found: C, 57.1; H, 5.1. Spectroscopic (IR/NMR) and conductivity data are given in the Supporting Information.

 $\tilde{l}(\eta^6$ -p- $\tilde{C}ymene)RuCl{\kappa}^2P,O-PPh_2(2-C_6H_4OH))]BF_4$, [2]BF₄ (Chart 3). A solution of compound 1 (103 mg, 0.188 mmol) in MeOH (4 mL) was treated with HBF₄ (48% w/w in H₂O, 50 μ L, ca. 0.38 mmol), and the resulting dark red solution was stirred at room temperature for 1 h. The progress of reaction was checked by ³¹P NMR, and volatiles were removed under vacuum. The residue was dissolved in a few milliliters Chart 3. Structure of $[2]BF_4^{a}$



^aNumbering refers to carbon atoms.

of CH₂Cl₂, then Et₂O was added under vigorous stirring, leading to the precipitation of the title compound as an orange solid. The suspension was filtered; the solid was washed with Et₂O, dried under vacuum (room temperature), and stored under N₂. Yield: 92 mg, 77%. Compound [2]BF₄ is soluble in MeOH, acetone, and chlorinated solvents and is insoluble in Et₂O and hexane. Anal. Calcd for C₂₈H₂₉BClF₄OPRu: C, 52.89; H, 4.60. Found: C, 52.4; H, 4.6. Spectroscopic (IR/NMR) and conductivity data are given in the Supporting Information.

 $[(\eta^6-p-cymene)RuCl_2[\kappa P-PPh_2(2-C_6H_4OH)]]$, 3 (Chart 4). In a 25 mL Schlenk tube, PPh_2(2-C_6H_4OH) (68 mg, 0.24 mmol) was added





^aNumbering refers to carbon atoms.

to a brick-red solution of $[(\eta^6-p-\text{cymene})\text{RuCl}_2]_2$ (62 mg, 0.101 mmol) in CDCl₃ (5 mL), and the reaction mixture was stirred at room temperature for 1 h. ¹H and ³¹P{¹H} NMR spectra of the resulting orange solution revealed the formation of a mixture of [2]Cl and 3 in 25:75 molar ratio; NMR data for 3 in this solution are given in the Supporting Information. Compound 3 is sensitive to the impurities formed in aged CDCl₃ solutions; stabilized CDCl₃ is required for NMR analysis. Then volatiles were removed under vacuum, and the resulting orange solid was washed with Et₂O and dried under vacuum (40 °C). The reaction was then repeated in CD_2Cl_2 , with a similar outcome. These solid materials isolated from solutions containing both [2]Cl and 3 were not characterized by CHN analysis and NMR spectroscopy; indeed, [2]Cl and 3 have the same formula (C28H29Cl2OPRu) and will immediately re-equilibrate when dissolved in a solvent for NMR analysis. However, X-ray quality crystals of 3. CH₃COCH₃ were collected from an acetone solution of this solid layered with petroleum ether and settled aside at -20 °C.

 $[(\eta^6-p-Cymene)Ru(NO_3)\{\kappa^2P,O-PPh_2(2-C_6H_4O)\}]$, **4** (Chart 5). A solution of compound **1** (76 mg, 0.14 mmol) in MeOH (3 mL) was treated with AgNO₃ (25 mg, 0.15 mmol). The mixture was stirred at





^aNumbering refers to carbon atoms.

room temperature under protection from the light for 1.5 h affording a red-orange solution and colorless solid (AgCl). The suspension was filtered on a small pad of Celite, and the filtrate solution was taken to dryness under vacuum. The residue was dissolved in CH₂Cl₂, and the resulting solution was filtered on a small pad of Celite. The title compound was obtained from the filtrate solution as a foamy yellow-brown solid after volatiles were removed under vacuum (40 °C). Yield: 75 mg, 94%. Compound 4 is soluble in MeOH and chlorinated solvents and insoluble in Et₂O and hexane. Partial degradation with formation of a green soluble derivative was observed upon contact of the solid with commercial BHT-stabilized Et₂O. Anal. Calcd for C₂₈H₂₈NO₄PRu: C, 58.53; H, 4.91; N, 2.44. Found: C, 58.2; H, 4.9; N, 2.4. Spectroscopic (IR/NMR) and conductivity data are given in the Supporting Information.

 $[(\eta^6-p-cymene)RuCl_2[\kappa P-PPh_2(2-C_6H_4OC(=O)Me)]]$, **5** (Chart 6). In a 25 mL Schlenk tube, acetyl chloride (50 μ L, 0.70 mmol) was

Chart 6. Structure of 5^a



^aNumbering refers to carbon atoms.

added to a solution of compound 1 (88 mg, 0.16 mmol) in CH_2Cl_2 (6 mL). The resulting red solution was stirred at room temperature for 22 h, and the progress of reaction was checked by ³¹P NMR. Therefore, Et₃N (0.10 mL, 0.72 mmol) was added; the reaction mixture was stirred for 10 min then extracted with H_2O (3 \times 20 mL). HCl generated by excess acetyl chloride upon air exposition is detrimental to the Ru compound. Adding NaHCO3 in the aqueous phase during the extraction step is not sufficient. Volatiles were removed under vacuum from the organic phase; the residue was dissolved in CH₂Cl₂ and loaded on top of a silica column (d = 1 cm, h = 5 cm). Impurities were eluted with CH2Cl2 then a red band was eluted with CH2Cl2:acetone 9:1 v/v. Volatiles were removed under vacuum, and the residue was dissolved in few mL of CH₂Cl₂. Addition of Et₂O (2 mL) followed by hexane under vigorous stirring caused the precipitation of the title compound as an orange solid. The suspension was filtered; the solid was washed with hexane, dried under vacuum (40 °C) and stored under N2. Yield: 66 mg, 66%. Compound 5 is soluble in acetone and chlorinated solvents, poorly soluble in Et₂O and insoluble in hexane and H_2O . Anal. Calcd for $C_{30}H_{31}Cl_2O_2PRu$: C, 57.51; H, 4.99. Found: C, 57.4; H, 5.1. Spectroscopic (IR/NMR) data are given in the Supporting Information. Compound 5 is sensitive to the impurities formed in aged CDCl₃ solutions; stabilized CDCl₃ is required for NMR analysis.

Attempted Reactions of 1 with NH₄Cl, NH₄[HF₂], HF, and Mel. A dark red solution of 1 (50 mg, 0.091 mmol) and the selected compound (NH₄Cl: 34 mg, 0.64 mmol; NH₄[HF₂]: 10 mg, 0.19 mmol; HF ca. 1 M in H₂O: 0.15 mL, ca. 0.15 mmol) in MeOH (5 mL) was stirred at room temperature for 20 h. Aliquots were periodically taken for ³¹P{¹H} NMR analysis (C₆D₆ capillary), revealing that protonation of Ru–P,O did not occur [δ /ppm = 51.4]. Therefore, volatiles were removed under vacuum, and the residue was suspended in CH₂Cl₂. The suspension was filtered over a small pad of Celite, and volatiles were removed under vacuum from the filtrate solution. The resulting orange solid was identified as pure starting material 1 by ¹H and ³¹P NMR spectroscopy (CH₃OD). Reactions with MeI (25 μ L, 0,40 mmol) in MeOH or acetone (5 mL) were carried out under protection from the light following an analogous procedure.

Behavior of [2]X (X = Cl, BF_4) in Different Solvents: NMR Study. General Procedure. Compound [2]X (X = Cl, BF_4 ; 5.0 mg) was dissolved in the selected deuterated solvent (0.5 mL; $c_{R_{11}} = 10$ g. L^{-1} corresponding to 17 and 16 mM for [2]Cl and [2]BF₄, respectively) at room temperature. The solutions were subsequently analyzed by ¹H and ³¹P{¹H} NMR spectroscopy (t < 15 min).²⁶ Molar ratios of Ru compounds were calculated on ¹H signals for analogous CH or CH₃ groups of the *p*-cymene ligand. Results are presented in Scheme 2; NMR data for each solution are given in the Supporting Information.

[2]Cl. (CD₃)₂CO, CD₂Cl₂, and CDCl₃: orange-red solutions, containing [2]Cl and 3 (Scheme 2a). [2]Cl/3 molar ratio = 25:75 ((CD₃)₂CO), 35:65 (CD₂Cl₂), 30:70 (CDCl₃). CD₃OD and CD₃OD/ D₂O 4:1 v/v: orange-green solutions; no other Ru species besides [2] Cl was identified (Scheme 2b). No changes in the NMR spectra of the CD₃OD/D₂O 4:1 v/v solution were observed after 48 h at room temperature. CD₃CN: orange-yellow solution, containing a third Ru product identified as $[(\eta^6-p-cymene)RuCl{\kappa P-PPh_2(2-C_6H_4OH)}-(MeCN)]Cl, [3-MeCN]Cl (Scheme 2c). [2]Cl/3/[3-MeCN]Cl molar ratio = 30:40:30.$

[2]BF₄. CD₃OD, (CD₃)₂CO, CD₂Cl₂, and CDCl₃: orange solutions. No other Ru species beside [2]BF₄ was identified (Scheme 2b). CD₃CN: orange solution turning to yellow within minutes, with quantitative formation of $[(\eta^6-p-cymene)RuCl{\kappa P-PPh_2(2-C_6H_4OH)}(MeCN)]BF_4$, [3-MeCN]BF₄ (Scheme 2c) and other minor products.

Diffusion NMR Measurements. ¹H diffusion NMR measurements were performed by using the double-stimulated echo sequence with longitudinal eddy current delay at 298 K without spinning.⁴⁸ The dependence of the resonance intensity (I) on a constant waiting time and on a varied gradient strength G is described by the following equation:

$$\ln \frac{I}{I_0} = (\gamma \delta)^2 D_t \left(\Delta - \frac{\delta}{3} \right) G^2$$

where I is the intensity of the observed spin echo, I_0 is the intensity of the spin echo in the absence of gradient, D_t is the self-diffusion coefficient, Δ is the delay between the midpoints of the gradients (0.2 s), δ is the length of the gradient pulse (4 ms), and γ is the magnetogyric ratio. The shape of the gradients was rectangular, and their strength G was varied during the experiments.

The self-diffusion coefficient, D_v was estimated by evaluating the proportionality constant for a sample of HDO (5%) in D₂O (known diffusion coefficients in the range 274–318 K)⁴⁹ under the exact same conditions as the samples of interest. The solvent or TMS was taken as internal standard. The hydrodynamic volume of the species has been calculated from the experimental value of D_t through the procedure previously described.³⁰⁶

Computational Studies. All the geometries were optimized with ORCA 3.0.3,⁵⁰ using the BP86 functional⁵¹ in conjunction with an augmented triple- ζ quality basis set. The dispersion corrections were taken into account using the Grimme D3-parametrized XC functionals.⁵² The energies of the optimized geometries were evaluated by the M062X functional⁵³ and the same basis set. All the structures were confirmed to be local energy minima (no imaginary frequencies).

X-ray Crystallography. Crystal data and collection details for 3-CH₃COCH₃ and 3·[2]Cl are reported in Table S2. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON100 detector using Mo K α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).⁵⁴ The structures were solved by direct methods and refined by full-matrix least-squares based on all data using $F^{2.55}$ Hydrogen atoms were fixed at calculated positions and refined by a riding model. H(1) was preliminarily located in the difference map and, then, refined isotropically by a riding model. The correct location of H(1) is further supported by the presence of H-bonds. All nonhydrogen atoms were refined with anisotropic displacement parameters. The quality of the crystals of $3 \cdot [2]$ Cl is very low. Thus, the data have been cut at Θ = 23.898°, and some high-residual electron densities remain close to the heavy Ru atoms. These maxima are located in positions which are not realistic for any atom, and they are series termination errors which are common with heavy atoms such as Ru, especially when the quality of the crystals is low. Nonetheless, the fact that the structure and bonding parameters of 3, as found in $3 \cdot [2]$ Cl and $3 \cdot CH_3COCH_3$ are rather similar, suggests that also the structure of [2]Cl is reliable. The presence of hydrogens on the O atoms is confirmed by the formation of hydrogen bonds with the Cl-atoms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00071.

IR and NMR spectra of Ru compounds 1-5 (PDF) Computed Cartesian coordinates of all of the molecules reported in this study (XYZ)

Accession Codes

CCDC 1817661–1817662 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The University of Pisa is gratefully acknowledged for financial support.

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