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Bis(allyl)ruthenium(IV) Complexes Containing Water-Soluble Phosphane Ligands: Synthesis, Structure, and Application as Catalysts in the Selective Hydration of Organonitriles into Amides

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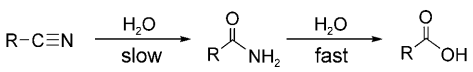
Dedicated to Professor José Barluenga on the occasion of his 70th birthday

Abstract: The novel mononuclear ruthenium(IV) complexes $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(L)]$ [L = (*meta*-sulfonatophenyl)diphenylphosphane sodium salt (TPPMS) (**2a**), 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (PTA) (**2b**), 1-benzyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane chloride (PTA-Bn) (**2c**), 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA) (**2d**), and 2,4,10-trimethyl-1,2,4,5,7,10-hexaaza-3-phosphatricyclo[3.3.1.1^{3,7}]decane (THPA) (**2e**)] have been synthesized by treatment of the dimeric precursor $[\{RuCl(\mu\text{-}Cl)(\eta^3:\eta^3\text{-}C_{10}H_{16})\}_2]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) (**1**) with two equivalents of the corresponding water-soluble phosphane. Reaction of **1** with one equivalent of the cage-type diphosphane ligand 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]octane (THDP) allowed also the high-yield preparation of the dinuclear derivative $[\{RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})\}_2(\mu\text{-THDP})]$ (**2f**). All these new complexes have been analytically and spectroscopically (IR and multinuclear NMR) characterized. In addition, the structure of **2b**, **2c**, **2d**, and **2f** was unequivocally confirmed by X-ray diffraction methods. Complexes **2a–f** are active catalysts for the selective hydration of nitriles to amides in pure aqueous medium under neutral conditions. The wide scope of this catalytic transformation has been evaluated by using the most active catalysts $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(THPA)]$ (**2e**) and $[\{RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})\}_2(\mu\text{-THDP})]$ (**2f**). Advantages of using MW versus conventional thermal heating are also discussed.

Keywords: amides · homogeneous catalysis · hydration · nitriles · ruthenium

Introduction

Hydration of nitriles to access amides is a process of great significance, because amides are versatile intermediates used in the production of pharmacological products, polymers, detergents, lubricants, and drug stabilizers.[1] Traditionally, this reaction is catalyzed by strong acids and bases under harsh conditions, methods which are not compatible with many sensitive functional groups and usually cause over-hydrolysis of the amides into the corresponding carboxylic acids, a faster reaction specially under basic conditions (see Scheme 1).[2] Moreover, from an industrial perspective, the final neutralization step required either in the acid- or base-catalyzed reactions leads to extensive salt formation with inconvenient product contamination and pollution effects.



Scheme 1. Nitrile hydration and amide hydrolysis reactions.

To overcome these limitations, different methods based on the use of enzymes,[3] heterogeneous catalysts,[4] and transition-metal complexes[5] have been developed. In particular, a variety of homogeneous catalysts, mainly of Group 8–12 metals, operating in organic media and showing a high selectivity to the amide, have been described in the literature.[5,6] From a mechanistic point of view, although several reaction pathways have been proposed for these metal-catalyzed transformations, coordination of the nitrile to the metal is a

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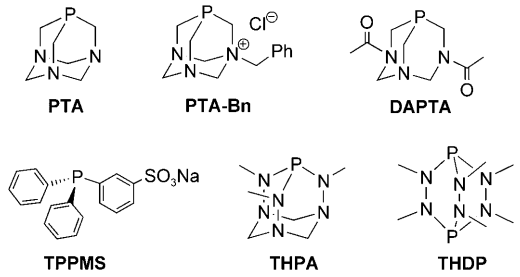
common prerequisite for most of them. In this way, the C≡N bond is activated towards the nucleophilic addition of water, or the hydroxyl group if basic conditions are used, thus improving the kinetics of the hydration process versus the hydrolysis (see Scheme 1).

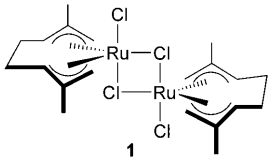
Owing to practical and environmental concerns, current research has focused on the search of catalytic systems able to operate directly in water under neutral conditions.[7] However, few promising methodologies have been proposed to date.[8,9] In this context, in the course of our current studies directed to the application of ruthenium complexes in catalytic aqueous organic synthesis,[10] we have recently reported that half-sandwich ruthenium(II) species $[RuCl_2(\eta^6\text{-arene})(L)]$, containing the hydrosoluble *P*-donor ligands PTA (1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane), PTA-Bn (1-benzyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane chloride) and DAPTA (3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) (see Scheme 2),[11,12] are excellent precatalysts for the selective



Scheme 2. Structure of the water-soluble phosphanes PTA, PTA-Bn, DAPTA, TPPMS, THPA, and THDP.

hydration of organonitriles to amides under these challenging conditions.[13] Interestingly, the presence of the nitrogen-containing phosphanes PTA, PTA-Bn, and DAPTA turned out to be key to attain good conversions, as related (η^6-arene)ruthenium(II) complexes bearing the sulfonated phosphane TPPMS ((*meta*-sulfonatophenyl)diphenylphosphane sodium salt) proved much less effective.[13] This fact strongly suggests that the hydration process occurs through a bifunctional catalysis mechanism,[14] that is, the metal acts as a Lewis acid activating the nitrile and the nitrogen-containing ligand acts as a Lewis base directing the attack of water through hydrogen bonding. Such a cooperative effect, also proposed by Oshiki and Breit and their co-workers in related Ru^{II}-catalyzed nitrile hydration reactions,[6a,m,o] has been largely exploited in homogeneous catalysis during the last years. In this sense, the transfer hydrogenation processes through an outer-sphere mechanism, described by Noyori and co-workers, and the selective hydration of alkynes to aldehydes (*anti*-Markovnikov addition), developed by Grotjahn's group, are probably the most illustrative and successful examples of this concept.[14]

With the aim of finding more efficient catalysts for this relevant transformation, we wondered about the effect of an increase in the Lewis acid character of the metal center in the activity of these bifunctional systems. Our attention was then turned to the chloro-bridged bis(allyl)-ruthenium(IV) dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl; **1** in Scheme 3). Although comparatively much less developed,[15] the reactivity of complex **1** is closely related to that of the more classical arene–ruthenium(II) species $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$, thus allowing the easy preparation of mononuclear derivatives $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)]$ by simple cleavage of the chloride bridges with appropriate two-electron donor ligands. Thus, herein we report on the reactivity of $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**) towards the hydrophilic phosphanes depicted in Scheme 2, as well as an evaluation of the ability of the resulting ruthenium(IV) complexes to catalyze the selective hydration of organonitriles into the corresponding amides in pure aqueous medium at neutral pH.

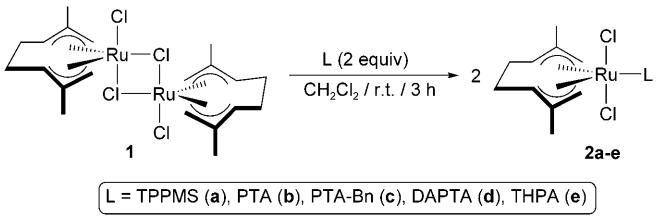


Scheme 3. Structure of the bis(allyl)ruthenium(IV) dimer **1**.

Results and Discussion

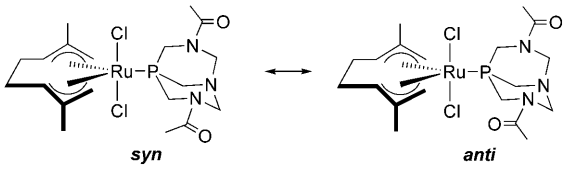
Synthesis and characterization of the bis(allyl)-ruthenium(IV) complexes $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)]$ (L = TPPMS, PTA, PTA-Bn, DAPTA, THPA) and $[\{RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2(\mu\text{-THDP})]$: Treatment of the purple dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**) with two equivalents of the monodentate *P*-donor ligands TPPMS, PTA, PTA-Bn, DAPTA, and THPA (2,4,10-trimethyl-1,2,4,5,7,10-hexaaza-3-phosphatricyclo[3.3.1.1^{3,7}]decane),[16] in dichloromethane at room temperature, results in the formation of bright orange solutions from which the mononuclear complexes $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)]$ (L = TPPMS (**2a**), PTA (**2b**), PTA-Bn (**2c**), DAPTA (**2d**), THPA (**2e**)) could be isolated, as air-stable solids in 67–90% yield, after partial removal of the solvent in vacuo and subsequent precipitation with hexane (Scheme 4).

The new compounds **2a–e** were fully characterized by means of elemental analyses and multinuclear NMR spectroscopy (details are given in the Experimental Section). Complexes **2a–c** and **2e** showed a singlet resonance in their $^{31}P\{^1H\}$ NMR spectra, strongly deshielded with respect to that of the corresponding free phosphane ($\Delta\delta$ = 30–50 ppm),



Scheme 4. Synthesis of the mononuclear bis(allyl)ruthenium(IV) complexes **2a–e**.

thus supporting the selective *P*-coordination of the ligands. In addition, both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra showed a single set of signals for the two allylic moieties suggesting that the two halves of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton are in equivalent environments, as expected for the formation of a simple equatorial adduct. In contrast, for complex $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(DAPTA)]$ (**2d**), two singlets were observed at room temperature in its $^{31}P\{^{1}H\}$ NMR spectrum (approximately in a 1.2:1 ratio). Similarly, a doubling on the number of signals expected for the bis(allyl) moiety was also observed in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Variable-temperature $^{31}P\{^{1}H\}$ NMR measurements showed that the two singlets observed at room temperature converge to a single signal at temperatures above 353 K, indicating that they correspond to conformational isomers. These isomers are most likely owed to the *syn* and *anti* conformations adopted by the acyl groups of the DAPTA ligand (see Scheme 5), a fact that has already been observed both within the free phosphane[17] and in some of its metal-complexes.[18]



Scheme 5. *syn* and *anti* conformations of the DAPTA ligand in complex **2d**.

The proposed structures for complexes **2b**, **2c**, and **2d** were unequivocally confirmed by means of X-ray diffraction methods. Single crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into saturated solutions of these compounds in dichloromethane. ORTEP plots of the molecular structures are shown in Figures 1–3, whereas selected bonding parameters are listed in Table 1.

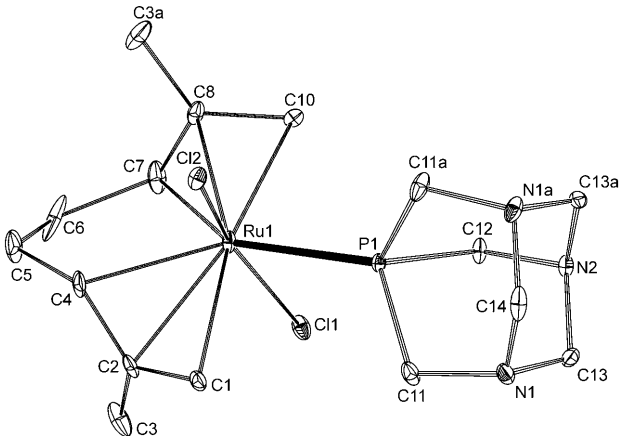


Figure 1. ORTEP-type view of the structure of compound **2b** showing the crystallographic labeling scheme. Atoms labeled with an "a" are related to those indicated by a crystallographic plane of symmetry. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **2b**, **2c**, **2d**, and **2f**.

	2b	**2c**	**2d**	**2f**
		bond lengths		
Ru–Cl1	2.483(3)	2.4307(9)	2.4081(9)	2.502(2)
Ru–Cl2	2.372(4)	2.4218(9)	2.4362(9)	2.331(3)
Ru–P1	2.3779(13)	2.3421(9)	2.3516(9)	2.3945(9)
Ru–C1	2.268(10)	2.204(4)	2.235(4)	2.104(8)
Ru–C2	2.312(8)	2.255(4)	2.276(4)	2.186(7)
Ru–C4	2.275(8)	2.264(4)	2.283(4)	2.179(7)
Ru–C7	2.229(8)	2.257(4)	2.284(4)	2.312(7)
Ru–C8	2.125(8)	2.259(4)	2.281(4)	2.379(6)
Ru–C10	2.147(12)	2.243(4)	2.237(4)	2.381(9)
C1–C2	1.398(13)	1.412(7)	1.418(6)	1.434(11)
C2–C4	1.429(14)	1.399(6)	1.405(6)	1.423(15)
C7–C8	1.397(14)	1.399(8)	1.405(6)	1.411(10)
C8–C10	1.440(15)	1.402(8)	1.406(6)	1.409(11)
		bond angles		
Cl1-Ru-Cl2	162.94(13)	166.44(4)	171.10(3)	172.87(9)
Cl1-Ru-P1	80.11(8)	85.94(3)	89.54(3)	91.16(5)
Cl1-Ru-C*[a]	92.37(8)	94.92(3)	93.41(3)	92.03(5)
Cl1-Ru-C**[a]	91.12(10)	90.03(3)	88.82(3)	82.51(5)
Cl2-Ru-P1	83.70(8)	80.68(3)	81.56(3)	83.41(10)
Cl2-Ru-C*[a]	90.27(8)	89.31(3)	90.24(3)	94.50(13)
Cl2-Ru-C**[a]	100.48(10)	97.16(3)	94.87(3)	94.88(14)
P1-Ru-C*[a]	117.12(1)	117.25(2)	112.95(3)	117.86(3)
P1-Ru-C**[a]	114.50(1)	112.96(2)	115.74(3)	109.01(2)
C*-Ru-C**[a]	128.09(2)	129.767(13)	131.273(13)	132.906(13)
C1-C2-C4	113.2(9)	115.6(4)	117.3(4)	114.7(9)
C7-C8-C10	116.3(9)	115.1(5)	117.1(4)	116.7(8)

[a] C* and C** denote the centroids of the allyl units (C1, C2, C4, and C7, C8, C10, respectively).

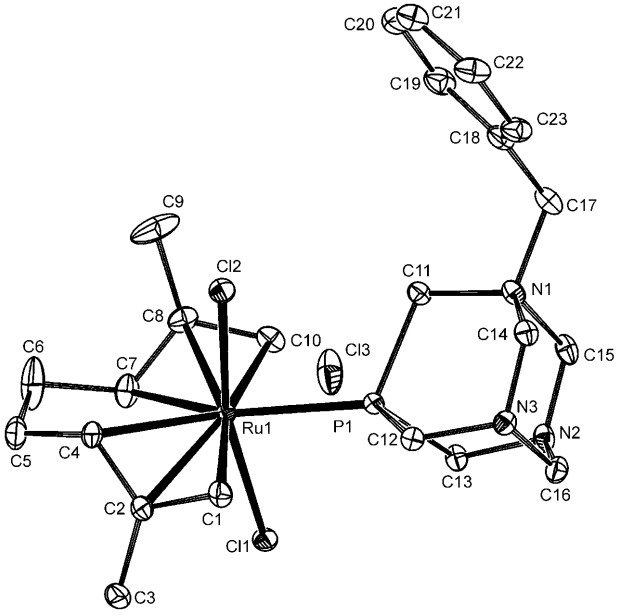


Figure 2. ORTEP-type view of the structure of compound **2c** showing the crystallographic labeling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level.

The geometry about the respective ruthenium(IV) atoms is best described as a distorted trigonal bipyramid by considering the allyl groups as monodentate ligands bound to the metal through their centers of mass (C* and C**; see footnote of Table 1). In all cases, the chloride ligands occupy the

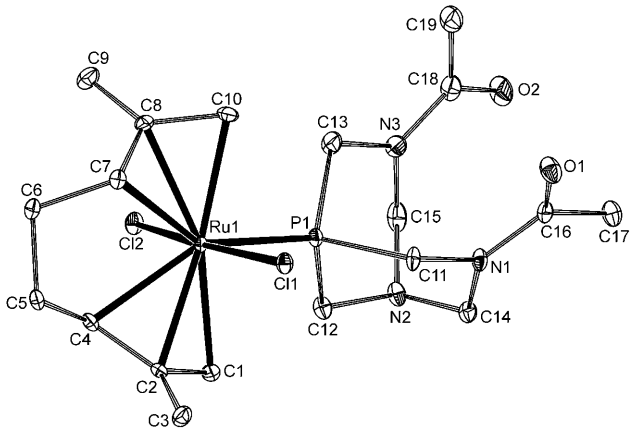


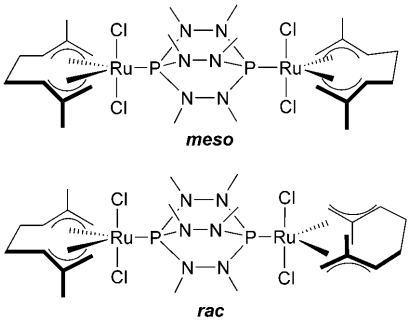
Figure 3. ORTEP-type view of the structure of compound **2d** showing the crystallographic labeling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level.

axial positions (Cl1-Ru-Cl2 bond angles ranging from 162.94(13) to 171.10(3)°), whereas the octadienediyl moiety and the *P*-donor ligand are located at the equatorial sites. Both allyl groups of the organic $C_{10}H_{16}$ fragment are η^3-bound to the ruthenium atom with Ru–C and C–C distances in the ranges 2.147(12)–2.312(8) Å and 1.397(14)–1.440(15) Å, respectively (Table 1). These values, together with the internal allylic C-C-C angles (113.2(9)–117.3(4)°), compare well with those observed in other structures containing the "Ru(η^3:η^3-$C_{10}H_{16}$)" unit.[19] Concerning the structure of the DAPTA complex **2d** (Figure 3), the $COCH_3$ groups of the ligand are *anti* with respect to each other, as they are in solid state structure of the free phosphane.[17]

Quite recently, Majoral and ourselves, have studied the suitability of the almost unexplored cage-type ligand tris(1,2-dimethylhydrazino)diphosphane P(NMeNMe)$_3$P (THDP in Scheme 2) to design water-tolerant transition-metal catalysts.[10j] To gain a deeper knowledge on the potentiality of this ligand in aqueous catalysis, the reactivity of THDP towards [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**1**) was also explored. Thus, as shown in Equation (1), we have found that **1** readily reacts with one equivalent of THDP, in dichloromethane at room temperature, to generate the dinuclear derivative [{RuCl$_2$(η^3:η^3-$C_{10}H_{16}$)}$_2$(μ-THDP)] (**2f**) in which the cage-like diphosphane is acting as a bridging ligand. All attempts to generate the mononuclear derivative [RuCl$_2$(η^3:η^3-$C_{10}H_{16}$){κ^1-(*P*)-THDP}] by using excess of THDP (up to 15 equiv) failed, the reactions leading to mixtures containing the dinuclear complex **2f** and the unreacted diphosphane. This coordination feature was also found starting from the Ru^{II} dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$].[10j]

$$1 + \mathrm{THDP} \xrightarrow[\mathrm{RT}]{\mathrm{CH_2Cl_2}} [\{\mathrm{RuCl_2}(\eta^3 : \eta^3\text{-}\mathrm{C_{10}H_{16}})\}_2(\mu\text{-THDP})] \ (\mathbf{2f}) \quad (1)$$

Compound **2f**, isolated in 71% yield, is an air-stable yellow solid soluble in common polar solvents. It has been characterized by using elemental analyses and IR and NMR ($^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$) spectroscopy (details are given in the Experimental Section). The dinuclear nature of **2f** was confirmed by comparing the relative intensities of the octadienediyl and diphosphane resonances (2:1) in the ^1H NMR spectrum. However, a closer examination of the NMR data revealed the presence of two different isomers in solution in an approximate 5:1 ratio. This is evidenced by: i) the appearance of one singlet ($\delta_P = 135.9$ ppm; major) and two doublets (AB system; $\delta_P = 132.8$ and 135.7 ppm ($^3J(P,P) = 102.1$ Hz); minor) in the $^{31}P\{^1H\}$ NMR spectrum, and ii) the doubling of some proton and carbon resonances for the organic octadienediyl unit. No interconversion was observed by variable-temperature $^{31}P\{^1H\}$ NMR experiments suggesting that, contrary to **2d**, conformational issues are not responsible of the mixture observed in solution. Taking into account the chirality associated to the metal coordinated 2,7-dimethylocta-2,6-diene-1,8-diyl unit (in solution dimer **1** itself exits in two diasteromeric forms),[15,20] two diastereoisomers with overall C_i (*meso*) and C_2 (*rac*) symmetry are possible for **2f** (see Scheme 6). Thus, although the *meso* form could account for the singlet signal observed in the $^{31}P\{^1H\}$ NMR spectrum, the absence of an inversion center in the *rac* one makes the two phosphorus atoms of the bridging THDP ligand inequivalents, and therefore an AB system should be expected, as observed experimentally.[21]



Scheme 6. The *meso* and *rac* forms of the dinuclear complex **2f**.

To establish conclusively the structure of the product formed we carried out a single-crystal structural analysis. The X-ray study (see Figure 4 and Table 1) showed that in the crystalline material only one of the isomers is present. That isomer has overall overall C_i symmetry (*meso* form), whereas the organic octadienediyl units have the expected local C_2 symmetry. The geometry about the crystallographically unique metal ion is that of a distorted trigonal bipyramid, with the chloride ligands occupying again the axial positions and the bis-allyl chain and THDP located at the equatorial sites.

As previously observed in the solid-state structure of the related Ru^{II} complex [{RuCl$_2$(η^6-*p*-cymene)}$_2$(μ-THDP)],[10j] the two P(NMe)$_3$ units of the bridged THDP ligand in **2f** do not adopt an eclipsed orientation. As shown in Figure 5,

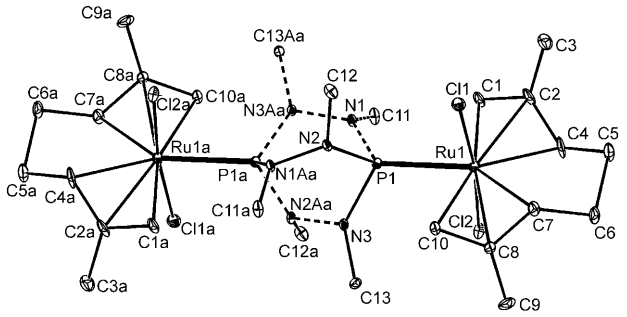


Figure 4. ORTEP-type view of the structure of compound **2f** showing the crystallographic labeling scheme. Atoms labeled with an "a" are related to those indicated by a crystallographic inversion center. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level.

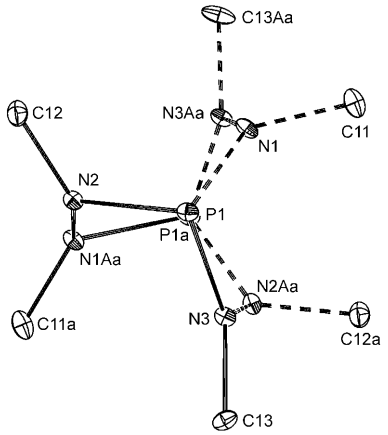


Figure 5. Partial view of the THDP-ligand skeleton along the P1–P1a axis in complex **2f**.

they are rotated relative to each other by 18.6° (torsion angle N2-P1-P1a-N1a).

Mononuclear **2a–d** and dinuclear **2f** complexes were further studied by means of cyclic voltammetry. In all cases a single irreversible reduction (E_{pc} values are given in Table 2) was observed over a variety of scan speeds (0.1–1.5 $V s^{-1}$), indicating that the electron-transfer reactions are followed by rapid chemical decomposition of the complexes. As previously observed by other authors, such a decomposition process most probably involves the irreversible loss of the bis(allyl) ligand.[21d,e,22] Finally, it must be noted that the solubility of these complexes in water is only modest (0.5–5.0 $mg mL^{-1}$), with the TPPMS derivative **2a** showing the highest value at room temperature (see Table 2).

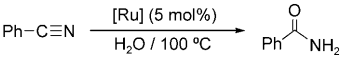
Table 2. Electrochemical data and solubility in water values for complexes **2a–f**.

Complex	E_{pc} [V][a]	S [$mg mL^{-1}$][b]	Complex	E_{pc} [V][a]	S [$mg mL^{-1}$][b]
2a	−1.82	5.0	**2d**	−2.05	1.0
2b	−1.37	0.5	**2e**	−2.00	2.5
2c	−1.50	2.5	**2f**	−2.32	1.0

[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. Indicated potentials are referenced relative to the potential of the $[Cp_2Fe]/[Cp_2Fe]^+$ couple. [b] Solubility in water at 20°C.

Catalytic hydration of nitriles: To prove the catalytic potential of the novel bis(allyl)-ruthenium(IV) complexes **2a–f**, we first carried out the hydration of benzonitrile into benzamide, as a model reaction using a ruthenium loading of 5 mol% of Ru. Thus, as shown in Table 3, performing the catalytic reactions at 100°C in pure aqueous medium, all the complexes synthesized were able to provide benzamide as the unique reaction product (benzoic acid was not detected by GC/MSD in the crude reaction mixtures). However, marked differences in activity were observed depending of the nature of hydrosoluble ligand attached to ruthenium. Thus, as observed in our previous work,[13] good conversions (≥94%) could only be attained with those catalysts bearing the nitrogen-containing phosphanes, complexes **2b–f** (Table 3, entries 3–7), the use of the TPPMS complex **2a** (Table 3, entry 2) or the dimeric precursor **1** (Table 3, entry 1) leading to remarkably lower conversions (up to 42% GC-yield) after 24 h of heating. This fact, along with the absence of direct relationships between the measured E_{pc} potentials and solubilities in water, supports the proposed cooperative effect of the ligand through a bifunctional catalysis mechanism. Interestingly, the catalytic activity of **2b–d** was lower than those previously reported for their Ru^{II} counterparts $[RuCl_2(\eta^6\text{-arene})(L)]$ (arene = benzene, mesitylene, *p*-cymene, hexamethylbenzene; L = PTA, PTA-Bn, DAPTA), which, under the same reaction conditions, were able to generate benzamide in almost quantitative yields after only 2–19 h (versus 24 h using **2b–d**).[13] This seems to indicate that the nucleophilic addition of water on the coordinated nitrile is not the rate-limiting step of these catalytic reactions, otherwise the higher Lewis acid character of the ruthenium(IV) centers should favor the addition. In contrast, complexes **2e–f**, containing the more sterically congested phosphanes THPA and THDP, proved to be as competitive as the arene-ruthenium(II) catalysts, leading to the

Table 3. Ruthenium(IV)-catalyzed hydration of benzonitrile.[a]



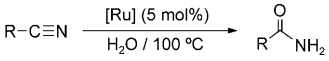
Entry	Catalyst	t [h]	Yield [%][b]
1	$[\{RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**)	24	18
2	$[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(TPPMS)]$ (**2a**)	24	42
3	$[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(PTA)]$ (**2b**)	24	94
4	$[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(PTA\text{-}Bn)]$ (**2c**)	24	97
5	$[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(DAPTA)]$ (**2d**)	24	97
6	$[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(THPA)]$ (**2e**)	2	99
7	$[\{RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2(\mu\text{-}THDP)]$ (**2f**)	4 (2)	98 (92)

[a] Reactions were performed under N_2 atmosphere at 100°C using 1 mmol of benzonitrile (0.33 M in water). Substrate/Ru ratio: 100/5. [b] Determined by GC.

desired benzamide in 98–99% yield after only 2–4 h of heating (Table 3, entries 6 and 7).

Complexes **2e–f** were also effective in the selective hydration of a variety of other aromatic and aliphatic nitriles, thus confirming their potential for practical applications (see Table 4). Thus, as observed for benzonitrile (Table 4, entry 1), other aromatic (Table 4, entries 2–14) and heteroaromatic (Table 4, entries 15 and 16) substrates could be selectively converted into the corresponding amides (94–99% GC-yields) in short reaction times, with no remarkable influence of the position and electronic nature of the substituents being observed. Subsequent purification by column chromatography on silica gel provided analytically pure samples of the amides in 75–90% isolated yield.

Table 4. Catalytic hydration of nitriles by complexes **2e**,**f**.[a]



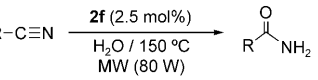
Entry	Substrate	Catalyst	*t* [h]	Yield [%][b]
1	R = Ph	**2e**	2	99 (88)
		2f	4	98 (85)
2	R = 2-C_6H_4F	**2e**	2	99 (84)
		2f	5	96 (80)
3	R = 4-C_6H_4F	**2e**	3	99 (89)
		2f	6	98 (88)
4	R = 3-C_6H_4Cl	**2e**	1	99 (87)
		2f	3	99 (89)
5	R = 4-C_6H_4Br	**2e**	2	99 (90)
		2f	2	97 (88)
6	R = 3-$C_6H_4NO_2$	**2e**	2	99 (89)
		2f	3	98 (86)
7	R = 2-Me-4-$C_6H_3NO_2$	**2e**	1	98 (83)
		2f	4	97 (80)
8	R = 4-$C_6H_4C(=O)Et$	**2e**	1	99 (93)
		2f	2	98 (91)
9	R = 4-C_6H_4Me	**2e**	3	98 (88)
		2f	3	94 (86)
10	R = 3-$C_6H_4NH_2$	**2e**	1	96 (79)
		2f	3	99 (80)
11	R = 2-C_6H_4OH	**2e**	2	99 (81)
		2f	3	99 (79)
12	R = 4-C_6H_4OMe	**2e**	2	96 (84)
		2f	6	96 (87)
13	R = 4-C_6H_4SMe	**2e**	2	99 (77)
		2f	4	96 (75)
14	R = benzo[1,3]dioxole-5-yl	**2e**	1	98 (83)
		2f	4	97 (80)
15	R = 3-C_5H_4N	**2e**	1	99 (90)
		2f	2	98 (90)
16	R = 5-Me-2-furyl	**2e**	2	99 (93)
		2f	3	99 (92)
17	R = *n*-C_5H_{11}	**2e**	24	63(50)
		2f	24	94 (83)
18	R = Cy	**2e**	24	57 (44)
		2f	24	83 (69)
19	R = CH_2-4-C_6H_4Cl	**2e**	4	97 (88)
		2f	3	99 (90)
20	R = CH_2SO_2Ph	**2e**	2	97 (85)
		2f	5	96 (83)
21	R = CH_2CH_2OPh	**2e**	3	96 (79)
		2f	4	96 (78)
22	R = (*E*)-CH=CHPh	**2e**	7	95 (83)
		2f	7	98 (88)

[a] Reactions were 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] Determined by GC (isolated yields are given in parentheses).

The presence of common functional groups, such as halide (Table 4, entries 2–5), nitro (Table 4, entries 6 and 7), ketone (Table 4, entry 8), amino (Table 4, entry 10), hydroxy (Table 4, entry 11), ether (Table 4, entries 12 and 14), or thioether (Table 4, entry 13), were tolerated regardless of the catalyst employed. Interestingly, starting from these aromatic and heteroaromatic substrates, the use of the mononuclear complex [$RuCl_2(\eta^3{:}\eta^3$-$C_{10}H_{16})$(THPA)] (**2e**) resulted in all cases more advantageous in terms of both reaction rates and yields. In contrast, the dinuclear species [{$RuCl_2(\eta^3{:}\eta^3$-$C_{10}H_{16})$}$_2$(μ-THDP)] (**2f**) was more active in the hydration of the aliphatic derivatives hexanenitrile (94 versus 63%; Table 4, entry 17) and cyclohexanecarbonitrile (83 versus 57%; Table 4, entry 18). However, these particular substrates required longer reaction times (24 h) and produced the corresponding amides in lower yields as compared to the aromatic ones. Sulfonyl-substituted (Table 4, entry 20), as well as α,β-unsaturated (Table 4, entry 22), nitriles were also tolerated confirming the wide scope of this catalytic transformation.

The combined use of microwaves (MWs), as a nonclassical low-energy-consuming heating source, and water, as an environmentally friendly solvent, to perform organic reactions has recently emerged as a promising new field of research within the "Green Chemistry" context.[23] In this sense, as shown in Table 5, our catalytic hydration reactions can be conveniently performed in water under MW-irradiation. The working conditions employed (80 W/150 °C) allowed to reduce considerably the reaction times, as clearly exemplified in the hydration of the aliphatic derivatives hexanenitrile (Table 5, entry 10) and cyclohexanecarbonitrile (Table 5, entry 11) by the dinuclear complex **2f**, which re-

Table 5. Catalytic hydration of nitriles by complex **2f** under MW irradiation.[a]



Entry	Substrate	*t* [min]	Yield [%][b]
1	R = Ph	35	96
2[c]	R = Ph	90	95
3	R = 3-C_6H_4Cl	20	98
4	R = 4-C_6H_4F	30	97
5	R = 3-$C_6H_4NO_2$	30	95
6	R = 2-C_6H_4OH	30	99
7	R = 4-C_6H_4OMe	60	96
8	R = 4-C_6H_4SMe	30	99
9	R = benzo[1,3]dioxole-5-yl	45	95
10	R = *n*-C_5H_{11}	420	98
11	R = Cy	420	99
12	R = CH_2SO_2Ph	45	95
13	R = (*E*)-CH=CHPh	180	90

[a] Reactions were 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. A CEM Discover S-Class microwave was used (80 W, 150 °C, with cooling to optimize the power). [b] Determined by GC. [c] Reaction performed with a [Substrate]:[Ru] ratio = 100:2.

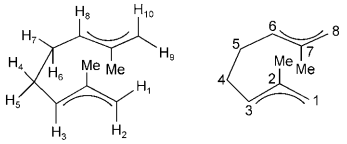
quired only 7 h of irradiation to be almost quantitatively transformed into the corresponding amides (98–99% GC yield). Finally, it is also important to note that, in contrast to the classical thermal conditions, a reduction of the catalysts loading is not associated with a dramatic increase in the reaction times. As an example, using only 1 mol% of **2f** (2 mol% of Ru instead of 5 mol%), benzamide is formed in 95% yield after irradiation for only 90 min.

Conclusion

We have developed new ruthenium-based catalytic systems that efficiently catalyze, in a neutral aqueous media, the selective hydration of a broad scope of nitriles, including aromatic, heteroaromatic and aliphatic substrates. To the best of our knowledge, these systems constituted by ruthenium(IV) complexes $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(L)]$ (L = hydrosoluble phosphane ligand), along with the ruthenium(II) examples $[RuCl_2(\eta^6\text{-arene})(L)]$ previously reported by us,[13] are the most efficient catalysts for this transformation in aqueous media. In addition, the high tolerance towards functional groups and their accessibility (easily prepared from commercially available metal precursors $[\{RuCl(\mu\text{-}Cl)(\eta^3:\eta^3\text{-}C_{10}H_{16})\}_2]$ and $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$) confers this selective and efficient synthetic approach of amides genuine potential for practical application avoiding the use of classical organic solvents.

Experimental Section

General: Synthetic procedures were performed under an atmosphere of dry nitrogen by 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 $[\{RuCl(\mu\text{-}Cl)(\eta^3:\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**),[24] TPPMS,[25] PTA,[26] PTA-Bn,[27] DAPTA,[17] THPA,[28] and THDP,[29] which were prepared by following methods reported in the literature. Infrared spectra were recorded by using a Perkin–Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out by using a Perkin–Elmer 2400 microanalyzer. CV measurements (25 °C) were carried out by using 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 (SCE) separated from the solution by a porous septum. Current and voltage parameters were controlled using a PAR system M273. GC/MSD measurements were performed by using a Agilent 6890N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using a HP-1MS column. 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 standards. DEPT experiments have been carried out for all the compounds reported in this paper. The numbering for protons and carbons of the 2,7-dimethyloctа-2,6-diene-1,8-diyl skeleton is as follows:



General procedure for the preparation of mononuclear complexes $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(L)]$ (L = TPPMS (2a), PTA (2b), PTA-Bn (2c), DAPTA (2d), THPA (2e)): A solution of the dimeric precursor $[\{RuCl(\mu\text{-}Cl)(\eta^3:\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**) (0.308 g, 0.5 mmol) and the appropriate monodentate phosphane (1 mmol) in dichloromethane (30 mL) was stirred at room temperature for 3 h. Concentration to approximately 5 mL followed by the addition of hexane (50 mL) led to the precipitation of a yellow solid, which was washed with hexane (3×10 mL) and vacuum-dried. Characterization data are as follows:

$[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(TPPMS)]$ (2a): Yield: 67% (0.450 g); IR (KBr): $\tilde{\nu}$ = 523 (w), 618 (m), 677 (m), 694 (s), 746 (m), 786 (m), 861 (w), 994 (m), 1034 (s), 1097 (s), 1141 (s), 1190 (vs), 1310 (w), 1346 (w), 1382 (m), 1433 (m), 1481 (m), 1630 (m), 2852 (w), 2910 (w), 3058 cm^{-1} (w); ^{31}P{^{1}H} NMR (C_6D_6): δ = 26.8 ppm (s); ^{1}H NMR (C_6D_6): δ = 2.17 (m, 2H, H_4 and H_6), 2.25 (s, 6H, Me), 3.15–3.27 (m, 4H, H_2, H_{10}, H_5 and H_7), 4.60 (d, 2H, ^3J(H,P) = 9.8 Hz, H_1 and H_9), 5.42 (m, 2H, H_3 and H_8), 6.89–7.90 (m, 12H, CH of TPPMS), 8.00, 8.85 ppm (br, 1 H each, CH of TPPMS); ^{13}C{^{1}H} NMR (C_6D_6): δ = 20.9 (s, Me), 37.0 (s, C_4 and C_5), 67.8 (d, ^2J(C,P) = 8.6 Hz, C_1 and C_8), 108.5 (d, ^2J(C,P) = 10.9 Hz, C_3 and C_6), 125.1 (s, C_2 and C_7), 127.2–135.3 ppm (m, C and CH of TPPMS); elemental analysis calcd (%) for $RuC_{28}H_{30}O_3Cl_2PSNa$: C 50.00, H 4.50; found: C 49.86, H 4.62; solubility in water at 20 °C: 5 mg mL^{-1}.

$[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(PTA)]$ (2b): Yield: 86% (0.401 g); IR (KBr): $\tilde{\nu}$ = 473 (m), 572 (m), 582 (s), 727 (w), 745 (m), 814 (m), 896 (w), 947 (s), 974 (vs), 1019 (s), 1098 (m), 1244 (m), 1282 (w), 1380 (w), 1418 (m), 1445 (w), 2893 (w), 2913 (w), 3026 cm^{-1} (w); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −56.1 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 2.23 (s, 6H, Me), 2.39 (m, 2H, H_4 and H_6), 2.97 (d, 2H, ^3J(H,P) = 4.0 Hz, H_2 and H_{10}), 3.01 (m, 2H, H_5 and H_7), 3.96 (d, 2H, ^3J(HP) = 8.0 Hz, H_1 and H_9), 4.12–4.42 (m, 12H, PCH_2N and NCH_2N), 4.91 ppm (m, 2H, H_3 and H_8); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.6 (s, Me), 36.4 (s, C_4 and C_5), 52.6 (d, ^1J(C,P) = 15.9 Hz, PCH_2N), 59.1 (d, ^2J(C,P) = 7.0 Hz, C_1 and C_8), 73.1 (d, ^3J(C,P) = 5.7 Hz, NCH_2N), 109.4 (d, ^2J(C,P) = 9.5 Hz, C_3 and C_6), 120.6 ppm (s, C_2 and C_7); elemental analysis calcd (%) for $RuC_{16}H_{28}N_3Cl_2P$: C 41.29, H 6.06, N 9.03; found: C 41.50, H 5.91, N 9.23; solubility in water at 20 °C: 0.5 mg mL^{-1}.

$[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(PTA\text{-}Bn)]$ (2c): Yield: 92% (0.544 g); IR (KBr): $\tilde{\nu}$ = 486 (m), 551 (w), 571 (m), 608 (w), 709 (w), 732 (vs), 756 (s), 820 (m), 902 (w), 991 (w), 1035 (s), 1071 (m), 1124 (m), 1266 (w), 1312 (m), 1383 (w), 1485 (m), 2854 (w), 2922 (w), 2977 (w), 3059 cm^{-1} (w); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −29.8 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 2.15 (s, 6H, Me), 2.78 (m, 2H, H_4 and H_6), 2.89 (d, 2H, ^3J(H,P) = 4.0 Hz, H_2 and H_{10}), 3.39 (m, 2H, H_5 and H_7), 4.21–4.39 (m, 4H, PCH_2N), 4.49 (d, 2H, ^3J(H,P) = 8.8 Hz, H_1 and H_9), 4.84–5.48 (m, 10H, PCH_2N, NCH_2Ph, H_3, H_8 and NCH_2N), 5.94 (m, 2H, NCH_2N), 7.38–7.64 ppm (m, 5H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.5 (s, Me), 36.4 (s, C_4 and C_5), 49.4 (d, ^1J(C,P) = 18.4 Hz, PCH_2N), 49.9 (d, ^1J(C,P) = 15.9 Hz, PCH_2N), 53.4 (d, ^1J(C,P) = 14.3 Hz, PCH_2N), 60.6 (br, C_1 and C_8), 64.7 (s, NCH_2Ph), 70.0, 78.5 and 78.8 (s, NCH_2N), 110.5 (d, ^2J(C,P) = 9.5 Hz, C_3 and C_6), 122.0 (s, C_2 and C_7), 125.0 (s, C of Ph), 129.3, 130.6, 133.1 ppm (s, CH of Ph); elemental analysis calcd (%) for $RuC_{23}H_{35}Cl_3N_3P$: C 46.67, H 5.96, N 7.10; found: C 46.90, H 6.12, N 7.24; solubility in water at 20 °C: 2.5 mg mL^{-1}.

$[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(DAPTA)]$ (2d): Two conformers were observed in solution for this complex (≈1.2:1 ratio). Yield: 90% (0.483 g); IR (KBr): $\tilde{\nu}$ = 469 (w), 532 (w), 564 (w), 626 (m), 699 (w), 799 (m), 868 (m), 891 (s), 999 (s), 1048 (s), 1100 (m), 1208 (m), 1238 (s), 1332 (s), 1356 (m), 1418 (s), 1651 (vs), 2857 (w), 2898 (w), 2972 cm^{-1} (w); *NMR data for the major conformer*: ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −30.9 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 2.11–2.20 (m, 12H, Me and COMe), 2.79 (m, 2H, H_4 and H_6), 2.98 (d, 2H, ^3J(H,P) = 5.1 Hz, H_2 and H_{10}), 3.43 (m, 2H, H_5 and H_7), 3.70–4.19 (m, 5H, PCH_2N and NCH_2N), 4.21 (d, 2H, ^3J(H,P) = 8.0 Hz, H_1 and H_9), 4.74–5.00 (m, 5H, PCH_2N, NCH_2N, H_3 and H_8), 5.79 ppm (m, 2H, PCH_2N and NCH_2N); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.7 (s, Me), 21.5 (s, CO*Me*), 36.5 (s, C_4 and C_5), 39.6 (d, ^1J(C,P) = 20.3 Hz, PCH_2N), 44.4 (d, ^1J(C,P) = 19.7 Hz, PCH_2N), 49.5 (d, ^1J(C,P) = 24.7 Hz, PCH_2N), 59.9 (d, ^2J(C,P) = 6.3 Hz, C_1 and C_8), 62.0 (br, NCH_2N), 110.3 (d, ^2J(C,P) = 6.9 Hz, C_3 and C_6), 121.9 (s, C_2 and C_7), 169.5, 170.3 ppm (s, *C*OMe); *NMR data for the minor conformer*: ^{31}P{^{1}H} NMR ($CDCl_3$): δ =

−31.2 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 2.11–2.20 (m, 12H, Me and COMe), 2.79 (m, 2H, H_4 and H_6), 3.01 (d, 2H, ^3J(H,P) = 5.1 Hz, H_2 and H_{10}), 3.43 (m, 2H, H_5 and H_7), 3.70–4.19 (m, 5H, PCH_2N and NCH_2N), 4.21 (d, 2H, ^3J(H,P) = 8.0 Hz, H_1 and H_9), 4.74–5.00 (m, 5H, PCH_2N, NCH_2N, H_3 and H_8), 5.79 ppm (m, 2H, PCH_2N and NCH_2N); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.7 (s, Me), 21.7 (s, CO*Me*), 36.4 (s, C_4 and C_5), 38.9 (d, ^1J(C,P) = 19.7 Hz, PCH_2N), 44.2 (d, ^1J(C,P) = 19.7 Hz, PCH_2N), 49.7 (d, ^1J(C,P) = 25.2 Hz, PCH_2N), 60.1 (d, ^2J(C,P) = 6.3 Hz, C_1 and C_8), 67.0 (br, NCH_2N), 110.5 (d, ^2J(C,P) = 6.9 Hz, C_3 and C_6), 121.7 (s, C_2 and C_7), 169.6, 170.3 ppm (s, *C*OMe); elemental analysis calcd (%) for $RuC_{19}H_{32}N_3Cl_2O_2P$: C 42.46, H 6.00, N 7.82; found: C 42.19, H 6.21, N 7.82; solubility in water at 20 °C: 1 mg mL^{-1}.

[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(THPA)] (2e): Yield: 67% (0.342 g); IR (KBr): $\tilde{\nu}$ = 468 (m), 583 (w), 613 (s), 629 (s), 645 (m), 671 (w), 789 (w), 803 (m), 887 (s), 922 (s), 940 (m), 982 (w), 1027 (w), 1072 (m), 1130 (w), 1158 (m), 1384 (m), 1426 (m), 1499 (w), 2913 (w), 2927 (w), 3025 cm^{-1} (w); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 135.4 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 2.15 (s, 6H, Me), 2.63 (m, 2H, H_4 and H_6), 3.14 (d, 3H, ^3J(H,P) = 10.0 Hz, NMe), 3.17 (d, 3H, ^3J(H,P) = 11.2 Hz, NMe), 3.39–3.48 (m, 4H, H_2, H_5, H_7 and H_{10}), 4.36 (d, 2H, ^3J(H,P) = 12.0 Hz, H_1 and H_9), 4.85 (m, 2H, H_3 and H_8), 5.21 (br, 2H, NCH_2N), 5.55–5.92 ppm (m, 4H, NCH_2N); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.3 (s, Me), 36.3 (s, C_4 and C_5), 41.0 (br, NMe), 46.8 (s, NMe), 62.8 (d, ^2J(C,P) = 4.4 Hz, C_1 and C_8), 67.0 (br, NCH_2N), 76.1 (s, NCH_2N), 110.1 (d, ^2J(C,P) = 12.7 Hz, C_3 and C_6), 126.7 ppm (s, C_2 and C_7); elemental analysis calcd (%) for $RuC_{16}H_{31}N_6Cl_2P$: C 37.65, H 6.12, N 16.47; found: C 37.78, H 6.00, N 16.31; solubility in water at 20 °C: 2.5 mg mL^{-1}.

Preparation of the dinuclear complex [{$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$}$_2$(μ-THDP)] (2f): A solution of complex [{RuCl(μ-Cl)($\eta^3{:}\eta^3$-$C_{10}H_{16}$)}$_2$] (**1**) (0.308 g, 0.5 mmol) and the diphosphine THDP (0.118 g, 0.5 mmol) in dichloromethane (30 mL) was stirred at room temperature for 2 h. Concentration to ≈5 mL followed by the addition of hexane (50 mL) led to the precipitation of a yellow solid, which was washed with hexane (3×10 mL) and vacuum-dried. Complex **2f** is formed as a nonseparable mixture of two diastereoisomers (*meso* and *rac* forms) in ≈5:1 ratio. Yield: 71% (0.303 g); IR (KBr): $\tilde{\nu}$ = 466 (w), 492 (m), 594 (s), 613 (s), 744 (s), 759 (s), 820 (w), 861 (m), 915 (m), 937 (m), 1020 (m), 1053 (m), 1138 (w), 1182 (w), 1231 (w), 1308 (w), 1383 (m), 1443 (m), 2849 (w), 2898 (w), 3004 cm^{-1} (w);

NMR data for the major diastereoisomer (meso form): ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 135.9 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 2.20 (br, 6H, Me), 2.64 (br, 2H, H_4 and H_6), 3.14–3.23 (m, 22H, NMe, H_2, H_{10}, H_5 and H_7), 3.52 (br, 2H, H_1 and H_9), 4.68 (br, 2H, H_3 and H_8) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.1 (s, Me), 36.4 (s, C_4 and C_5), 41.3 (s, NMe), 64.5 (br, C_1 and C_8), 109.8 (br, C_3 and C_6), 126.8 ppm (s, C_2 and C_7);

NMR data for the minor diastereoisomer (rac form): ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 132.8, 135.7 ppm (d, ^3J(P,P) = 102.1 Hz); ^{1}H NMR ($CDCl_3$): δ = 2.20 (br, 6H, Me), 2.64 (br, 2H, H_4 and H_6), 3.14–3.23 (m, 22H, NMe, H_2, H_{10}, H_5 and H_7), 3.52 (br, 2H, H_1 and H_9), 4.68 ppm (br, 2H, H_3 and H_8); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.5 (s, Me), 36.1 (s, C_4 and C_5), 41.7 (s, NMe), 66.2 (br, C_1 and C_8), 109.8 (br, C_3 and C_6), 125.9 ppm (s, C_2 and C_7); elemental analysis calcd (%) for $Ru_2C_{26}H_{50}N_6Cl_4P_2$: C 36.63, H 5.91, N 9.86; found: C 36.79, H 6.08, N 10.01; solubility in water at 20 °C: 1 mg mL^{-1}.

General procedure for the catalytic hydration of nitriles under thermal conditions: 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 stirred at 100 °C for the indicated time (see Tables 3 and 4). The course of the reaction was monitored by regular sampling and analysis by GC/MSD. After elimination of the solvent after 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 ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data with those reported in the literature and by their fragmentation in GC/MSD.

General procedure for the catalytic hydration of nitriles under MW irradiation: Under nitrogen atmosphere, a pressure-resistant septum-sealed glass microwave reactor vial was charged with the corresponding nitrile (1 mmol), water (3 mL), complex **2f** (21 mg, 0.025 mmol; 5 mol% of Ru) and a magnetic stirring bar. The vial was then placed inside the cavity of a CEM Discover S-Class microwave synthesizer and power was held at 80 W until the desired temperature was reached (150 °C). Microwave power was automatically regulated for the remainder of the experiment to maintain the temperature (monitored by a built-in infrared sensor; P_{max} = 20 psi). The course of the reaction was monitored by regular sampling and analysis by GC/MSD.

X-ray crystal structure determinations: Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane (**2b**, **2c**, and **2d**) or pentane (**2f**) into a saturated solution of the complexes in dichloromethane. In all cases, data collection was performed by using a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using $Cu_{K\alpha}$ 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.[30] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[30] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[26] The software package WINGX[31] was used for space group determination, structure solution and refinement. The structure for the complexes **2c** and **2d** were solved Patterson interpretation and phase expansion using DIRDIF.[32] For **2b** and **2f** the structures were solved by direct methods using SIR2004.[33] In the crystal of **2b** a CH_2Cl_2 solvent molecule per unit formula of the complex is present. This molecule, along with the octadienediyl chain, is disordered in two positions with an occupancy factor of 0.5. Similarly, in the crystal of **2f**, with the exception of the Ru and P atoms, and the methyl groups, the rest of atoms are also disordered in two positions with an occupancy factor of ca. 0.5. Isotropic least-squares refinement on F^2 using SHELXL97[34] 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 **2b**, **2c**, and **2f** the H atoms were geometrically located and their coordinates were refined riding on their parent atoms. For **2d**, the coordinates of H atoms were found from different Fourier maps and included in a refinement with isotropic parameters. In all cases the maximum residual electron density is located near heavy atoms.

Crystal data for 2b: $RuC_{16}H_{28}N_3Cl_2P{\cdot}CH_2Cl_2$, M = 550.28 g mol^{-1}, T = 120(2) K, orthorhombic, *Pnma*, crystal size 0.26×0.08×0.08 mm, a = 29.6657(5), b = 10.0708(2), c = 7.1548(1) Å, Z = 4, V = 2137.55(6) Å^3, ρ_{calcd} = 1.710 g cm^{-3}, μ = 11.304 mm^{-1}, final $R1$ = 0.0436 [$I > 2\sigma(I)$] and 0.0481 (all data), and $wR2$ = 0.1040 [$I > 2\sigma(I)$] and 0.1088 (all data).

Crystal data for 2c: $RuC_{23}H_{35}Cl_3N_3P$, M = 591.93 g mol^{-1}, T = 293(2) K, monoclinic, $P2_1/c$, crystal size 0.028×0.083×0.117 mm, a = 12.9696(4), b = 14.4861(3), c = 14.0113(4) Å, β = 107.552(3)°, Z = 4, V = 2509.87(3) Å^3, ρ_{calcd} = 1.566 g cm^{-3}, μ = 8.719 mm^{-1}, final $R1$ = 0.0417 [$I > 2\sigma(I)$] and 0.0452 (all data), and $wR2$ = 0.1126 [$I > 2\sigma(I)$] and 0.1149 (all data).

Crystal data for 2d: $RuC_{19}H_{32}N_3Cl_2O_2P$, M = 537.42 g mol^{-1}, T = 120(2) K, monoclinic, $P2_1/c$, crystal size 0.13×0.11×0.05 mm, a = 20.0690(2), b = 8.9949(1), c = 12.3476(1) Å, β = 94.903(1)°, Z = 4, V = 2220.82(4) Å^3, ρ_{calcd} = 1.607 g cm^{-3}, μ = 8.774 mm^{-1}, final $R1$ = 0.0270 [$I > 2\sigma(I)$] and 0.0347 (all data), and $wR2$ = 0.0698 [$I > 2\sigma(I)$] and 0.0785 (all data).

Crystal data for 2f: $Ru_2C_{26}H_{50}N_6Cl_4P_2$, M = 852.60 g mol^{-1}, T = 100(2) K, monoclinic, $P2_1/c$, crystal size 0.022×0.087×0.137 mm, a = 13.9680(2), b = 8.3530(1), c = 14.2890(2) Å, β = 93.4870(1)°, Z = 2, V = 1664.08(4) Å^3, ρ_{calcd} = 1.702 g cm^{-3}, μ = 11.433 mm^{-1}, final $R1$ = 0.0371 [$I > 2\sigma(I)$] and 0.0415 (all data), and $wR2$ = 0.0958 [$I > 2\sigma(I)$] and 0.0995 (all data).

CCDC-773996 (**2b**), CCDC-773997 (**2c**) CCDC-773998 (**2d**) CCDC-773999 (**2f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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