ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 3955–3965 3955
DOI: 10.1021/om1006227

Arene−Ruthenium(II) Complexes Containing Amino−Phosphine Ligands as Catalysts for Nitrile Hydration Reactions

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Received June 29, 2010

Three different series of novel mononuclear arene-ruthenium(II) complexes containing amino-phosphine ligands, namely, $[RuCl_2\{\kappa^1(P)\text{-}2\text{-}Ph_2PC_6H_4CH_2NHR\}(\eta^6\text{-arene})]$, $[RuCl_2\{\kappa^1(P)\text{-}3\text{-}Ph_2PC_6H_4CH_2NHR\}(\eta^6\text{-arene})]$, and $[RuCl_2\{\kappa^1(P)\text{-}4\text{-}Ph_2PC_6H_4CH_2NHR\}(\eta^6\text{-arene})]$ (arene = C_6H_6, *p*-cymene, 1,3,5-$C_6H_3Me_3$, C_6Me_6; R = ^{i}Pr, ^{t}Bu; all combinations), have been synthesized and fully characterized. These readily accessible species are efficient catalysts for the selective hydration of organonitriles into amides under challenging reaction conditions, i.e., pure aqueous medium in the absence of any cocatalyst, being much more active than their corresponding nonfunctionalized triphenylphosphine counterparts $[RuCl_2(PPh_3)(\eta^6\text{-arene})]$. The results obtained in this study indicate that the (amino-phosphine)ruthenium(II) complexes operate through a "bifunctional catalysis" mechanism in which the ruthenium center acts as a Lewis acid, activating the nitrile molecule, and the P-donor ligand acts as a Brønsted base, the pendant amino group generating the real nucleophile of the hydration process, i.e., the OH^- group.

Introduction

Hydration of nitriles is one of the most appealing routes presently available for the large-scale production of amides, which are versatile synthetic intermediates used in the manufacture of several pharmacological products, polymers, detergents, lubricants, and drug stabilizers.[1] As an example, hydration of acrylonitrile produces annually more than 2×10^5 tons of acrylamide, representing the main industrial route for this chemical.[2,3] Traditionally, these hydration processes have been catalyzed by strong acids and bases under harsh conditions, methods that are not compatible with many sensitive functional groups.[4] In addition, the base-catalyzed reactions usually cause overhydrolysis of the amides into the corresponding carboxylic acids, a kinetically favored reaction compared to the hydration one (see Scheme 1).[1,4] Although under acidic conditions it is possible to stop the process at the amide stage, in these cases it is necessary to control carefully the temperature and stoichiometry employed in order to avoid the formation of polymeric side products.[5] It is also important to note that, from an industrial perspective, the final neutralization step required in either the acid- or base-catalyzed reactions leads to extensive salt formation with inconvenient product contamination and pollution effects.

To circumvent all these limitations, several protocols using enzymes,[2,6] heterogeneous catalysts,[7] and transition-metal complexes[8] have been developed. In particular, a large variety of homogeneous catalysts highly selective toward amide formation have been described,[9] with Murahashi's ruthenium dihydride $[RuH_2(PPh_3)_4]$,[10] Parkins's platinum hydride $[PtH(PMe_2OH)\{(PMe_2O)_2H\}]$,[11] the acetylacetonate complex *cis*-$[Ru(acac)_2(PPh_2py)_2]$,[12] and the Rh(I)-based system $[\{Rh(\mu\text{-OMe})(cod)\}_2]/PCy_3$ (cod = 1,5-cyclooctadiene),[9h] showing remarkable activities under mild conditions. In

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(1) See, for example: (a) *The Chemistry of Amides*; Zabicky, J., Ed.; Wiley: New York, 1970. (b) *The Amide Linkage: Structural Significance in Chemistry, Biochemistry and Materials Science*; Greenberg, A.; Breneman, C. M.; Liebman, J. F., Eds.; Wiley: New York, 2000. (c) *Polyesters and Polyamides*; Deopura, B. L.; Gupta, B.; Joshi, M.; Alagirusami, R., Eds.; CRC Press: Boca Raton, 2008. (d) Johansson, I. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 2004; Vol. *2*, pp 442−463.

(2) Yamada, H.; Kobayashi, M. *Biosci., Biotechnol., Biochem.* **1996**, *60*, 1391.

(3) Hydration of 3-cyanopyridine and adiponitrile into nicotinamide and 5-cyanovaleramide, respectively, are other relevant examples of the industrial applications of this process. See: van Pelt, S.; van Rantwijk, F.; Sheldon, R. A. In *Focus in Catalysis Applications* (supplement to Chim. Oggi **2008**, 26); pp 2−4.

(4) See, for example: (a) Bailey, P. D.; Mills, T. J.; Pettecrew, R.; Price, R. A. In *Comprehensive Organic Functional Group Transformations II*; Katritzky, A. R.; Taylor, R. J. K., Eds.; Elsevier: Oxford, 2005; Vol. *5*, pp 201−294. (b) *Methoden Org. Chem.* (*Houben Weyl*); Dopp, D.; Dopp, H., Eds.; Thieme Verlag: Stuttgart, 1985; Vol. *E5* (2), pp 1024−1031.

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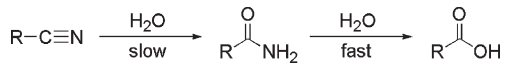
Published on Web 08/03/2010

Scheme 1. Nitrile Hydration and Amide Hydrolysis Reactions



addition to these examples, all operating in organic media, some metal complexes able to promote selective nitrile hydrations directly in water have also been disclosed, mainly thanks to the use of hydrosoluble ligands or surfactants.[13]

From a mechanistic point of view, although different reaction pathways have been proposed for these metal-catalyzed transformations, coordination of the nitrile to the metal is a common prerequisite for all of them.[8−13] In this way, the C≡N unit becomes more electrophilic and susceptible to nucleophilic attack by water (or the hydroxyl group if basic conditions are used), thus improving the kinetics of the hydration process versus the hydrolysis (see Scheme 1). Recent work has also suggested that this nucleophilic addition step can be facilitated by the presence of functionalized ligands able to activate the water molecule via hydrogen bonding (see Figure 1).[9m,12,13a,g,i] Such a cooperative effect of the ligand represents a new example of the so-called "bifunctional catalysis"; that is, the metal ion acts as a Lewis acid and the ligand as a Lewis base, a concept largely exploited in homogeneous catalysis during the last years.[14]

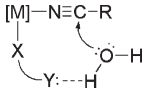


Figure 1. Cooperative effect of the ligand.

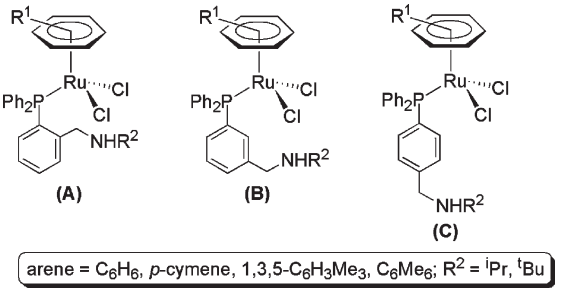


Figure 2. Structure of the (η^6-arene)-Ru(II) complexes synthesized in this work.

With this mechanistic idea in mind, and continuing with our interest in this key catalytic transformation,[13g,i] we wondered about the potential of (η^6-arene)-Ru(II) complexes **A**−**C**, containing readily accessible amino-phosphine ligands (Figure 2), as catalysts for the selective hydration of nitrile to amides.[15] We reasoned that, while the presence of a pendant amino group on these P-donor ligands would ensure the activation of the water molecule via hydrogen bonding, the exact location of the amino substituent on the aromatic ring should drastically affect the efficiency of these catalysts, conditioning the effective approach of the activated hydrogen-bonded water molecule to the coordinated nitrile. In this way, very useful information on the real operativity of a bifunctional catalysis mechanism could be easily gained experimentally. Results from this study are presented herein.

Results and Discussion

Synthesis of the Amino-phosphine Ligands. Amino-phosphine ligands **7**−**9a**,**b** have been synthesized following classical

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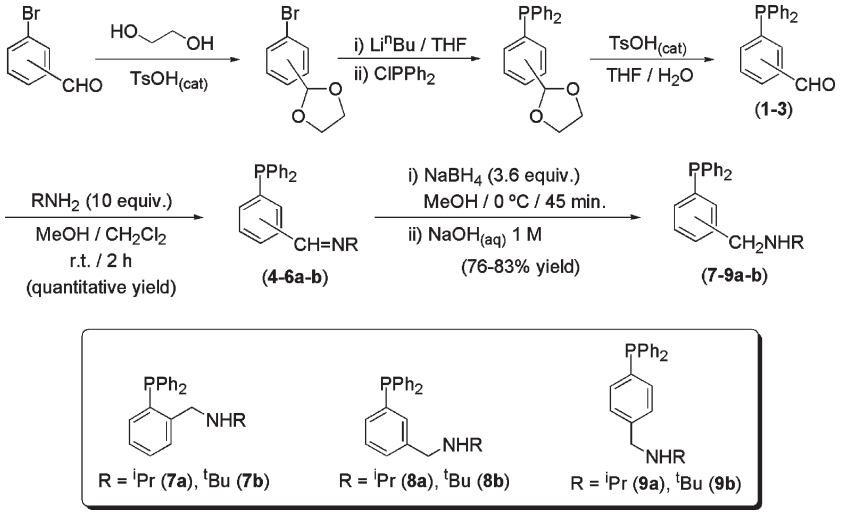
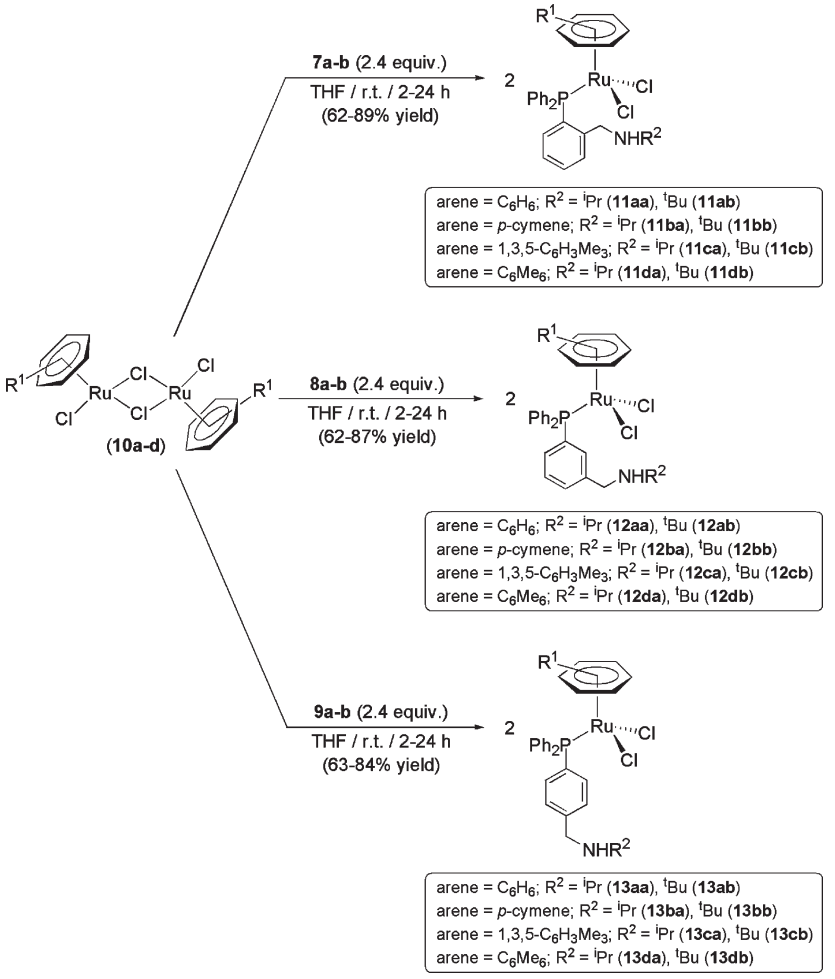
Scheme 2. General Procedure for the Preparation of Amino-phosphine Ligands 7−9a,b



Scheme 3. Synthesis of the Mononuclear (η^6-Arene)ruthenium(II) Complexes 11aa−13db



methodologies (see Scheme 2),[16] based on the condensation of known (formylphenyl)diphenylphosphines **1**−**3**[17] with isopropylamine or *tert*-butylamine. In this way, the corresponding phosphine-substituted Schiff bases **4**−**6a**,**b** were quantitatively formed and subjected to reduction of the C═N bond by means

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of $NaBH_4$/MeOH, thus affording the desired amino-phosphines **7**−**9a**,**b** as air-stable, pale yellow oils in 62−89% yield. Characterization of the novel compounds 3-$Ph_2PC_6H_4CH{=}NR$ (**5a**,**b**), 4-$Ph_2PC_6H_4CH{=}NR$ (**6a**,**b**), 3-$Ph_2PC_6H_4CH_2NHR$ (**8a**,**b**), and 4-$Ph_2PC_6H_4CH_2NHR$ (**9a**,**b**) was straightforward following their analytical and spectroscopic data (details are given in the Experimental Section). Significant features are (i) ($^{31}P\{^1H\}$ NMR) the presence of a singlet signal at ca. −5 ppm, (ii) (^1H NMR) the appearance of singlet or broad resonances at ca. 8 (**5**−**6a**,**b**) and 4 ppm (**8**−**9a**,**b**), respectively, attributed to the iminic CH=N and methylenic CH_2N protons, and (iii) ($^{13}C\{^1H\}$ NMR) the presence of characteristic singlet signals at *ca.* 155 (**5**−**6a**,**b**) and 51 (**8**−**9a**,**b**) ppm for the iminic and methylenic carbons, respectively.

Synthesis of the Arene-ruthenium(II) Complexes. The ability of dimers [{RuCl(μ-Cl)(η^6-arene)}$_2$] to form mononuclear ruthenium(II) species of general composition [$RuCl_2$(η^6-arene)L] (L = 2e$^-$ donor ligand) via cleavage of the chloride bridges is well known.[18] In accord, we have found that the reaction of [{RuCl(μ-Cl)(η^6-arene)}$_2$] (arene = C_6H_6 (**10a**),[19] *p*-cymene (**10b**),[20] 1,3,5-$C_6H_3Me_3$ (**10c**),[21] C_6Me_6 (**10d**)[20]) with 2.4 equiv of the amino-phosphine ligands **7**−**9a**,**b**, in tetrahydrofuran at room temperature, leads to the selective formation of the novel mononuclear Ru(II) derivatives **11aa**−**13db** (see Scheme 3).

Complexes **11aa**−**13db**, isolated as air-stable orange solids in 62−89% yield, are soluble in polar solvents, such as dichloromethane, chloroform, THF, alcohols, and even water (ca. 1 mg/mL), and insoluble in *n*-alkanes and diethyl ether. The formulation proposed for these species is based on analytical data, as well as IR and multinuclear NMR ($^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$) spectroscopy (details are given in the Experimental Section). In particular, the $^{31}P\{^1H\}$ NMR spectra of all these derivatives exhibit a singlet resonance (δ 23.7−33.4 ppm) strongly deshielded with respect to that of the corresponding free amino-phosphine ($\Delta\delta$ = 29−39 ppm), thus supporting the selective P-coordination of the ligands to ruthenium. Their ^1H and $^{13}C\{^1H\}$ NMR spectra are also consistent with the proposed structures, showing the expected resonances for the corresponding amino-phosphine and η^6-coordinated arene groups. At this point, we must note that, although the N−H proton of the amino-phosphine ligands was not detected in any case by ^1H NMR spectroscopy, the presence of this group was confirmed by the appearance of a characteristic ν(N−H) absorption band at 3174−3317 cm^{-1} in the IR spectra.

Moreover, the structure of the *p*-cymene complexes [$RuCl_2\{\kappa^1(P)$-2-$Ph_2PC_6H_4CH_2NH^tBu\}(\eta^6$-*p*-cymene)] (**11bb**), [$RuCl_2\{\kappa^1(P)$-3-$Ph_2PC_6H_4CH_2NH^tBu\}(\eta^6$-*p*-cymene)] (**12bb**), and [$RuCl_2\{\kappa^1(P)$-4-$Ph_2PC_6H_4CH_2NH^tBu\}(\eta^6$-*p*-cymene)] (**13bb**) could be unequivocally confirmed by means of X-ray diffraction methods. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into saturated solutions of these compounds in dichloromethane. ORTEP views of the molecules, along with selected structural parameters, are shown in Figures 3−5. The unexpected protonation of the amino group of **11bb** by traces of HCl present in dichloromethane occurred during crystallization, and consequently the structure of the corresponding ammonium salt [$RuCl_2\{\kappa^1(P)$-2-$Ph_2PC_6H_4CH_2NH_2^tBu\}(\eta^6$-*p*-cymene)]-[Cl] (**11bb·HCl**) was obtained (Figure 3). The three molecules exhibit an usual pseudooctahedral three-legged pianostool geometry around the metal with values of the interligand angles Cl(1)−Ru−P(1), Cl(2)−Ru−P(1), and Cl(1)−Ru−Cl(2), and those between the centroid of the *p*-cymene ring C* and the legs, typical of a pseudo-octahedron. The observed N(1)−C(29) and N(1)−C(30) bond distances (1.446(5)−1.530(3) Å) fall also within the expected range for a nitrogen−carbon (sp^3) single bond.[22]

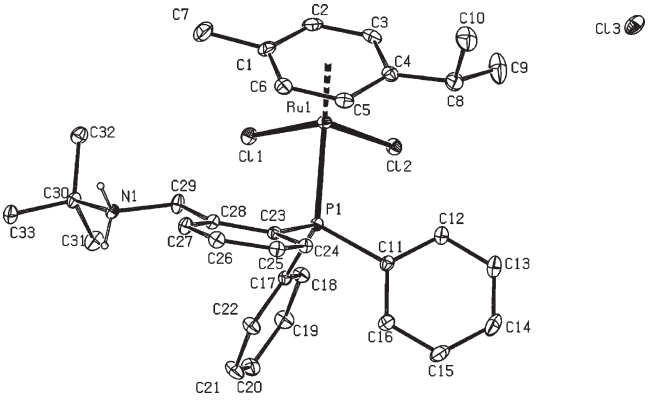

Figure 3. ORTEP-type view of the structure of complex **11bb·**HCl showing the crystallographic labeling scheme. Hydrogen atoms, except those on N(1), have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Ru−C* = 1.7179(2); Ru−Cl(1) = 2.4025(8); Ru−Cl(2) = 2.4061(7); Ru−P(1) = 2.3743(7); C(29)−N(1) = 1.489(4); N(1)−C(30) = 1.530(3); C*−Ru−Cl(1) = 124.09(2); C*−Ru−Cl(2) = 126.21(2); C*−Ru−P(1) = 128.579(18); Cl(1)−Ru−Cl(2) = 85.42(3); Cl(1)−Ru−P(1) = 89.61(2); Cl(2)−Ru−P(1) = 90.11(2); C(11)−P(1)−C(17) = 97.88(12); C(11)−P(1)−C(23) = 103.38(12); C(11)−P(1)−Ru(1) = 116.74(10); C(17)−P(1)−C(23) = 105.49(12); C(17)−P(1)−Ru(1) = 120.82(9); C(23)−P(1)−Ru(1) = 110.46(8); C(28)−C(29)−N(1) = 113.5(2); C(29)−N(1)−C(30) = 117.1(3). C* denotes the centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

Complexes **11aa**−**13db** were further studied by means of cyclic voltammetry (CV). Two independent electrochemical processes were in all cases observed (representative cyclic voltammograms are shown in Figure 6). The first oxidation wave observed in the voltammograms, which corresponds to the oxidation of the amino group,[23] is irreversible and disappears after successive scans, while the second one is reversible, or quasi-reversible, and corresponds to the Ru^{2+}/Ru^{3+}

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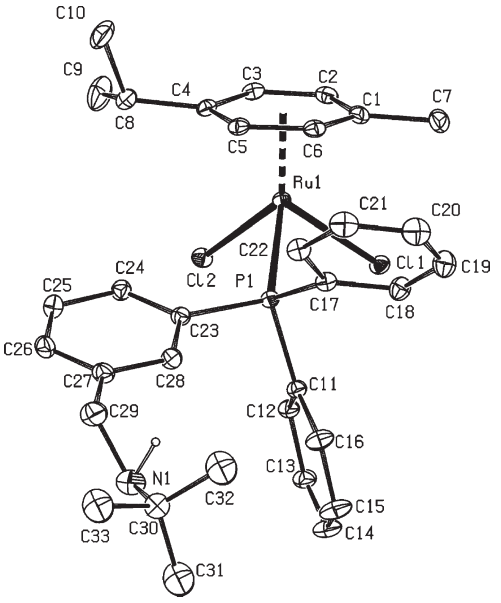

Figure 4. ORTEP-type view of the structure of complex **12bb** showing the crystallographic labeling scheme. Hydrogen atoms, except that on N(1), have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Ru−C* = 1.7114(2); Ru−Cl(1) = 2.4090(7); Ru−Cl(2) = 2.4232(7); Ru−P(1) = 2.3743(7); C(29)−N(1) = 1.448(7); N(1)−C(30) = 1.500(7); C*−Ru−Cl(1) = 124.72(2); C*−Ru−Cl(2) = 126.31(2); C*−Ru−P(1) = 127.945(19); Cl(1)−Ru−Cl(2) = 88.63(3); Cl(1)−Ru−P(1) = 86.39(2); Cl(2)−Ru−P(1) = 90.27(3); C(11)−P(1)−C(17) = 104.18(15); C(11)−P(1)−C(23) = 101.64(14); C(11)−P(1)−Ru(1) = 120.08(10); C(17)−P(1)−C(23) = 104.55(15); C(17)−P(1)−Ru(1) = 107.76(11); C(23)−P(1)−Ru(1) = 116.97(10); C(27)−C(29)−N(1) = 114.3(4); C(29)−N(1)−C(30) = 116.2(5). C* denotes the centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

redox system. Formal potentials ($E^{\circ\prime}$) of the latter, given versus the $[Cp_2Fe]/[Cp_2Fe]^+$ redox couple,[24] are collected in Table 1. In complete accord with the increasing electron-releasing properties of the arene ring, within the three series of complexes studied, $E^{\circ\prime}$ values decrease in the sequence C_6H_6 > *p*-cymene ≈ 1,3,5-$C_6H_3Me_3$ > C_6Me_6. Similar trends have been previously reported for related (η^6-arene)ruthenium(II)

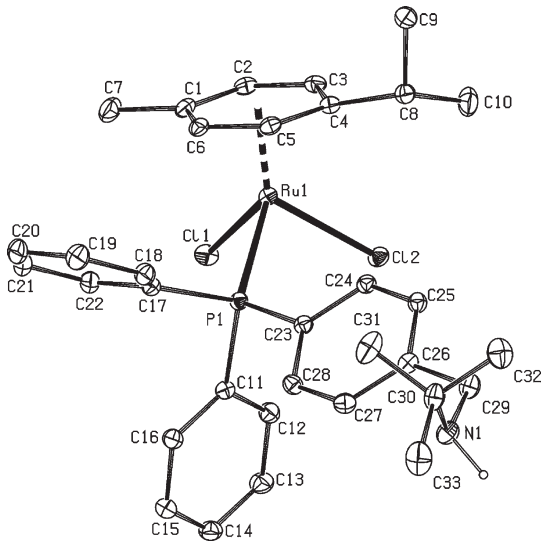

Figure 5. ORTEP-type view of the structure of complex **13bb** showing the crystallographic labeling scheme. Hydrogen atoms, except that on N(1), have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Ru−C* = 1.7235(2); Ru−Cl(1) = 2.4061(7); Ru−Cl(2) = 2.4236(7); Ru−P(1) = 2.3606(7); C(29)−N(1) = 1.446(5); N(1)−C(30) = 1.479(5); C*−Ru−Cl(1) = 124.87(2); C*−Ru−Cl(2) = 127.65(2); C*−Ru−P(1) = 128.800(18); Cl(1)−Ru−Cl(2) = 87.67(3); Cl(1)−Ru−P(1) = 85.89(3); Cl(2)−Ru−P(1) = 88.36(2); C(11)−P(1)−C(17) = 101.87(13); C(11)−P(1)−C(23) = 101.41(13); C(11)−P(1)−Ru(1) = 121.86(9); C(17)−P(1)−C(23) = 105.92(13); C(17)−P(1)−Ru(1) = 108.53(10); C(23)−P(1)−Ru(1) = 115.48(9); C(26)−C(29)−N(1) = 115.0(3); C(29)−N(1)−C(30) = 117.8(3). C* denotes the centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

complexes.[25] These observations are also consistent with theoretical studies that indicate that the HOMO energy level decreases when substituting Me by H in an arene−metal complex.[26] It is also worthy of note that the exact location of the CH_2NHR substituent on the aromatic ring of the P-donor ligands exerts some influence on the formal potentials of these complexes, those derived from the *para*-substituted phosphines being, in general, more easily oxidized than their *meta*- and *ortho*-substituted counterparts (in the order $E^{\circ\prime}_{para}$ < $E^{\circ\prime}_{meta}$ < $E^{\circ\prime}_{ortho}$).

Catalytic Hydration of Nitriles in Aqueous Medium. The catalytic potential of the novel (η^6-arene)ruthenium(II) complexes **11aa**−**13bd** was then evaluated using the hydration of benzonitrile into benzamide as model reaction. In a typical experiment, the ruthenium precursor (5 mol % of Ru) was added to a 0.33 M aqueous solution of benzonitrile and the mixture heated in an oil bath at 100 °C. The course of the reaction was monitored by regular sampling and analysis by gas chromatography (GC). The results obtained are summarized in Table 2.

All complexes synthesized proved to be active catalysts in this transformation, providing benzamide as the unique reaction product (benzoic acid was not detected by GC in the crude reaction mixtures) in 43−99% GC yield after 24 h of heating (entries 1−24). Among them, complexes [$RuCl_2$-{κ^1(*P*)-2-$Ph_2PC_6H_4CH_2NH^tBu$}(η^6-C_6Me_6)] (**11db**), [$RuCl_2$-{κ^1(*P*)-3-$Ph_2PC_6H_4CH_2NH^tBu$}(η^6-1,3,5-$C_6H_3Me_3$)] (**12cb**), and [$RuCl_2${κ^1(*P*)-4-$Ph_2PC_6H_4CH_2NH^iPr$}(η^6-*p*-cymene)]

(23) Related irreversible oxidations were observed when cyclic voltammograms of *N*-isopropylbenzylamine (E_{pa} = 1.72 V) and *N*-benzyl-*tert*-butylamine (E_{pa} = 1.81 V) were run under identical experimental conditions.

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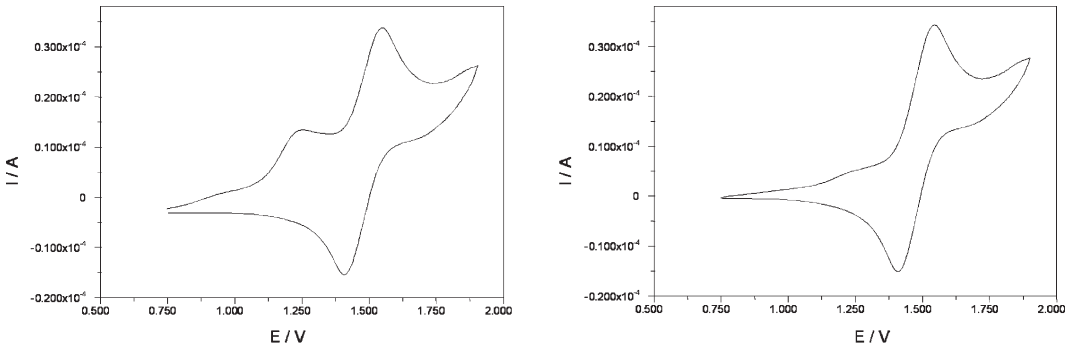


Figure 6. Cyclic voltammograms obtained for $[RuCl_2\{\kappa^1(P)\text{-}2\text{-}Ph_2PC_6H_4CH_2NH^iPr\}(\eta^6\text{-}C_6H_6)]$ (**11aa**) after one (left) and three successive scans (right). Measured at 0.1 V s^{-1} in dichloromethane with a 0.03 M solution of $[^nBu_4N][PF_6]$ as the supporting electrolyte.

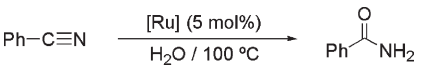
Table 1. Electrochemical Data for Complexes 11aa−13db[a]

complex	$E^{\circ\prime}$ (V)[b]	i_{pa}/i_{pc}	ΔE_p (mV)	complex	$E^{\circ\prime}$ (V)[b]	i_{pa}/i_{pc}	ΔE_p (mV)
11aa	1.27	0.8	125	**12ca**	1.07	1.0	95
11ab	1.30	0.8	161	**12cb**	0.94	1.0	165
11ba	1.12	0.8	202	**12da**	0.82	0.8	162
11bb	1.07	0.8	168	**12db**	0.78	0.8	161
11ca	1.18	0.8	156	**13aa**	1.06	1.0	150
11cb	1.09	0.9	147	**13ab**	0.99	1.0	164
11da	0.97	0.9	146	**13ba**	0.95	1.1	162
11db	0.91	0.8	144	**13bb**	0.91	1.0	144
12aa	1.14	1.0	137	**13ca**	0.95	1.0	162
12ab	1.10	1.0	156	**13cb**	0.96	1.2	171
12ba	0.99	1.0	162	**13da**	0.78	1.0	155
12bb	0.95	1.0	168	**13db**	0.80	1.1	232

[a] Measured at 0.1 V s^{-1} in dichloromethane with a 0.03 M solution of $[^nBu_4N][PF_6]$ as the supporting electrolyte. [b] Formal potentials ($E^{\circ\prime}$) are referenced relative to the potential of the $[Cp_2Fe]/[Cp_2Fe]^+$ couple (E° = 0.21 V) run under identical conditions ($E^{\circ\prime} = E^\circ(Ru^{III}/Ru^{II}) - E^\circ(Fe^{III}/Fe^{II})$).

(**13ba**) showed the best performances, generating benzamide in >90% yield after only 7 h (entries 8, 14, and 19, respectively). Although those complexes derived from the *ortho*-substituted phosphines $2\text{-}Ph_2PC_6H_4CH_2NHR$ (entries 1−8) are in general less active than their *meta*- (entries 9−16) and *para*-substituted counterparts (entries 17−24),[27] no direct relationships between the structure or electronic nature of these species and their catalytic activity become really evident from the data obtained. Solubility grounds do not explain the reactivities observed since homogeneity of the aqueous phase was in all cases observed.[28a,b]

Table 2. Ruthenium-Catalyzed Hydration of Benzonitrile in Water[a]



entry	catalyst	yield (%)[b]	entry	catalyst	yield (%)[b]
1	**11aa**	65 (96)	19	**13ba**	93 (97)
2	**11ab**	23 (75)	20	**13bb**	83 (95)
3	**11ba**	34 (65)	21	**13ca**	83 (95)
4	**11bb**	34 (77)	22	**13cb**	84 (93)
5	**11ca**	13 (43)	23	**13da**	62 (88)
6	**11cb**	47 (81)	24	**13db**	56 (84)
7	**11da**	61 (85)	25	**14a**	21 (45)
8	**11db**	92 (99)	26	**14b**	11 (45)
9	**12aa**	85 (96)	27	**14c**	10 (21)
10	**12ab**	61 (79)	28	**14d**	24 (48)
11	**12ba**	89 (97)	29	**14a**[c]	61 (85)
12	**12bb**	77 (95)	30	**14a**[d]	35 (55)
13	**12ca**	88 (96)	31	**14b**[c]	28 (62)
14	**12cb**	94 (97)	32	**14b**[d]	52 (77)
15	**12da**	46 (75)	33	**14c**[c]	45 (80)
16	**12db**	76 (98)	34	**14c**[d]	44 (86)
17	**13aa**	72 (87)	35	**14d**[c]	52 (95)
18	**13ab**	44 (70)	36	**14d**[d]	46 (89)

[a] Reactions performed under N_2 atmosphere at 100 °C using 1 mmol of benzonitrile (0.33 M in water). Substrate/Ru ratio: 100/5. [b] Yield after 7 h of heating (yield after 24 h in parentheses). In both cases, yields are reported as uncorrected GC areas. [c] Reactions performed in the presence of 5 mol % of $PhCH_2NH^iPr$. [d] Reactions performed in the presence of 5 mol % of $PhCH_2NH^tBu$.

Interestingly, when the related triphenylphosphine-Ru(II) complexes $[RuCl_2(PPh_3)(\eta^6\text{-arene})]$ (arene = C_6H_6 (**14a**),[19] *p*-cymene (**14b**),[19] 1,3,5-$C_6H_3Me_3$ (**14c**),[29] C_6Me_6 (**14d**)[30]) were used as catalysts under identical reaction conditions, benzamide was formed in remarkably lower yields (21−48% after 24 h; entries 25−28).[28c] This fact clearly evidences that a cooperative effect of the amino-phosphine ligands is taking place. However, since the position of the amino susbtituent in the aromatic ring (*ortho*, *meta*, or *para*) does not exert a marked influence on the catalytic activity, such a cooperative effect of the amino-functionalized ligands **7**−**9a**,**b** seems to be unrelated to the effective approach of the nucleophilic water molecule to the coordinated nitrile, via hydrogen bonding. On the other hand, we have also observed that the effectiveness of $[RuCl_2(PPh_3)(\eta^6\text{-arene})]$ (**14a**−**d**) is greatly improved

(27) Formation of a stable six-membered chelate ring by intramolecular coordination of the pendant amino group to ruthenium could be responsible for this behavior. In the case of complex $[RuCl_2\{\kappa^1(P)\text{-}2\text{-}Ph_2PC_6H_4CH_2NH^tBu\}(\eta^6\text{-}C_6Me_6)]$ (**11db**), one of the most active catalysts found in this study, such a chelation process is sterically disfavored by the presence of the bulky η^6-coordinated hexamethylbenzene and the *tert*-butyl substituent on the amino-phosphine ligand.

(28) (a) A two-phase system (water/organic products) is observed, the reaction taking place probably at the interface. (b) We note that the addition of surfactants does not improve the catalytic activity of these complexes. On the contrary, it significantly decreases. For example, in the presence of sodium dodecyl sulfate and cetyltrimethylammonium bromide (0.05 M solutions), complex $[RuCl_2\{\kappa^1(P)\text{-}3\text{-}Ph_2PC_6H_4CH_2NH^tBu\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (**12cb**) (5 mol %) generates benzamide in only 58% and 60% GC yield, respectively, after 24 h of heating at 100 °C (to be compared with entry 14 in Table 2). (c) Complexes $[RuCl_2(PPh_3)(\eta^6\text{-arene})]$ (**14a**−**d**) are completely insoluble in water at room temperature, but they become partially soluble at 100 °C. Therefore, unlike the case of amino-phosphine derivatives **11aa**−**13db**, the aqueous phase during the catalytic reactions using $[RuCl_2(PPh_3)(\eta^6\text{-arene})]$ (**14a**−**d**) is not completely homogenous, and consequently, solubility issues cannot be completely discarded to explain the different reactivities observed.

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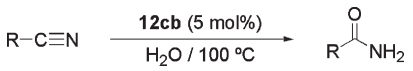
Table 3. Catalytic Hydration of Nitriles in Water Using Complex 12cb[a]



entry	substrate	yield after 7 h (%)[b]	yield after 24 h (%)[b]
1	R = Ph	94	97 (84)
2	R = 2-C_6H_4F	48	90 (79)
3	R = 3-C_6H_4Cl	77	99 (87)
4	R = 4-C_6H_4Cl	64	94 (80)
5	R = 3-C_6H_4Br	87	99 (88)
6	R = 3-$C_6H_4NO_2$	89	99 (90)
7	R = 4-$C_6H_4CO_2Et$	50	83 (70)
8	R = 3-C_6H_4OMe	71	98 (86)
9	R = C_6F_5	92	99 (90)
10	R = 3-pyridyl	98	99 (88)
11	R = CH_2-4-C_6H_4Cl	90	99 (91)
12	R = CH_2-2-Thienyl	96	99 (87)
13	R = $(CH_2)_2OPh$	81	89 (74)
14	R = *n*-C_5H_{11}	41	55 (40)
15	R = (*E*)-CH=CHPh	53	80 (72)

[a] Reactions performed under N_2 atmosphere at 100 °C using 1 mmol of the corresponding nitrile (0.33 M in water). Substrate/Ru ratio: 100/5. [b] Yields are reported as uncorrected GC areas (isolated yields are given in parentheses).

when the catalytic reactions are performed in the presence of 5 mol % of *N*-isopropylbenzylamine or *N*-benzyl-*tert*-butylamine (entries 29−36), i.e., in basic media. Consequently, we can conclude that the beneficial effect of the coordinated amino-phosphines **7**−**9a**,**b** is more likely related with the activation of water by deprotonation, thus generating in the reaction media the more nucleophilic hydroxyl group.[31]

Using the most active complex [$RuCl_2\{\kappa^1(P)$-3-$Ph_2PC_6H_4CH_2NH^tBu\}(\eta^6$-1,3,5-$C_6H_3Me_3$)] (**12cb**), the generality of this catalytic transformation was also evaluated (see Table 3). Thus, as observed for benzonitrile (entry 1), other aromatic (entries 2−9) and heteroaromatic (entry 10) substrates could be selectively converted into the corresponding amides (83−99% GC yields) after 24 h of heating, regardless of the position and electronic nature of the substituents present in the aromatic ring. Common functional groups (halide, nitro, ester, ether) were tolerated, and no overhydrolysis to carboxylic acids was observed, thus demonstrating the wide scope and synthetic utility of this procedure. Subsequent purification by column chromatography on silica gel provided analytically pure samples of the corresponding amides in 70−88% isolated yields. As shown in entries 11−15, this aqueous process is not restricted to aromatic organonitriles, the hydration of substrates containing alkyl- and alkenyl-CN bonds being also conveniently achieved under the standard reaction conditions. However, we must note that in the case of the aliphatic derivative hexanenitrile (entry 14) only a modest yield of hexanamide could be reached (55% by CG).

Conclusions

In summary, in this work three series of novel arene-ruthenium(II) complexes containing amino-phosphine ligands, namely, [$RuCl_2\{\kappa^1(P)$-2-$Ph_2PC_6H_4CH_2NHR\}(\eta^6$-arene)] (**11aa**−**11db**), [$RuCl_2\{\kappa^1(P)$-3-$Ph_2PC_6H_4CH_2NHR\}(\eta^6$-arene)] (**12aa**−**12db**), and [$RuCl_2\{\kappa^1(P)$-4-$Ph_2PC_6H_4CH_2NHR\}(\eta^6$-arene)] (**13aa**−**13db**), have been synthesized. These readily accessible species are efficient catalysts for the selective conversion of organonitriles into amides under challenging reaction conditions, i.e., pure aqueous medium in the absence of any cocatalyst, being much more active than their corresponding nonfunctionalized triphenylphosphine counterparts [$RuCl_2(PPh_3)(\eta^6$-arene)]. Experimental results seem to indicate that complexes **11aa**−**13db** operate through a "bifunctional catalysis" mechanism in which the ruthenium center acts as a Lewis acid, activating the nitrile molecule, and the amino-phoshine ligand acts as a Brønsted base, the pendant amino group generating the real nucleophilic species of the process, i.e., the OH^- group.

Experimental Section

Synthetic procedures 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 and used without further purification with the exception of compounds 2-$Ph_2PC_6H_4CHO$ (**1**),[17a,c] 3-$Ph_2PC_6H_4CHO$ (**2**),[17d] 4-$Ph_2PC_6H_4CHO$ (**3**),[17b] 2-$Ph_2PC_6H_4CH$=N^iPr (**4a**),[16a,c] 2-$Ph_2PC_6H_4CH$=N^tBu (**4b**),[16a,c] 2-$Ph_2PC_6H_4CH_2NH^iPr$ (**7a**),[16d] 2-$Ph_2PC_6H_4CH_2NH^tBu$ (**7b**),[16b,e] [{RuCl(μ-Cl)(η^6-arene)}$_2$] (arene = C_6H_6 (**10a**),[19] *p*-cymene (**10b**),[20] 1,3,5-$C_6H_3Me_3$ (**10c**),[21] C_6Me_6 (**10d**)[20]), and [$RuCl_2(PPh_3)(\eta^6$-arene)] (arene = C_6H_6 (**14a**),[19] *p*-cymene (**14b**),[19] 1,3,5-$C_6H_3Me_3$ (**14c**),[29] C_6Me_6 (**14d**)[30]), which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX300 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 standard. DEPT experiments have been carried out for all the compounds reported in this paper.

Synthesis of Imino-phosphines 3-$Ph_2PC_6H_4CH$=NR (R = ^{i}Pr (5a), ^{t}Bu (5b)) and 4-$Ph_2PC_6H_4CH$=NR (R = ^{i}Pr (6a), ^{t}Bu (6b)). A solution of the corresponding diphenylphosphinobenzaldehyde (**2**, **3**; 0.50 g, 1.72 mmol) in 20 mL of a MeOH/CH_2Cl_2 mixture (1:1 v/v) was treated, at room temperature, with the appropriate primary amine (17 mmol) for 2 h. Volatiles were then removed under vacuum, yielding phosphino-imines **5**−**6a**,**b** as colorless oils in quantitative yield. **5a:** Anal. Calcd for $C_{22}H_{22}NP$: C, 79.74; H, 6.69; N, 4.23. Found: C, 79.65; H, 6.84; N, 4.37. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.4 (s) ppm. ^{1}H NMR ($CDCl_3$): δ 1.27 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CHMe_2), 3.54 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, C*H*Me$_2$), 7.32−7.89 (m, 14H, CH_{arom}), 8.25 (s, 1H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.3 (s, CHMe_2), 61.7 (s, *C*HMe$_2$), 127.0−135.6 (m, CH_{arom} and C_{arom}), 157.9 (s, CH=N) ppm. **5b:** Anal. Calcd for $C_{23}H_{24}NP$: C, 79.97; H, 7.00; N, 4.06. Found: C, 80.15; H, 7.12; N, 4.17. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.9 (s) ppm. ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 9H, CMe_3), 7.29−7.98 (m, 14H, CH_{arom}), 8.22 (s, 1H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.4 (s, CMe_3), 57.3 (s, *C*Me$_3$), 127.7−138.0 (m, CH_{arom} and C_{arom}), 154.5 (s, CH=N) ppm. **6a:** Anal. Calcd for $C_{22}H_{22}NP$: C, 79.74; H, 6.69; N, 4.23. Found: C, 79.58; H, 6.87; N, 4.40. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.4 (s) ppm. ^{1}H NMR ($CDCl_3$): δ 1.37 (br, 6H, CHMe_2), 3.62 (br, 1H, C*H*Me$_2$), 7.39−7.81 (m, 14H, CH_{arom}), 8.36 (s, 1H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.4 (s, CHMe_2), 61.8 (s, *C*HMe$_2$), 128.1−134.1 (m, CH_{arom} and C_{arom}), 157.8 (s, CH=N) ppm. **6b:** Anal. Calcd for $C_{23}H_{24}NP$: C, 79.97; H, 7.00; N, 4.06. Found: C, 80.10; H, 7.19; N, 4.23. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.4 (s) ppm. ^{1}H

(31) pH measurements on 0.016 M aqueous solutions of complexes **11aa**−**13db** (the same concentration used in the catalytic experiments) confirm this hypothesis. The values obtained, ranging from 7.12 to 7.37, indicate that when dissolved in water **11aa**−**13db** are able to generate a slightly basic media.

NMR ($CDCl_3$): δ 1.19 (s, 9H, C*Me*$_3$), 7.41−7.83 (m, 14H, CH_{arom}), 8.36 (s, 1H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.9 (s, C*Me*$_3$), 57.3 (s, *C*Me$_3$), 127.9−140.0 (m, CH_{arom} and C_{arom}), 154.7 (s, CH=N) ppm.

Synthesis of Amino-phosphines 3-Ph$_2$PC$_6$H$_4$CH$_2$NHR (R = ^{i}Pr (8a), ^{t}Bu (8b)) and 4-Ph$_2$PC$_6$H$_4$CH$_2$NHR (R = ^{i}Pr (9a), ^{t}Bu (9b)). A solution of the corresponding imino-phosphine (**5**−**6a**,**b**; 1.5 mmol) in 20 mL of methanol was treated by $NaBH_4$ (0.208 g, 5.5 mmol) at 0 °C for 45 min. The reaction was then quenched with aqueous NaOH (5 mL, 1 M), the organic layer was extracted with dichloromethane (3 × 15 mL), and the combined phases were dried over $MgSO_4$. Solvent removal under reduced pressure afforded amino-phosphines **8**−**9a**,**b** as pale yellow oils. **8a:** Yield: 0.400 g (80%). Anal. Calcd for $C_{22}H_{24}NP$: C, 79.25; H, 7.26; N, 4.20. Found: C, 79.33; H, 7.39; N, 4.41. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.4 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.10 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 2.84 (m, 1H, C*H*Me$_2$), 3.79 (br, 2H, CH_2), 7.19−7.38 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.9 (s, CH*Me*$_2$), 48.0 (s, *C*HMe$_2$), 51.4 (s, CH_2), 128.5−132.3 (m, CH_{arom} and C_{arom}) ppm. **8b:** Yield: 0.395 g (76%). Anal. Calcd for $C_{23}H_{26}NP$: C, 79.51; H, 7.54; N, 4.03. Found: C, 79.67; H, 7.59; N, 4.12. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.3 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.16 (s, 9H, CMe$_3$), 3.72 (br, 2H, CH_2), 7.12−7.38 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.6 (s, C*Me*$_3$), 47.5 (s, CH_2), 51.2 (s, *C*Me$_3$), 128.8−134.2 (m, CH_{arom} and C_{arom}) ppm. **9a:** Yield: 0.415 g (83%). Anal. Calcd for $C_{22}H_{24}NP$: C, 79.25; H, 7.26; N, 4.20. Found: C, 79.41; H, 7.15; N, 4.33. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −6.2 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.24 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 3.02 (m, 1H, C*H*Me$_2$), 3.95 (br, 2H, CH_2), 7.47−7.88 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.1 (s, CH*Me*$_2$), 48.4 (s, *C*HMe$_2$), 51.3 (s, CH_2), 128.4−143.0 (m, CH_{arom} and C_{arom}) ppm. **9b:** Yield: 0.412 g (79%). Anal. Calcd for $C_{23}H_{26}NP$: C, 79.51; H, 7.54; N, 4.03. Found: C, 79.59; H, 7.65; N, 4.17. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.1 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.28 (s, 9H, CMe$_3$), 3.83 (br, 2H, CH_2), 7.36−7.45 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.4 (s, C*Me*$_3$), 47.1 (s, CH_2), 50.7 (s, *C*Me$_3$), 128.5−143.0 (m, CH_{arom} and C_{arom}) ppm.

Synthesis of Complexes [RuCl$_2${κ^1(*P*)-2-Ph$_2$PC$_6$H$_4$CH$_2$NHR}-(η^6-arene)] (arene = C$_6$H$_6$, R = ^{i}Pr (11aa), ^{t}Bu (11ab); arene = *p*-cymene, R = ^{i}Pr (11ba), ^{t}Bu (11bb); arene = 1,3,5-C$_6$H$_3$Me$_3$, R = ^{i}Pr (11ca), ^{t}Bu (11cb); arene = C$_6$Me$_6$, R = ^{i}Pr (11da), ^{t}Bu (11db)). A solution of the corresponding dimer [{RuCl(μ-Cl)(η^6-arene)}$_2$] (**10a**−**d**; 0.5 mmol) in 40 mL of tetrahydrofuran was treated, at room temperature, with the appropriate amino-phosphine ligand **7a**,**b** (1 mmol) for 2 h (24 h when **10a** is used as starting material). The resulting solution was then evaporated to dryness, thus yielding a microcrystalline orange-red solid, which was washed with a 1:2 mixture of diethyl ether/hexane (3 × 10 mL) and vacuum-dried. **11aa:** Yield: 0.426 g (73%). Anal. Calcd for $RuC_{28}H_{30}Cl_2NP$: C, 57.64; H, 5.18; N, 2.40. Found: C, 57.71; H, 5.22; N, 2.53. IR (Nujol, cm^{-1}): ν 3204 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.9 (s) ppm. ^1H NMR (CD_2Cl_2): δ 0.88 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 2.50 (m, 1H, C*H*Me$_2$), 3.59 (br, 2H, CH_2), 5.47 (s, 6H, C_6H_6), 7.35−7.86 (m, 14H, CH_{arom}) ppm; NH signal not observed. **11ab:** Yield: 0.382 g (64%). Anal. Calcd for $RuC_{29}H_{32}Cl_2NP$: C, 58.29; H, 5.40; N, 2.34. Found: C, 58.20; H, 5.48; N, 2.45. IR (Nujol, cm^{-1}): ν 3211 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.3 (s) ppm. ^1H NMR (CD_2Cl_2): δ 0.84 (s, 9H, CMe$_3$), 3.44 (br, 2H, CH_2), 5.44 (s, 6H, C_6H_6), 7.38−7.94 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 27.8 (s, C*Me*$_3$), 45.9 (s, CH_2), 51.2 (s, *C*Me$_3$), 89.4 (d, $^2J_{CP}$ = 3.1 Hz, C_6H_6), 128.0−134.4 (m, CH_{arom} and C_{arom}) ppm. **11ba:** Yield: 0.441 g (69%). Anal. Calcd for $RuC_{32}H_{38}Cl_2NP$: C, 60.09; H, 5.99; N, 2.19. Found: C, 59.91; H, 6.12; N, 2.31. IR (Nujol, cm^{-1}): ν 3317 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 27.4 (s) ppm. ^1H NMR (CD_2Cl_2): δ 0.79 (br, 6H, CH*Me*$_2$), 1.28 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.82 (s, 3H, Me of cym), 2.29 (br, 1H, C*H*Me$_2$), 2.93 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, C*H*Me$_2$), 3.40 (br, 2H, CH_2), 4.83 and 5.33 (d, 2H each, $^3J_{HH}$ = 6.0 Hz, CH of cym), 7.33−7.91 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.8 (s, Me of cym), 21.6 and 21.9 (both s, CH*Me*$_2$), 30.6 (s, *C*HMe$_2$ of cym), 49.7 (s, *C*HMe$_2$), 49.9 (s, CH_2), 86.9 and 88.3 (s, CH of cym), 98.2 and 111.7 (s, C of cym), 127.7−134.1 (m, CH_{arom} and C_{arom}) ppm. **11bb:** Yield: 0.463 g (71%). Anal. Calcd for $RuC_{33}H_{40}Cl_2NP$: C, 60.64; H, 6.17; N, 2.14. Found: C, 60.77; H, 6.09; N, 2.20. IR (Nujol, cm^{-1}): ν 3260 (N−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.5 (s) ppm. ^1H NMR ($CDCl_3$): δ 0.75 (s, 9H, CMe$_3$), 1.27 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$ of cym), 1.84 (s, 3H, Me of cym), 2.89 (sept, 1H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$ of cym), 3.22 (br, 2H, CH_2), 4.84 and 5.31 (d, 2H each, $^3J_{HH}$ = 4.8 Hz, CH of cym), 7.35−7.95 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.8 (s, Me of cym), 21.9 (s, CH*Me*$_2$ of cym), 28.5 (s, C*Me*$_3$), 30.5 (s, *C*HMe$_2$ of cym), 46.0 (s, CH_2), 50.2 (s, *C*Me$_3$), 87.3 and 87.9 (s, CH of cym), 98.0 and 110.9 (s, C of cym), 126.2−137.2 (m, CH_{arom} and C_{arom}) ppm. **11ca:** Yield: 0.400 g (64%). Anal. Calcd for $RuC_{31}H_{36}Cl_2NP$: C, 59.52; H, 5.80; N, 2.24. Found: C, 59.60; H, 5.86; N, 2.32. IR (Nujol, cm^{-1}): ν 3298 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.7 (s) ppm. ^1H NMR (CD_2Cl_2): δ 0.69 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 2.02 (s, 9H, C_6H_3*Me*$_3$), 3.24 (m, 3H, C*H*Me$_2$ and CH_2), 4.60 (s, 3H, C_6H_3Me$_3$), 7.39−8.30 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.3 (s, C_6H_3*Me*$_3$), 22.4 (s, CH*Me*$_2$), 49.0 (s, *C*HMe$_2$), 50.6 (s, CH_2), 84.8 (d, $^2J_{CP}$ = 4.5 Hz, CH of $C_6H_3Me_3$), 104.6 (s, C of $C_6H_3Me_3$), 126.3−145.6 (m, CH_{arom} and C_{arom}) ppm. **11cb:** Yield: 0.396 g (62%). Anal. Calcd for $RuC_{32}H_{38}Cl_2NP$: C, 60.09; H, 5.99; N, 2.19. Found: C, 60.15; H, 5.87; N, 2.22. IR (Nujol, cm^{-1}): ν 3248 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.7 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.19 (s, 9H, CMe$_3$), 2.02 (s, 9H, C_6H_3*Me*$_3$), 3.16 (br, 2H, CH_2), 4.61 (s, 3H, C_6H_3Me$_3$), 7.39−8.31 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.3 (s, C_6H_3*Me*$_3$), 28.5 (s, C*Me*$_3$), 46.2 (s, CH_2), 50.0 (s, *C*Me$_3$), 84.8 (d, $^2J_{CP}$ = 3.4 Hz, CH of $C_6H_3Me_3$), 104.7 (d, $^2J_{CP}$ = 3.4 Hz, C of $C_6H_3Me_3$), 125.9−147.0 (m, CH_{arom} and C_{arom}) ppm. **11da:** Yield: 0.594 g (89%). Anal. Calcd for $RuC_{34}H_{42}Cl_2NP$: C, 61.16; H, 6.34; N, 2.10. Found: C, 60.97; H, 6.36; N, 2.19. IR (Nujol, cm^{-1}): ν 3270 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.1 (s) ppm. ^1H NMR (CD_2Cl_2): δ 0.68 (br, 6H, CH*Me*$_2$), 1.75 (s, 18H, C_6*Me*$_6$), 3.01 (m, 1H, C*H*Me$_2$), 3.72 (br, 2H, CH_2), 7.15−7.91 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.7 (s, C_6*Me*$_6$), 22.6 (s, CH*Me*$_2$), 48.7 (s, *C*HMe$_2$), 50.8 (s, CH_2), 96.5 (s, C_6Me$_6$), 125.6−139.5 (m, CH_{arom} and C_{arom}) ppm. **11db:** Yield: 0.538 g (79%). Anal. Calcd for $RuC_{35}H_{44}Cl_2NP$: C, 61.67; H, 6.51; N, 2.05. Found: C, 61.60; H, 6.64; N, 2.15. IR (Nujol, cm^{-1}): ν 3291 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.1 (s) ppm. ^1H NMR (CD_2Cl_2): δ 0.67 (s, 9H, CMe$_3$), 1.73 (s, 18H, C_6*Me*$_6$), 3.26 (br, 2H, CH_2), 7.15−7.85 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.8 (s, C_6*Me*$_6$), 28.5 (s, C*Me*$_3$), 46.1 (s, CH_2), 50.0 (s, *C*Me$_3$), 96.5 (d, $^2J_{CP}$ = 3.0 Hz, C_6Me$_6$), 125.5−147.0 (m, CH_{arom} and C_{arom}) ppm.

Synthesis of Complexes [RuCl$_2${κ^1(*P*)-3-Ph$_2$PC$_6$H$_4$CH$_2$NHR}-(η^6-arene)] (arene = C$_6$H$_6$, R = ^{i}Pr (12aa), ^{t}Bu (12ab); arene = *p*-cymene, R = ^{i}Pr (12ba), ^{t}Bu (12bb); arene = 1,3,5-C$_6$H$_3$Me$_3$, R = ^{i}Pr (12ca), ^{t}Bu (12cb); arene = C$_6$Me$_6$, R = ^{i}Pr (12da), ^{t}Bu (12db)). Complexes **12aa**−**12db**, isolated as orange microcrystalline solids, were prepared as described for **11aa**−**11db** starting from the appropriate [{RuCl(μ-Cl)(η^6-arene)}$_2$] dimer (**10a**−**d**; 0.5 mmol) and amino-phosphine ligand **8a**,**b** (1.2 mmol). **12aa:** Yield: 0.414 g (71%). Anal. Calcd for $RuC_{28}H_{30}Cl_2NP$: C, 57.64; H, 5.18; N, 2.40. Found: C, 57.72; H, 5.09; N, 2.51. IR (Nujol, cm^{-1}): ν 3293 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.0 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.05 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 2.77 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 3.79 (br, 2H, CH_2), 5.42 (s, 6H, C_6H_6), 7.35−7.79 (m, 14H, CH_{arom}) ppm; NH signal not observed.

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 22.7 (s, CH*Me*$_2$), 48.1 (s, *C*HMe$_2$), 50.8 (s, CH_2), 89.3 (d, $^2J_{CP}$ = 4.0 Hz, C_6H_6), 128.0−141.1 (m, CH_{arom} and C_{arom}) ppm. **12ab:** Yield: 0.370 g (62%). Anal. Calcd for $RuC_{29}H_{32}Cl_2NP$: C, 58.29; H, 5.40; N, 2.34. Found: C, 58.35; H, 5.29; N, 2.33. IR (Nujol, cm^{-1}): ν 3280 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.3 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.14 (s, 9H, CMe_3), 3.75 (br, 2H, CH_2), 5.43 (s, 6H, C_6H_6), 7.35−7.87 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 29.0 (s, C*Me*$_3$), 46.6 (s, CH_2), 50.7 (s, *C*Me$_3$), 89.3 (s, C_6H_6), 128.0−142.3 (m, CH_{arom} and C_{arom}) ppm. **12ba:** Yield: 0.498 g (78%). Anal. Calcd for $RuC_{32}H_{38}Cl_2NP$: C, 60.09; H, 5.99; N, 2.19. Found: C, 60.22; H, 6.08; N, 2.01. IR (Nujol, cm^{-1}): ν 3302 (N−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.2 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.06 and 1.11 (d, 6H each, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.90 (s, 3H, Me of cym), 2.82 (m, 2H, C*H*Me$_2$), 3.78 (br, 2H, CH_2), 5.04 and 5.22 (d, 2H each, $^3J_{HH}$ = 6.0 Hz, CH of cym), 7.32−7.92 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.5 (s, Me of cym), 21.7 and 22.8 (s, CH*Me*$_2$), 30.3 (s, *C*HMe$_2$ of cym), 47.9 (s, *C*HMe$_2$), 51.0 (s, CH_2), 87.3 and 89.0 (s, CH of cym), 96.4 and 110.2 (s, C of cym), 127.8−142.2 (m, CH_{arom} and C_{arom}) ppm. **12bb:** Yield: 0.471 g (72%). Anal. Calcd for $RuC_{33}H_{40}Cl_2NP$: C, 60.64; H, 6.17; N, 2.14. Found: C, 60.51; H, 6.23; N, 2.20. IR (Nujol, cm^{-1}): ν 3302 (N−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.5 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.12 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$ of cym), 1.17 (s, 9H, CMe_3), 1.90 (s, 3H, Me of cym), 2.87 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, C*H*Me$_2$ of cym), 3.75 (br, 2H, CH_2), 5.03 and 5.23 (d, 2H each, $^3J_{HH}$ = 6.2 Hz, CH of cym), 7.31−7.94 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.7 (s, Me of cym), 21.8 (s, CH*Me*$_2$ of cym), 29.0 (s, C*Me*$_3$), 30.4 (s, *C*HMe$_2$ of cym), 46.8 (s, CH_2), 50.6 (s, *C*Me$_3$), 87.5 and 88.9 (s, CH of cym), 96.4 and 110.3 (s, C of cym), 127.7−142.1 (m, CH_{arom} and C_{arom}) ppm. **12ca:** Yield: 0.406 g (65%). Anal. Calcd for $RuC_{31}H_{36}Cl_2NP$: C, 59.52; H, 5.80; N, 2.24. Found: C, 59.44; H, 5.92; N, 2.30. IR (Nujol, cm^{-1}): ν 3306 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.1 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.09 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 2.03 (s, 9H, C_6H_3*Me*$_3$), 2.82 (m, 1H, C*H*Me$_2$), 3.82 (br, 2H, CH_2), 4.71 (s, 3H, C_6*H*$_3$Me$_3$), 7.40−7.86 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.2 (s, C_6H_3*Me*$_3$), 22.6 (s, CH*Me*$_2$), 48.1 (s, *C*HMe$_2$), 50.8 (s, CH_2), 85.4 (d, $^2J_{CP}$ = 4.5 Hz, CH of $C_6H_3Me_3$), 104.5 (d, $^2J_{CP}$ = 2.3 Hz, C of $C_6H_3Me_3$), 127.6−141.0 (m, CH_{arom} and C_{arom}) ppm. **12cb:** Yield: 0.409 g (64%). Anal. Calcd for $RuC_{32}H_{38}Cl_2NP$: C, 60.09; H, 5.99; N, 2.19. Found: C, 59.92; H, 6.06; N, 2.25. IR (Nujol, cm^{-1}): ν 3312 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.4 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.19 (s, 9H, CMe_3), 2.02 (s, 9H, C_6H_3*Me*$_3$), 3.80 (br, 2H, CH_2), 4.72 (s, 3H, C_6*H*$_3$Me$_3$), 7.37−7.95 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.2 (s, C_6H_3*Me*$_3$), 28.9 (s, C*Me*$_3$), 46.7 (s, CH_2), 50.7 (s, *C*Me$_3$), 85.3 (d, $^2J_{CP}$ = 4.0 Hz, CH of $C_6H_3Me_3$), 104.6 (d, $^2J_{CP}$ = 3.0 Hz, C of $C_6H_3Me_3$), 127.6−141.8 (m, CH_{arom} and C_{arom}) ppm. **12da:** Yield: 0.580 g (87%). Anal. Calcd for $RuC_{34}H_{42}Cl_2NP$: C, 61.16; H, 6.34; N, 2.10. Found: C, 61.31; H, 6.26; N, 2.22. IR (Nujol, cm^{-1}): ν 3270 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.8 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.12 (d, 6H, $^3J_{HH}$ = 9.0 Hz, CH*Me*$_2$), 1.77 (s, 18H, C_6Me_6), 2.79 (m, 1H, C*H*Me$_2$), 3.79 (br, 2H, CH_2), 7.40−7.78 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ 12.7 (s, C_6*Me*$_6$), 19.2 (s, CH*Me*$_2$), 45.7 (s, *C*HMe$_2$), 48.3 (s, CH_2), 95.3 (s, C_6Me$_6$), 125.9−133.8 (m, CH_{arom} and C_{arom}) ppm. **12db:** Yield: 0.559 g (82%). Anal. Calcd for $RuC_{35}H_{44}Cl_2NP$: C, 61.67; H, 6.51; N, 2.05. Found: C, 61.56; H, 6.47; N, 2.13. IR (Nujol, cm^{-1}): ν 3230 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.3 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.15 (s, 9H, CMe_3), 1.75 (s, 18H, C_6Me_6), 3.73 (br, 2H, CH_2), 7.40−7.82 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.8 (s, C_6*Me*$_6$), 28.8 (s, C*Me*$_3$), 46.9 (s, CH_2), 50.6 (s, *C*Me$_3$), 96.7 (d, $^2J_{CP}$ = 3.0 Hz, C_6Me$_6$), 127.5−141.7 (m, CH_{arom} and C_{arom}) ppm.

Synthesis of Complexes [RuCl$_2$\{κ^1(*P*)-4-Ph$_2$PC$_6$H$_4$CH$_2$NHR\}-(η^6-arene)] (arene = C$_6$H$_6$, R = ^{i}Pr (13aa), ^{t}Bu (13ab); arene = *p*-cymene, R = ^{i}Pr (13ba), ^{t}Bu (13bb); arene = 1,3,5-C$_6$H$_3$Me$_3$, R = ^{i}Pr (13ca), ^{t}Bu (13cb); arene = C$_6$Me$_6$, R = ^{i}Pr (13da), ^{t}Bu (13db)). Complexes **13aa**−**13db**, isolated as orange microcrystalline solids, were prepared as described for **11aa**−**11db** starting from the appropriate [{RuCl(μ-Cl)(η^6-arene)}$_2$] dimer (**10a**−**d**; 0.5 mmol) and amino-phosphine ligand **9a**,**b** (1.2 mmol). **13aa:** Yield: 0.391 g (67%). Anal. Calcd for $RuC_{28}H_{30}Cl_2NP$: C, 57.64; H, 5.18; N, 2.40. Found: C, 57.50; H, 5.31; N, 2.55. IR (Nujol, cm^{-1}): ν 3270 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 26.8 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.21 (br, 6H, CH*Me*$_2$), 2.91 (br, 1H, C*H*Me$_2$), 3.81 (br, 2H, CH_2), 5.43 (s, 6H, C_6H_6), 7.41−7.77 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 28.5 (s, CH*Me*$_2$), 46.5 (s, CH_2), 48.5 (s, *C*HMe$_2$), 89.3 (s, C_6H_6), 126.1−143.5 (m, CH_{arom} and C_{arom}) ppm. **13ab:** Yield: 0.376 g (63%). Anal. Calcd for $RuC_{29}H_{32}Cl_2NP$: C, 58.29; H, 5.40; N, 2.34. Found: C, 58.13; H, 5.51; N, 2.44. IR (Nujol, cm^{-1}): ν 3275 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 26.8 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.22 (s, 9H, CMe_3), 3.83 (br, 2H, CH_2), 5.43 (s, 6H, C_6H_6), 7.40−7.77 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 28.2 (s, C*Me*$_3$), 46.4 (s, CH_2), 52.4 (s, *C*Me$_3$), 89.3 (s, C_6H_6), 128.1−142.5 (m, CH_{arom} and C_{arom}) ppm. **13ba:** Yield: 0.454 g (71%). Anal. Calcd for $RuC_{32}H_{38}Cl_2NP$: C, 60.09; H, 5.99; N, 2.19. Found: C, 60.18; H, 5.91; N, 2.23. IR (Nujol, cm^{-1}): ν 3317 (N−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.13 (d, 12H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.90 (s, 3H, Me of cym), 2.88 (m, 2H, C*H*Me$_2$), 3.83 (br, 2H, CH_2), 5.02 and 5.22 (d, 2H each, $^3J_{HH}$ = 6.0 Hz, CH of cym), 7.35−7.88 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.6 (s, Me of cym), 21.8 and 22.5 (s, CH*Me*$_2$), 30.4 (s, *C*HMe$_2$ of cym), 48.4 (s, *C*HMe$_2$), 50.7 (s, CH_2), 87.3 and 89.2 (s, CH of cym), 96.3 and 110.2 (s, C of cym), 127.6−143.0 (m, CH_{arom} and C_{arom}) ppm. **13bb:** Yield: 0.490 g (75%). Anal. Calcd for $RuC_{33}H_{40}Cl_2NP$: C, 60.64; H, 6.17; N, 2.14. Found: C, 60.80; H, 6.02; N, 2.25. IR (Nujol, cm^{-1}): ν 3317 (N−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.13 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$ of cym), 1.20 (s, 9H, CMe_3), 1.89 (s, 3H, Me of cym), 2.88 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, C*H*Me$_2$ of cym), 3.76 (br, 2H, CH_2), 5.01 and 5.21 (d, 2H each, $^3J_{HH}$ = 5.4 Hz, CH of cym), 7.30−7.87 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.5 (s, Me of cym), 21.7 (s, CH*Me*$_2$ of cym), 28.8 (s, C*Me*$_3$), 30.3 (s, *C*HMe$_2$ of cym), 46.6 (s, CH_2), 50.6 (s, *C*Me$_3$), 87.3 and 89.1 (s, CH of cym), 96.2 and 110.3 (s, C of cym), 127.6−144.0 (m, CH_{arom} and C_{arom}) ppm. **13ca:** Yield: 0.419 g (67%). Anal. Calcd for $RuC_{31}H_{36}Cl_2NP$: C, 59.52; H, 5.80; N, 2.24. Found: C, 59.61; H, 5.72; N, 2.11. IR (Nujol, cm^{-1}): ν 3301 (N−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.1 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.13 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 2.03 (s, 9H, C_6H_3*Me*$_3$), 2.89 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, C*H*Me$_2$), 3.82 (br, 2H, CH_2), 4.67 (s, 3H, C_6*H*$_3$Me$_3$), 7.36−7.79 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.2 (s, C_6H_3*Me*$_3$), 22.8 (s, CH*Me*$_2$), 48.5 (s, *C*HMe$_2$), 51.0 (s, CH_2), 85.5 (d, $^2J_{CP}$ = 5.0 Hz, CH of $C_6H_3Me_3$), 104.3 (s, C of $C_6H_3Me_3$), 127.3−143.9 (m, CH_{arom} and C_{arom}) ppm. **13cb:** Yield: 0.428 g (67%). Anal. Calcd for $RuC_{32}H_{38}Cl_2NP$: C, 60.09; H, 5.99; N, 2.19. Found: C, 59.89; H, 6.13; N, 2.21. IR (Nujol, cm^{-1}): ν 3294 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 32.1 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.19 (s, 9H, CMe_3), 2.02 (s, 9H, C_6H_3*Me*$_3$), 3.79 (br, 2H, CH_2), 4.68 (s, 3H, C_6*H*$_3$Me$_3$), 7.41−7.76 (m, 14H, CH_{arom}) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.3 (s, C_6H_3*Me*$_3$), 28.9 (s, C*Me*$_3$), 46.6 (s, CH_2), 50.6 (s, *C*Me$_3$), 85.6 (s, CH of $C_6H_3Me_3$), 104.4 (s, C of $C_6H_3Me_3$), 127.4−144.7 (m, CH_{arom} and C_{arom}) ppm. **13da:** Yield: 0.561 g (84%). Anal. Calcd for $RuC_{34}H_{42}Cl_2NP$: C, 61.16; H, 6.34; N, 2.10. Found: C, 61.29; H, 6.46; N, 2.01. IR (Nujol, cm^{-1}): ν 3290 (N−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.8 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.12 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.76 (s, 18H, C_6Me_6), 2.88 (m, 1H,

Table 4. Crystal Data and Structure Refinement Details for Compounds 11bb·HCl, 12bb, and 13bb

	11bb·HCl	**12bb**	**13bb**
chemical formula	$RuC_{33}H_{41}Cl_3NP$	$RuC_{33}H_{40}Cl_2NP$	$RuC_{33}H_{40}Cl_2NP$
fw	690.06	653.60	653.60
T, K	293(2)	293(2)	293(2)
wavelength, Å	1.5418	1.5418	1.5418
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
cryst size, mm	0.101 × 0.057 × 0.028	0.086 × 0.062 × 0.025	0.125 × 0.099 × 0.031
a, Å	18.1728(2)	9.8513(3)	11.6372(1)
b, Å	10.3861(1)	10.3852(3)	19.7352(2)
c, Å	18.3489(3)	15.9639(4)	13.9921(1)
α, deg	90	89.619(2)	90
β, deg	111.663(2)	76.419(2)	106.732(1)
γ, deg	90	79.882(2)	90
Z	4	2	4
V, Å^3	3218.65(7)	1561.85(8)	3077.41(5)
ρ_{calcd}, g cm^{-3}	1.424	1.390	1.411
μ, mm^{-1}	6.868	6.278	6.372
$F(000)$	1424	676	1352
θ range, deg	2.92 to 73.92	2.85 to 74.01	3.99 to 73.81
index ranges	$-22 \le h \le 22$	$-12 \le h \le 12$	$-14 \le h \le 14$
	$-12 \le k \le 12$	$-12 \le k \le 12$	$-23 \le k \le 15$
	$-22 \le l \le 17$	$-18 \le l \le 19$	$-17 \le l \le 16$
completeness to θ_{max}	96.9%	99.4%	96.9%
no. of data collected	18 786	18 252	17 444
no. of unique data	6320 (R_{int} = 0.0234)	6304 (R_{int} = 0.0254)	6042 (R_{int} = 0.0279)
no. of params/restraints	516/0	417/3	353/0
refinement method		full-matrix least-squares on F^2	
goodness of fit on F^2	1.083	1.033	1.063
weight function (a, b)	0.0535, 1.922	0.0638, 0.7391	0.0577, 1.1784
R1[a] [$I > 2\sigma(I)$]	0.0327	0.0354	0.0348
wR2[a] [$I > 2\sigma(I)$]	0.0923	0.0957	0.0880
R1 (all data)	0.0363	0.0392	0.0417
wR2 (all data)	0.0945	0.0992	0.0961
largest diff peak and hole, e Å^{-3}	1.263 and −0.779	0.787 and −0.648	0.809 and −0.379

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

C*H*Me$_2$), 3.81 (br, 2H, CH$_2$), 7.39−7.79 (m, 14H, CH$_{arom}$) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.8 (s, C$_6$*Me$_6$*), 22.1 (s, CH*Me$_2$*), 48.4 (s, CH$_2$), 50.5 (s, *C*HMe$_2$), 96.7 (d, $^2J_{CP}$ = 3.8 Hz, *C$_6$*Me$_6$), 127.4−135.2 (m, CH$_{arom}$ and C$_{arom}$) ppm. **13db:** Yield: 0.552 g (81%). Anal. Calcd for $RuC_{35}H_{44}Cl_2NP$: C, 61.67; H, 6.51; N, 2.05. Found: C, 61.78; H, 6.55; N, 1.97. IR (Nujol, cm^{-1}): ν 3174 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.2 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.21 (s, 9H, CMe$_3$), 1.77 (s, 18H, C$_6$Me$_6$), 3.80 (br, 2H, CH$_2$), 7.43−7.18 (m, 14H, CH$_{arom}$) ppm; NH signal not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.9 (s, C$_6$*Me$_6$*), 28.8 (s, C*Me$_3$*), 46.6 (s, CH$_2$), 50.9 (s, *C*Me$_3$), 96.7 (s, *C$_6$*Me$_6$), 127.5−144.2 (m, CH$_{arom}$ and C$_{arom}$) ppm.

Electrochemistry. CV measurements (25 °C) were carried out with a three-electrode system. The working electrode was a platinum disk electrode, the counter electrode was a platinum spiral, and the reference electrode was an aqueous saturated calomel electrode separated from the solution by a porous septum. Current and voltage parameters were controlled using a PAR system M273. In a typical experiment, 0.15 mmol of the complex was dissolved under a nitrogen atmosphere in 10 mL of freshly distilled and deoxygenated dichloromethane containing 1.15 g of pure [^{n}Bu$_4$N][PF$_6$] (0.3 mmol) as electrolyte. Formal CV potentials ($E^{\circ\prime}$) given in Table 1 are referenced relative to the potential of the $[Cp_2Fe]/[Cp_2Fe]^+$ couple (E° = 0.21 V) run under identical conditions ($E^{\circ\prime} = E^\circ(Ru^{III}/Ru^{II}) - E^\circ(Fe^{III}/Fe^{II})$).[24]

General Procedure for the Catalytic Hydration Reactions. Under nitrogen atmosphere, the corresponding nitrile (1 mmol), water (3 mL), and the appropriate ruthenium catalyst (5 mol % of Ru) were introduced into a sealed tube, and the reaction mixture was stirred at 100 °C for the indicated time (see Tables 2 and 3). The course of the reaction was monitored by regularly taking samples of 20 μL, which after extraction with CH_2Cl_2 (3 mL) were analyzed by GC. After elimination of the solvent under reduced pressure, the crude reaction mixture was purified by column chromatography over silica gel using diethyl ether as eluent. The identity of the resulting amides was assessed by comparison of their ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data with those reported in the literature and by their fragmentation in GC/MSD.

X-ray Crystal Structure Determination of Complexes 11bb·HCl, 12bb, and 13bb. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into saturated solutions of the appropriate complex in dichloromethane. The most relevant crystal and refinement data are collected in Table 4. For all crystals, data collection was performed on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα radiation (λ = 1.5418 Å). Images were collected at a 65 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (3−40 s). Data collection strategy was calculated with the program CrysAlis Pro CCD.[32] Data reduction and cell refinement were performed with the program CrysAlis Pro RED.[32] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[32] The software package WINGX[33] was used for space group determination, structure solution, and refinement. The structures of complexes **11bb·HCl** and **13bb** were solved by direct methods using SIR2004.[34] For **12bb** the structure was solved by Patterson interpretation and phase expansion using DIRDIF.[35]

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Isotropic least-squares refinement on F^2 using SHELXL97[36] 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. For **11bb**·HCl and **12bb** the coordinates of H atoms were found from different Fourier maps and included in a refinement with isotropic parameters (except those of the CH_3 groups of **12bb**, which were geometrically located and their coordinates refined riding on their parent atoms). For **13bb**, the H atoms were geometrically located and their coordinates were refined riding on their parent atoms (except H_{N1}, which was found from different Fourier maps and included in a refinement with isotropic parameters). The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are given in Table 4) with $\sigma(F_o^2)$ from counting statistics and $P = (\max(F_o^2,0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[37] Geometrical calculations were made with PARST.[38] The crystallographic plots were made with PLATON.[39]

Acknowledgment. Financial support from the Spanish MICINN (Projects CTQ2006-08485/BQU and CSD2007-00006) and the Gobierno del Principado de Asturias (FICYT Project IB08-036) is acknowledged.

Supporting Information Available: CIF file giving crystallographic data for compounds **11bb**·HCl, **12bb**, and **13bb**. This material is available free of charge via the Internet at http://pubs.acs.org.

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