

Article

# Selective Hydration of Nitriles to Corresponding Amides in Air with Rh(I)-N-Heterocyclic Complex Catalysts

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**Abstract:** A new synthetic method for obtaining [RhCl(cod)(NHC)] complexes (**1–4**) (cod =  $\eta^4$ -1,5-cyclooctadiene, NHC = *N*-heterocyclic carbene: IMes, SIMes, IPr, and SIPr, respectively) is reported together with the catalytic properties of **1–4** in nitrile hydration. In addition to the characterization of **1–4** in solution by <sup>13</sup>C NMR spectroscopy, the structures of complexes **3**, and **4** have been established also in the solid state with single-crystal X-ray diffraction analysis. The Rh(I)-NHC complexes displayed excellent catalytic activity in hydration of aromatic nitriles (up to TOF = 276 h<sup>-1</sup>) in water/2-propanol (1/1 *v/v*) mixtures in air.

**Keywords:** hydration; metal catalysis; *N*-heterocyclic carbenes; nitriles; rhodium; synthesis of organometallics

## 1. Introduction

From the viewpoint of the industrial and pharmacological applications, amides are important compounds in many fields and several ways are reported to obtain amides from nitriles [1,2]. Hydration of nitriles to amides is a 100% atom economic reaction, however the procedure is biased by selectivity issues. Traditionally, hydration of nitriles has been performed in the presence of strong inorganic acids (H<sub>2</sub>SO<sub>4</sub>) or bases (NaOH) under harsh conditions, that often results in over-hydrolysis and produces undesired carboxylic acids. To avoid this problem, in the last decades several remarkable catalytic systems have been developed to stop hydration at the amide stage, e.g., using enzymes as biocatalysts (nitrile hydratase, NHase) [3], nanocatalysts such as a Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles-supported Cu-NHC complex [4], or ruthenium hydroxide nanoparticles on magnetic silica [5], silver nanoparticles [6], and other heterogeneous [7–10] or homogenous catalysts. A broad spectrum of transition metal complexes based on rhodium [11,12], ruthenium [12–15], nickel [16], osmium [17], and gold [18] were employed as catalysts, and the field has been reviewed from various aspects [19–29].

Transition metal-free processes have been described, too, such as the CsOH/DMSO superbase system [30], NaOH as catalyst [31], or *t*BuOK under anhydrous conditions [32]. Nitrile hydratases catalyze the hydration of nitriles to the corresponding amides under softer conditions and have been successfully used, for example, for production of levetiracetam (Keppra<sup>®</sup>) for the treatment of epilepsy [3]. However, the application of most NHases is limited because of their substrate

specificity, and the rapid decay of the catalytic activity at temperatures higher than 10–30 °C, not mentioning their high cost. Despite all the mentioned results, the development of efficient new catalysts is still required. Although the homogenous organometallic catalysts give the target amides with high selectivity and in high yield, many of the reported reactions were carried out at high temperature (> 150 °C) [33], or in several cases required specific reaction conditions such as microwave irradiation, inert atmosphere or long reaction times. For example, Oshiki et al. described a very efficient catalyst [33], *cis*-[Ru(acac)<sub>2</sub>(PPh<sub>2</sub>py)<sub>2</sub>] (acac = acetylacetonate, PPh<sub>2</sub>py = diphenyl-2-pyridylphosphine) for hydration of benzonitrile at 180 °C in 1,2-dimethoxyethane under argon with the highest turnover frequency reported to date for this reaction, i.e., TOF = 20,900 h<sup>-1</sup> (TOF = mol amide × (mol catalyst × h)<sup>-1</sup>). However, this excellent activity was observed only at high temperature; the TOF value dropped to 222 h<sup>-1</sup> upon reducing the temperature to 150 °C, and no product was observed at 80 °C.

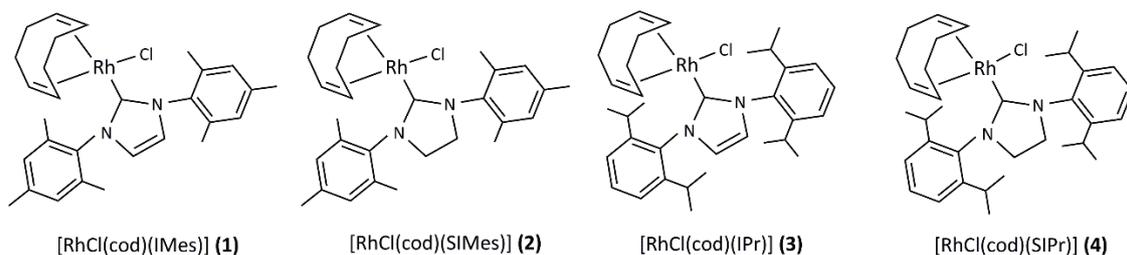
The field of transition metal complex-catalyzed nitrile hydration is dominated by ruthenium-based catalysts [7,10,12–14,33,34] and only a few rhodium catalysts can be found in the literature for this transformation. Ajjou et al. reported that the water-soluble rhodium complex generated in situ from [RhCl(cod)]<sub>2</sub> (cod = η<sup>4</sup>-1,5-cyclooctadiene) and P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)<sub>3</sub> (mtppts) very effectively catalyzed the hydration of nitriles under basic conditions. As an example, benzonitrile yielded the corresponding amide quantitatively in 24 h at 90 °C and at pH of ~11.7 [35]. Saito et al. described a Rh(I)-complex prepared in situ from [Rh(cod)(OMe)]<sub>2</sub> and PCy<sub>3</sub> (Cy = cyclohexyl), as a remarkable hydration catalyst for nitriles in 2-PrOH at 25 °C. The nitrile substrates included aromatic, aliphatic, and olefinic substituents, however, at this low temperature, 24–72 h reaction time was required to achieve quantitative yields [36]. Bera et al. have found that in the presence of a base, [Rh(cod)(κC<sub>2</sub>-PIN)Br] (PIN = 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene) showed outstanding catalytic activity for hydration of organonitriles in 2-PrOH. A turnover frequency of 20,000 h<sup>-1</sup> was possible to achieve for acrylonitrile and it was demonstrated that the naphthyridine group enhanced the hydration activity of the metal centre [37]. Recently, Cadierno et al. disclosed that [RhCl(cod){P(NMe<sub>2</sub>)<sub>3</sub>}] promoted very efficiently the selective hydration of an array of nitriles in water without the addition of a base or other additive [11].

In the last three decades, *N*-heterocyclic carbene (NHC) ligands and the transition metal complexes of them have attracted enormous interest in organometallic chemistry, as well as catalysis [38–41]. It is therefore surprising that Rh(I)-NHC complexes have not been employed for catalysis of nitrile hydration reactions in aqueous or partly aqueous systems. One reason for this relative lack of prominence may be in that generally, the Rh(I)-complexes—with a few exceptions—were found less reactive than the Ru(II)-based complex catalysts, and in the hydration of benzonitrile they were characterized with turnover frequencies TOF < 100 h<sup>-1</sup>. [RhCl(NHC)(cod)] complexes were first reported in 1974 by Lappert et al. [42], followed by pioneering contributions of Herrmann et al. [43]. Generally, [RhCl(cod)(NHC)] complexes are possible to be prepared by deprotonation of the imidazolium salts in the presence of [RhCl(cod)]<sub>2</sub>, and the reported procedures differ only in the nature of the deprotonation agent. The synthesis may involve the direct reaction of the free carbene (isolated or in situ generated) with [RhCl(cod)]<sub>2</sub> [44]; reaction of an imidazolium halide salt with a [Rh(μ-OR)(cod)]<sub>2</sub> alkoxide complex [45]; and transmetalation of [RhCl(cod)]<sub>2</sub> with silver-NHC complexes [46]. In 2009, it was discovered that imidazolium-2-cyanides can transfer NHC ligands to rhodium complexes and this finding opened a new pathway of synthesis of [RhCl(NHC)(cod)] complexes, too [47]. Plenio et al. also reported the one-step synthesis of [RhCl(NHC)(cod)] complexes using K<sub>2</sub>CO<sub>3</sub> as base in acetone at 60 °C [48]. *t*BuOK in THF could also be used at room temperature [49].

The first selective catalytic hydration of nitriles under anhydrous conditions in the presence of [RhCl(cod)(IMes)] as the catalyst was reported in 2009 by Lee et al. [50]. Hydration of nitriles was achieved with propionaldoxime as a water source; with 1 mol% catalyst, hydration of 4-methoxybenzonitrile yielded the respective amide with 87% conversion at 110 °C in 6 h. Later this group reported the selective hydration of nitriles into the respective amides on the catalytic action of

Wilkinson's catalyst with acetaldoxime as the water source; various functional groups were compatible with the reaction conditions [51].

To the best of our knowledge, there are no  $[\text{RhCl}(\text{cod})(\text{NHC})]$  type Rh(I)-catalysts reported until now for the selective hydration reaction of nitriles with water in aqueous or partly aqueous solvents. Therefore, we initiated a study of catalytic nitrile hydration with the use of the known  $[\text{RhCl}(\text{cod})(\text{NHC})]$  (**1–4**) complexes with the NHC ligands IMes, SIMes, IPr, and SIPr, respectively (Figure 1) [44,46,48,49,52–56]. In this article, we report on a simple, one-step synthetic procedure for obtaining these complexes using  $[\text{RhX}(\text{cod})]_2$  ( $\text{X} = \text{Cl}^-$ ,  $\text{OH}^-$ ) as a metal precursor, the respective imidazolium/imidazolium chlorides, and  $\text{K}_2\text{CO}_3$  as the deprotonating agent, in toluene at 70 °C. Successful application of complexes **1–4** for the selective hydration of several aromatic and heteroaromatic nitriles to the corresponding amides is also described in detail below.



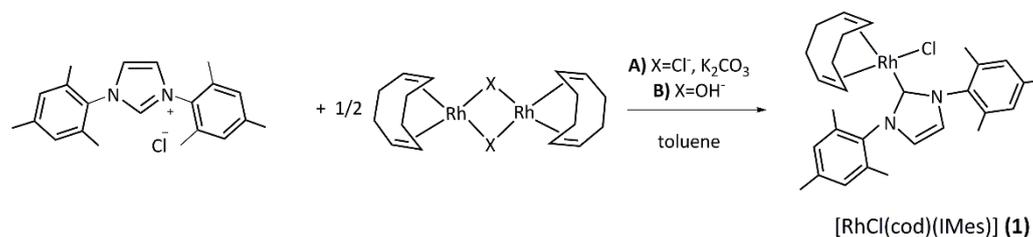
**Figure 1.** The Rh(I)-NHC complexes **1–4** used in our study as catalysts for selective nitrile hydration.

## 2. Results and Discussion

### 2.1. Synthesis and Characterization of the $[\text{RhCl}(\text{cod})(\text{NHC})]$ Complexes **1–4**

In this work, we explored the applicability of Rh(I)-N-heterocyclic complexes **1–4** (Figure 1) for catalysis of hydration of aromatic nitriles. We developed a synthetic method for obtaining these known compounds [44,46,48,49,52–56], which does not require the use of the isolated free carbenes or the use of the corresponding Ag(I)-NHC transmetallating agents.

In general, the synthesis of **1–4** (Scheme 1) involved stirring of the respective 1,3-diarylimidazolium or 1,3-diarylimidazolium salt in toluene at 70 °C together with  $[\text{RhCl}(\text{cod})]_2$  and  $\text{K}_2\text{CO}_3$  as an efficient and mild base (A) [47] or with  $[\text{Rh}(\text{OH})(\text{cod})]_2$  (no base added; B). After removal of the toluene solvent the products were dissolved in  $\text{CH}_2\text{Cl}_2$ -ethyl acetate and purified by passing through a short silica column; complexes **1–4** were isolated in 58–88% yield.

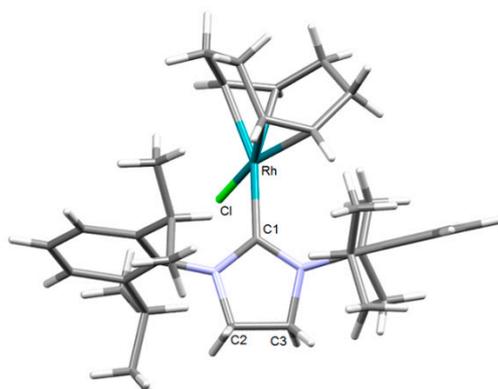


**Scheme 1.** Synthesis of **1** from  $[\text{RhCl}(\text{cod})]_2$  and  $[\text{IMesH}]\text{Cl}$  with  $\text{K}_2\text{CO}_3$  as deprotonating agent.

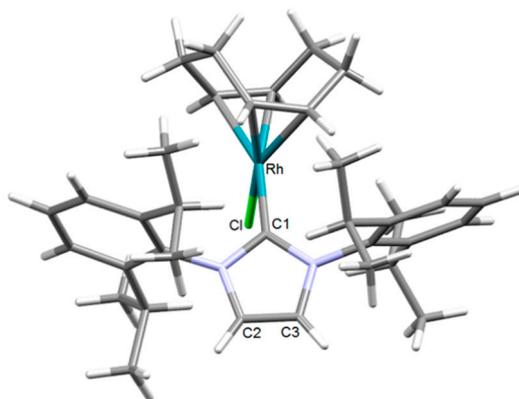
The purity of the complexes was checked by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of all complexes displayed the diagnostic Rh(I)-C(carbene) doublet resonances at 183.2 and 185.5 ppm (**1** and **3**), and 212.4 and 214.9 ppm (**2** and **4**), respectively (further spectral details in the Materials and Methods Section).

Single-crystals of **4** could be obtained by crystallization from chloroform at room temperature. In addition, both **3** and **4** yielded single-crystals from benzene, however, these crystals contained solvating benzene molecules, too. (Further experimental details of the X-ray structure analysis can be found in Supplementary Materials). The crystals were subjected to X-ray diffraction measurements.

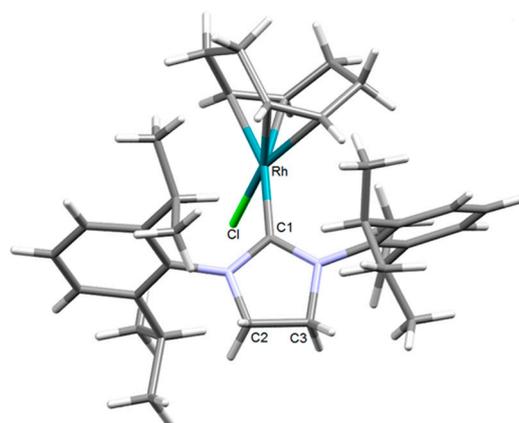
The respective capped sticks representations are shown on Figures 2–4, while the most important bond distances and bond angles are found in Tables 1–3.



**Figure 2.** Capped sticks representation of the solid-state structure of [RhCl(cod)(SIPr)] (4) crystallized from CHCl<sub>3</sub>.



**Figure 3.** Capped sticks representation of the solid-state structure of [RhCl(cod)(IPr)](3) crystallized from benzene ([RhCl(cod)(IPr)]\_benzene\_3; benzene molecules are omitted for clarity).



**Figure 4.** Capped sticks representation of the solid-state structure of [RhCl(cod)(SIPr)]\_benzene\_4 (benzene molecules are omitted for clarity).

**Table 1.** Comparison of the most important bond lengths (Å) angles (°) of [RhCl(cod)(IPr)] (3) [54] and [RhCl(cod)(SIPr)] (4) crystallized from CHCl<sub>3</sub> (this work).

	[RhCl(cod)(IPr)] (3) [54]		[RhCl(cod)(SIPr)] (4)	
Rh–C <sub>carbene</sub>	2.056(4)	2.052(1)	2.043(3)	2.053(1)
Rh–Cl	2.3467(12)	2.3713(12)	2.3721(11)	2.3466(10)
C2–C3	-	-	1.501(7)	1.487(7)
C2=C3	1.328(6)	1.324(5)	-	-
C <sub>carbene</sub> –Rh–Cl	85.61(11)	88.26(11)	86.92(9)	84.32(10)

**Table 2.** The most important bond lengths (Å) angles (°) of the four individual molecules in the unit cells of the benzene solvate of 3, i.e., [RhCl(cod)(IPr)]\_benzene\_3.

	[RhCl(cod)(IPr)]_benzene_3			
Rh–C <sub>carbene</sub>	2.050(4)	2.031(4)	2.032(4)	2.051(4)
Rh–Cl	2.3752(11)	2.3726(10)	2.3706(10)	2.3775(10)
C2=C3	1.330(6)	1.338(6)	1.339(6)	1.333(6)
C <sub>carbene</sub> –Rh–Cl	89.01(11)	88.33(11)	87.76(11)	89.43(10)

**Table 3.** The most important bond lengths (Å) angles (°) of the four individual molecules in the unit cells of the benzene solvate of 4, i.e., [RhCl(cod)(SIPr)]\_benzene\_4.

	[RhCl(cod)(SIPr)]_benzene_4			
Rh–C <sub>carbene</sub>	2.028(7)	2.034(7)	2.046(7)	2.044(7)
Rh–Cl	2.3800(17)	2.3746(17)	2.3797(18)	2.3781(4)
C2–C3	1.515(11)	1.505(11)	1.497(11)	1.524(10)
C <sub>carbene</sub> –Rh–Cl	87.40(19)	86.03(19)	88.80(18)	88.08(19)

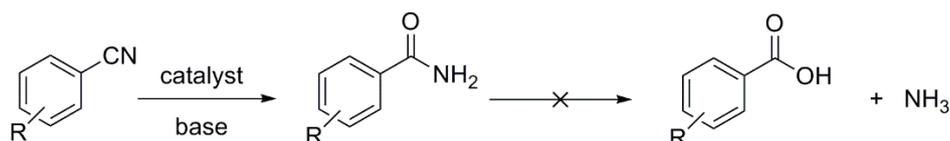
The solid-state crystal structure of 3 has already been determined by single crystal X-ray diffraction and was resolved without solvent [54]. This gives a possibility to compare the structures of 3 and 4 (Table 1). The unit cell of [RhCl(cod)(SIPr)] (4), obtained from chloroform, does not contain solvent molecules, and, in contrast to [RhCl(cod)(IPr)] (3) [54] (*P*<sub>2</sub><sub>1</sub>/*c*), it crystallizes in the monoclinic *P*<sub>2</sub><sub>1</sub>/*n* space group. There are two neutral Rh-complex molecules in the unit cells of both compounds. The lengths of the unit cell edges, and the unit cell angles show only slight differences. This is not surprising, since the sp<sup>2</sup> or sp<sup>3</sup> C-atoms in the IPr, and SIPr ligands, respectively, do not influence significantly the measures of the unit cell (the same is true for the two extra hydrogen atoms in SIPr). There are no significant differences in the Rh–C<sub>carbene</sub> and in the Rh–Cl bond lengths, either, however, the C2–C3 bond lengths in the [RhCl(cod)(SIPr)] (4) molecules are 1.501(7) Å, and 1.487(7) Å, respectively, which unambiguously refers to sp<sup>3</sup> carbon atoms. Saturation of the heterocyclic ring does not alter significantly the C<sub>carbene</sub>–Rh–Cl angles, either. Interestingly, the data of the unit cells of 3 and 4 are almost identical to those of [IrCl(cod)(IPr)] [57]; the data are compared in Tables S2 and S3.

Crystallization of [RhCl(cod)(IPr)] and [RhCl(cod)(SIPr)] from benzene leads to incorporation of solvent molecules into the lattice, yielding crystals of [RhCl(cod)(IPr)]\_benzene\_3 and [RhCl(cod)(SIPr)]\_benzene\_4. Unfortunately, the benzene molecules are disordered. Both [RhCl(cod)(IPr)]\_benzene\_3 and [RhCl(cod)(SIPr)]\_benzene\_4 crystallize in the monoclinic *CC* (no. 9) space group, and the unit cells contain four different neutral Rh(I)-complexes together with eight benzene molecules. In the four molecules of [RhCl(cod)(IPr)]\_benzene\_3 in the unit cell, there are no significant differences in the Rh–Cl bond lengths, however, the Rh–C<sub>carbene</sub> distances are slightly lower (2.031–2.051 Å) than the average Rh–C<sub>carbene</sub> distances in similar complexes, 2.049 Å (CSD Version 5.40, 2019). The crystal structure of [RhCl(cod)(SIPr)]\_benzene\_4 is very similar to that of [RhCl(cod)(IPr)]\_benzene\_3. In this case, too, the average Rh–C<sub>carbene</sub> distances (2.028–2.046 Å) are somewhat shorter than those in the benzene-free crystals of [RhCl(cod)(SIPr)] (3). The C2–C3 distance in [RhCl(cod)(IPr)]\_benzene\_3 is 1.330–1.339 Å which refers to carbon atoms with sp<sup>2</sup> hybridization,

while the corresponding C2–C3 bond length in [RhCl(cod)(SIPr)]\_benzene\_4, i.e., 1.524–1.497 Å, agrees well with the presence of sp<sup>3</sup>-hybridized carbon atoms.

## 2.2. Hydration of Aromatic Nitriles Catalyzed by the [RhCl(cod)(NHC)] Complexes 1–4

Due to the importance of amides in the synthesis of important pharmaceuticals, there is a strong incentive to develop new transition metal catalysts which are able to facilitate the selective hydration reaction of aliphatic, as well as aromatic nitriles to corresponding amides (Scheme 2) with high activity under mild conditions (i.e., at temperatures below 100 °C, and preferably close to room temperature).



**Scheme 2.** General scheme of the selective hydration of benzonitriles to benzamides.

It was found that complexes 1–4 efficiently catalyzed the hydration of benzonitrile to benzamide in a water/2-propanol = 1/1 mixture in air and under mild conditions ( $\leq 80$  °C). The choice of 2-propanol as the organic component of the solvent was based on its unique favourable effects on certain reactions, e.g., hydrogenation and transfer hydrogenation of ketones [58]. The reactions did not display an induction period (Figure S1) and they proved completely selective; no products other than benzamide were detected by GC-MS or <sup>1</sup>H NMR spectroscopy. With these catalysts, fast hydration of benzonitrile was observed only in the presence of bases. The data in Table 4 show that in the lack of a base no reaction of benzonitrile was observed in 1.5 h, and even after 2 h the conversion reached only 3%. Conversely, with bases such as *t*BuOK, KOH, Na<sub>2</sub>CO<sub>3</sub>, and NaOH at a [base]/[Rh] = 1/1 ratio, the conversions in 1.5 h were in the 50–60% range and were not strongly dependent on the choice of the particular base. The use of NaOH resulted in the highest conversion, and therefore it was chosen for further studies. The possible catalytic effect of the bases in Table 4 were also checked in the hydration of benzonitrile in the absence of catalysts 1–4. Under the conditions used, conversion of benzonitrile to benzamide was < 1% with all four bases (only a trace of product could be detected by gas chromatography). These results show that the contribution of base-catalyzed hydration is negligible compared to the metal-complex catalyzed transformation.

**Table 4.** Effect of various bases on the hydration of benzonitrile catalyzed by [RhCl(cod)(IMes)] (1).

Entry	Base	Conversion (%)	TOF <sup>a</sup> (h <sup>-1</sup> )
1	-	0(3 <sup>b</sup> )	0(4 <sup>b</sup> )
2	<i>t</i> BuOK	52	69
3	KOH	52	69
4	K <sub>2</sub> CO <sub>3</sub>	56	75
5	NaOH	59	79

Conditions: 1 mmol benzonitrile, 0.5 mol% [RhCl(cod)(IMes)] (1), 0.005 mmol base, 1.5 mL 2-PrOH, 1.5 mL H<sub>2</sub>O, 80 °C, 1.5 h. <sup>a</sup> Turnover frequencies were calculated from the conversions at the indicated reaction times. <sup>b</sup> 2 h.

The effects of various reaction parameters for the hydration of benzonitrile were studied in detail using complex 1 as the catalyst. The progress of the reactions could be conveniently monitored by gas chromatography. Representative results are summarized in Table 5.

**Table 5.** The effect of various reaction parameters on the hydration of benzonitrile catalyzed by [RhCl(cod)(IMes)] (1).

Entry	Catalyst (mol%)	Base <sup>a</sup>	Phosphine	T °C	t (min)	Conversion (%) <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )
1	1	NaOH	-	40	120	48 (0)	24
2	1	NaOH	-	50	120	72 (1)	36
3	1	NaOH	-	60	120	82 (1)	41
4	1	NaOH	-	70	120	91 (3)	45
5	1	NaOH	-	80	120	98 (6)	49
6	1	NaOH	-	80	10	46 (1)	276
7	1	NaOH	-	80	20	63 (1)	189
8	1	NaOH	-	80	30	74 (2)	148
9	1	NaOH	-	80	60	86 (3)	86
10	1	NaOH	-	80	90	94 (5)	63
11	5	-	-	reflux	60	0	0
12	5	-	-	reflux	120	18	2
13	5	-	-	reflux	180	26	2
14	5	NaOH	-	reflux	10	96	115
15	5	NaOH	-	reflux	20	97	58
16	5	NaOH	-	reflux	60	>99	20
17	5	-	0.05 mmol PTA	reflux	60	17	3
18	5	-	0.15 mmol PTA	reflux	60	70	14
19	5	-	0.25 mmol PTA	reflux	60	78	16
20	5	-	0.05 mmol <i>mtp</i> ppms	reflux	60	75	15
21	5	-	0.15 mmol <i>mtp</i> ppms	reflux	60	76	15
22	5	-	0.25 mmol <i>mtp</i> ppms	reflux	60	94	19

Conditions: 1 mmol benzonitrile, 2-PrOH/H<sub>2</sub>O = 1:1 V = 3 mL. <sup>a</sup> [NaOH]/[Rh] = 1; <sup>b</sup> Conversions of base-catalyzed hydrations in parentheses (NaOH only). <sup>c</sup> Turnover frequencies were calculated from the conversions at the indicated reaction times.

The data in Table 5 show that [RhCl(cod)(IMes)] (1) is an active catalyst for benzonitrile hydration. The TOF values (up to 276 h<sup>-1</sup>) compare well with those of most transition metal catalysts although fall behind the highest activities [33]. With increasing temperatures, the yield of benzamide increased and reached a maximum (98%) at 80 °C. It is also evident from Table 5, that under the applied reaction conditions, 2 h is the optimum reaction time for the catalytic hydration of benzonitrile to benzamide. For the entries 1–10 of Table 5, the effect of the base (NaOH) alone (i.e., in the absence of the Rh(I)-complex catalyst) has been checked and the results are shown in parentheses in the Conversion (%) column of the Table, next to the values obtained with catalyst 1 + NaOH. Here, again, it can be concluded, that the base-catalyzed hydration increases the total benzamide yield only to a minor extent even at higher reaction temperatures and longer reaction times (entries 5 and 10). In order to determine the efficiency of the catalyst in the absence of NaOH, we had to increase the catalyst concentration to 5 mol% (entries 11–13). Even then, no reaction was observed at reflux conditions (approximately 81 °C, see Experimental) in 60 min, and only 26% conversion of benzonitrile was obtained after 180 min reaction time. In contrast, the reaction with 1 + NaOH led to 86% conversion already after 10 min (entry 14).

Table 5 also shows the effect of the water-soluble tertiary phosphines PTA (1,3,5-triaza-7-phosphaadamantane) and *mtp*ppms-Na (sodium diphenylphosphinobenzene-3-sulfonate or monosulfonated triphenylphosphine Na-salt). Compared to catalyst 1 (entry 11, 0% conversion in 60 min), both PTA and *mtp*ppms increased the reaction rate and at a [phosphine]/[Rh] ratio their effect is about the same (entries 18 and 21). In general, however, *mtp*ppms proved to be more effective. Nevertheless, with regard to the rate increase, both phosphines were much inferior to NaOH (entry 14).

The precedents in the literature show that with bmim (1-butyl-3-methyl-imidazole-2-ylidene) as the NHC ligand, PTA and *mtp*ppms form [Rh(cod)(bmim)(PTA)]Cl, and [Rh(cod)(bmim)(*mtp*ppms)] (a neutral zwitterionic complex), respectively [59]. In accordance with these earlier results, we expect that tertiary phosphines coordinate to the central Rh(I) ion in [RhCl(cod)(NHC)] complexes. However, the resulting complex species are coordinatively saturated and coordination of the nitrile substrate and/or H<sub>2</sub>O or OH<sup>-</sup> to the metal ion in a Rh(I)-complex seems unlikely. In the case of [RuCl<sub>2</sub>(PTA)<sub>4</sub>]-catalyzed nitrile hydration, Frost suggested that the increased catalytic activity in the presence of a large excess of PTA was due to the pH shift into the alkaline region in concentrated PTA solutions caused by the protonation of PTA [34]. This may happen in our reactions with added PTA, too, however, it is certainly not the case with *mtp*ppms which is protonated only in concentrated aqueous acid solutions. Nevertheless, since the roles of PTA and *mtp*ppms were not clarified in detail, our observations on the effect of PTA and *mtp*ppms on the Rh(I)-complex catalyzed hydration of benzonitrile can be regarded only as an information of practical importance. Details of these phosphine effects were not scrutinized.

Table 6 presents the results of benzonitrile hydration with [RhCl(cod)(NHC)] complexes 1–4. It can be seen that in the presence of NaOH, high conversions (93 – >99%) could be obtained in reasonable reaction times (1–3 h) with all four catalysts (entries 2, 5, 8, 11). Conversely, in the absence of NaOH, each catalyst showed only low activity, and the highest conversion under such conditions was only 26% in 3 h (entry 1). It seems from the conversion data for the first hour of the reactions, that the evolution of the real catalytic species in the water/2-propanol mixed solvent from the precursor complexes 1–4 and NaOH needs noticeable time. It is fast with 1 and 2 (entries 2, 5), somewhat slower with 4 (entry 11) and significantly slower in the case of 3 (entry 8). Note, that even with catalyst 3, the conversion of benzonitrile to benzamide reached 93% in 3 h. Compared to NaOH, lower rates were achieved with PTA in the case of all four catalysts, similar to the observations discussed above in conjunction with Table 5.

**Table 6.** Hydration of benzonitrile with [RhCl(cod)(NHC)] catalyst 1–4.

Entry	Catalyst	Conversion (%)		
		1 h	2 h	3 h
1	<b>1</b>	0	18	26
2	<b>1</b> + NaOH	>99	-	-
3	<b>1</b> + PTA	70	71	77
4	<b>2</b>	0	0	10
5	<b>2</b> + NaOH	99	>99	-
6	<b>2</b> + PTA	69	78	88
7	<b>3</b>	0	1	2
8	<b>3</b> + NaOH	66	86	93
9	<b>3</b> + PTA	54	61	64
10	<b>4</b>	0	0	12
11	<b>4</b> + NaOH	94	98	-
12	<b>4</b> + PTA	1	47	53

Conditions: 1 mmol benzonitrile, 5 mol% [RhCl(cod)(NHC)], 1.5 mL 2-PrOH, 1.5 mL H<sub>2</sub>O, 0.05 mmol NaOH or 0.15 mmol PTA, reflux temperature.

[RhCl(cod)(IMes)] (**1**) proved suitable for hydration of benzonitriles with both electron donating and electron withdrawing substituents (Table 7). High conversions were achieved with as low as 1 mol% of catalyst. *Para*-chlorobenzonitrile showed more efficient conversion to *p*-chlorobenzamide than *p*-methylbenzonitrile which has an electron donating group in 4-position. Electron-withdrawing groups make the nitrile carbon more susceptible to nucleophilic attack by the activated water molecule or OH<sup>-</sup>. These findings are in agreement with the previously reported observations [6,10].

**Table 7.** Hydration of various nitriles into amides with catalyst **1** with NaOH and catalysis of the same reaction with NaOH only.

Entry	Nitrile	t(h)	1 + NaOH		NaOH
			Conversion (%)	TOF <sup>b</sup> (h <sup>-1</sup> )	Conversion <sup>c</sup> (%)
1	benzonitrile	1	93	93	3
2		2	98	49	6
3	4-chlorobenzonitrile	1	88	88	4
4		2	94	47	6
5	4-methylbenzonitrile	1	70	70	1
6		2	84	42	2
7	4-chlorophenyl-acetonitrile	1	58	58	0
8		2	62	31	2

Conditions:<sup>a</sup> 1 mol% [RhCl(cod)(IMes)] (**1**), 1 mmol nitrile, 0.01 mmol NaOH, 1 mL 2-PrOH, 1 mL H<sub>2</sub>O, 80 °C. <sup>c</sup> Same as in <sup>a</sup>, but without [RhCl(cod)(IMes)] (**1**). <sup>b</sup> Turnover frequencies were calculated from the conversions at the indicated reaction times.

The conversions of various pyridine-carbonitriles to the corresponding amides (picolinamide, nicotinamide, isonicotinamide) were explored with 5 mol% catalyst **1** and the results are summarized in Table 8. Remarkably, the reactions of 3- and 4-pyridinecarbonitrile proceeded efficiently even in the absence of NaOH; apparently the pyridine moiety provided the sufficient basicity. The coordinating ability of the pyridyl functionality of 2-pyridinecarbonitrile reduced the activity as a catalyst of the complex and the reaction resulted only in 9% picolinamide. However, heteroaromatic nitriles with the *N* heteroatom adjacent to the  $\beta$  or  $\gamma$  position of the CN group (3-pyridinecarbonitrile and 4-pyridinecarbonitrile) showed high reactivity. Addition of three equivalents of PTA increased the catalytic activity in all cases, and 3-pyridinecarbonitrile, too, was hydrated with > 99% conversion in only 1 h.

**Table 8.** Hydration of substituted pyridinecarbonitriles with catalyst **1** in the absence of added base.

Entry	Substrate	Phosphine	Conversion (%)		
			1 h	2 h	3 h
1	2-pyridinecarbonitrile	-	6	8	9
2	2-pyridinecarbonitrile	PTA	8	10	11
3	3-pyridinecarbonitrile	-	88	96	96
4	3-pyridinecarbonitrile	PTA	> 99	-	-
5	4-pyridinecarbonitrile	-	> 99	-	-
6	4-pyridinecarbonitrile	PTA	> 99	-	-
7 <sup>a</sup>	4-pyridinecarbonitrile	-	90	> 99	-

Conditions: 1 mmol nitrile, 5 mol% [RhCl(cod)(IMes)] (**1**), 1.5 mL 2-PrOH, 1.5 mL H<sub>2</sub>O, 0.15 mmol PTA, reflux temperature. <sup>a</sup> 1 mol% [RhCl(cod)(IMes)] (**1**).

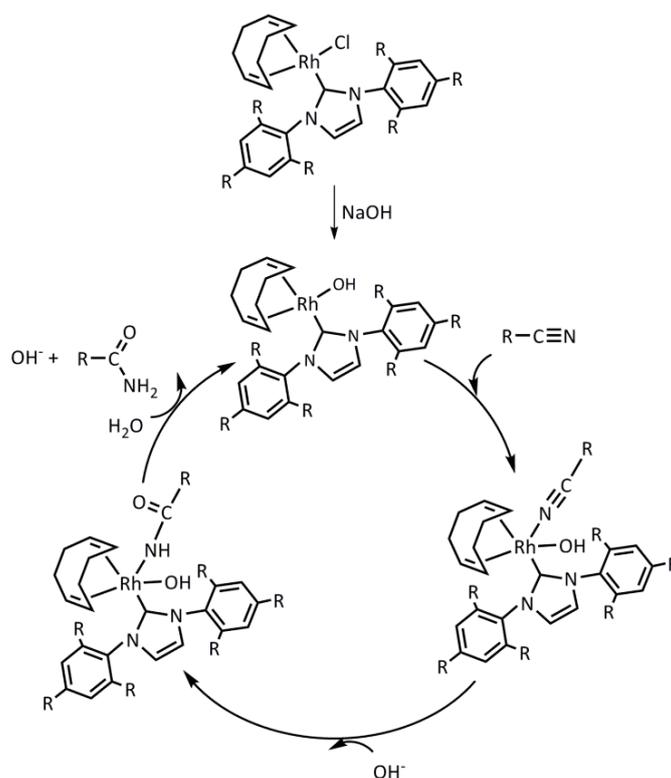
Finally, we studied the hydration of benzonitrile at 25 °C. It was found, that the use of 1 mol% catalyst **1** was sufficient to give a reasonable yield in 40 h (Table 9, entry 3). However, with a higher catalyst loading (2.5 mol%) 99% conversion was reached in 24 h (Table 9, entry 8). Lowering the concentration of 2-PrOH in the aqueous solvent mixture from 50% to 20% *v/v*, lead to a decrease in the conversion (entries 9, 10 vs. 1–3). The origin of this latter effect is presently unclear, since even at the lower 2-propanol concentration the reaction mixtures were homogeneous, and—formally—2-propanol is not involved in the hydration of benzonitrile.

**Table 9.** Hydration of benzonitrile at 25 °C catalyzed by [RhCl(cod)(IMes)] (1) with equimolar amounts of NaOH <sup>a</sup>.

Entry	1 (mol%) <sup>b</sup>	t (h)	Conversion (%)	TOF (h <sup>-1</sup> )
1	1	17	73	4.3
2	1	22	79	3.6
3	1	40	94	2.4
4	2	17	84	2.5
5	2	22	85	1.9
6	2.5	17	94	2.2
7	2.5	19	96	2.0
8	2.5	24	99	1.7
9 <sup>c</sup>	1	17	34	2.0
10 <sup>c</sup>	1	34	60	1.8

Conditions: 1 mmol benzonitrile, 1 mL 2-PrOH, 1 mL H<sub>2</sub>O, 25 °C; <sup>a</sup> [NaOH]/[Rh] = 1; <sup>b</sup> Relative to benzonitrile; <sup>c</sup> 20% v/v 2-PrOH.

The above results did not allow the suggestion of a detailed reaction mechanism. Nevertheless, the findings are in accord with the nucleophilic attack of a Rh(I)-coordinated hydroxide onto the nitrile carbon atom (Scheme 3), similar to the mechanism suggested in [17]. It is an important observation, that the hydration reactions proceed with high rate already with 1 equivalent of base per Rh(I). Since there is hardly any conversion of benzonitrile in the absence of a base, this points to an intermediate formation of a Rh(I)-OH hydroxo-complex. On the other hand, the complete selectivity of the reaction to benzamide shows that most probably the nitrile also coordinates to the Rh-based catalyst, thereby activating the nitrile carbon against a nucleophilic attack. It should also be mentioned, that at the moment the role of the cod ligand is unclear. It may stay coordinated to the rhodium throughout the catalytic cycle, but in the reductive milieu of basic 2-propanol it may also be hydrogenated and replaced by other ligands present in the solution.

**Scheme 3.** Suggested mechanism of nitrile hydration catalyzed by [RhCl(cod)(NHC)] complexes.

### 3. Materials and Methods

#### 3.1. Materials

All chemicals and reagents used in this work were purchased from Sigma-Aldrich, St. Louis, Missouri, USA; Molar Chemicals Kft., Halásztelek, Hungary and VWR International, West Chester, Pennsylvania, USA and were used as received without further purification. Analytical thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 F254 plates (Merck, Darmstadt, Germany), TLC plates were visualised by UV fluorescence at 254 nm. Column chromatography was performed on silica gel (70–230 mesh, 63–200  $\mu\text{m}$ , Sigma-Aldrich). The metal precursors  $[\text{RhCl}(\text{cod})]_2$  [60],  $[\text{Rh}(\text{OH})(\text{cod})]_2$  [61], the ligands PTA [62], and *mtppps*-Na [63] were prepared by the methods described in the literature.

#### 3.2. General Procedure for the Synthesis of $[\text{RhCl}(\text{cod})(\text{NHC})]$ Complexes

Starting from  $[\text{Rh}(\text{cod})\text{X}]_2$  ( $\text{X} = \text{Cl}^-$ ,  $\text{OH}^-$ ) and the appropriate 1,3-diaryl-imidazolium/imidazolinium salts the corresponding rhodium complexes **1–4**, were prepared in 58–88% yield (Scheme 1).

**Method A:** To a solution of 0.88 mmol of the imidazolium/imidazolinium salt in 30 mL of toluene were added 0.44 mmol of  $[\text{RhCl}(\text{cod})]_2$  and 8.88 mmol of  $\text{K}_2\text{CO}_3$  in one portion. The mixture was stirred at 70 °C for 3–24 h (followed by TLC). After removal of the solvent the product was purified by passing through a short silica column in dichloromethane:ethyl acetate = 1:1 as solvent. The coloured fraction of the complex was collected, evaporated to dryness, and the yellow solid was vacuum-dried, characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and HR ESI-MS.

**Method B:** To a solution of 0.88 mmol of the imidazolium/imidazolinium salt in 30 mL of toluene was added 0.44 mmol of  $[\text{Rh}(\text{OH})(\text{cod})]_2$  and the mixture was stirred at 70 °C for the required time (followed by TLC). After removal of the solvent the product was purified by passing through a short silica column in dichloromethane:ethyl acetate = 1:1 as solvent, and the complex was isolated and characterized as in Method A.

*Chloro*( $\eta^4$ -1,5-cyclooctadiene)(1,3-dimesitylimidazole-2-ylidene)rhodium(I),  $[\text{RhCl}(\text{cod})(\text{IMes})]$  (**1**). 302 mg (0.888 mmol) IMes HCl, 220 mg (0.444 mmol)  $[\text{RhCl}(\text{cod})]_2$ , 1228 mg (8.88 mmol)  $\text{K}_2\text{CO}_3$ , 3 h, yield of **1**: A) 345 mg (0.627 mmol) 71%; B) 399 mg (0.725 mmol), 83%.  $^1\text{H}$  NMR (360 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ /ppm: 7.12–7.11 (m, 4H,  $\text{H}_{\text{Ar}}$ ), 7.04 (s, 2H, NCH), 4.48 (br, 2H,  $\text{H}_{\text{cod}}$ ), 3.38 (br, 2H,  $\text{H}_{\text{cod}}$ ), 2.46–2.42 (m, 12H, Me), 2.18 (s, 6H, Me), 1.92–1.89 (m, 4H,  $\text{H}_{\text{cod}}$ ), 1.63–1.59 (m, 4H,  $\text{H}_{\text{cod}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ /ppm: 183.2 (d,  $^1J_{\text{Rh-C}} = 52.3$  Hz); 138.6; 137.4; 136.5; 134.5; 129.3; 128.3; 123.7; 95.7 (d,  $^1J_{\text{Rh-C}} = 7.2$  Hz); 68.1 (d,  $^1J_{\text{Rh-C}} = 14.3$  Hz); 32.6; 28.3; 20.8; 19.5; 17.9. MS(ESI), positive mode, in MeOH,  $m/z$  for **1**,  $[\text{M}]^+$  ( $\text{C}_{29}\text{H}_{36}\text{N}_2\text{Rh}$ ), calculated: 515.1928, found: 515.1928.

*Chloro*( $\eta^4$ -1,5-cyclooctadiene)(1,3-dimesitylimidazolidin-2-ylidene)rhodium(I),  $[\text{RhCl}(\text{cod})(\text{SIMes})]$  (**2**). 304 mg (0.888 mmol) SIMes HCl, 220 mg (0.444 mmol)  $[\text{RhCl}(\text{cod})]_2$ , 1228 mg (8.88 mmol)  $\text{K}_2\text{CO}_3$ , 22 h, yield of **2**: A) 350 mg (0.632 mmol), 71%, B) 428 mg (0.773 mmol), 88%.  $^1\text{H}$  NMR (360 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ /ppm: 7.09–7.06 (m, 4H,  $\text{H}_{\text{Ar}}$ ), 4.43 (br, 2H,  $\text{H}_{\text{cod}}$ ), 3.89 (br, 4H, NCH<sub>2</sub>), 3.46 (br, 2H,  $\text{H}_{\text{cod}}$ ), 2.62 (s, 6H, Me), 2.41–2.38 (m, 12H, Me), 1.85–1.80 (m, 4H,  $\text{H}_{\text{cod}}$ ), 1.64–1.55 (m, 4H,  $\text{H}_{\text{cod}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (90 MHz,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$ /ppm: 212.4 (d,  $^1J_{\text{Rh-C}} = 48.4$  Hz); 138.2; 137.7; 136.6; 135.4; 129.6; 128.5; 96.8 (d,  $^1J_{\text{Rh-C}} = 6.4$  Hz); 67.8 (d,  $^1J_{\text{Rh-C}} = 14.3$  Hz); 51.47; 32.6; 28.1; 20.8; 19.7; 18.2. MS(ESI), positive mode, in MeOH,  $m/z$  for **2**,  $[\text{M}]^+$  ( $\text{C}_{29}\text{H}_{38}\text{N}_2\text{Rh}$ ), calculated: 517.2085, found: 517.2085.

*Chloro*( $\eta^4$ -1,5-cyclooctadiene)(1,3-bis(2,6-diisopropylphenylimidazol)-2-ylidene)rhodium(I),  $[\text{RhCl}(\text{cod})(\text{IPr})]$  (**3**). 378 mg (0.888 mmol) IPr HCl, 220 mg (0.444 mmol)  $[\text{RhCl}(\text{cod})]_2$ , 1228 mg (8.88 mmol)  $\text{K}_2\text{CO}_3$ , 21 h, yield of **3**: A) 494 mg (0.777 mmol), 88%; B) 389 mg (0.612 mmol), 69%.  $^1\text{H}$  NMR (360 MHz,  $\text{dms}\text{-d}_6$ )  $\delta$ /ppm: 7.62 (s, 2H, NCH), 7.54 (t,  $J = 7.7$  Hz, 2H,  $\text{H}_{\text{Ar}}$ ), 7.39 (br, 4H,  $\text{H}_{\text{Ar}}$ ), 4.33 (br, 2H,  $\text{H}_{\text{cod}}$ ), 3.51 (br, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 3.23 (s, 2H,  $\text{H}_{\text{cod}}$ ), 2.35–2.31 (br, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.71–1.27 (m, 8H,  $\text{H}_{\text{cod}} + 12\text{H}$ ,

CH(CH<sub>3</sub>)<sub>2</sub>), 1.06 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (90 MHz, CDCl<sub>3</sub>), δ/ppm: 186.1 (d, <sup>1</sup>J<sub>Rh-C</sub> = 52.2 Hz); 147.9; 145.3; 136.4; 129.8; 124.6; 122.9; 96.4 (d, <sup>1</sup>J<sub>Rh-C</sub> = 7.2 Hz); 67.8 (d, <sup>1</sup>J<sub>Rh-C</sub> = 14.4 Hz); 32.7; 28.8; 28.3; 26.6; 22.8. MS(ESI), positive mode, in MeOH, *m/z* for **3**, [M]<sup>+</sup> (C<sub>35</sub>H<sub>48</sub>N<sub>2</sub>Rh), calculated: 599.2867, found: 599.2867.

*Chloro(η<sup>4</sup>-1,5-cyclooctadiene)(1,3-bis(2,6-diisopropylphenylimidazolidin)-2-ylidene)rhodium(I), [RhCl(cod)(SIPr)] (4)*. 380 mg (0.888 mmol) SIPr HCl, 220 mg (0.444 mmol) [RhCl(cod)]<sub>2</sub>, 1228 mg (8.88 mmol) K<sub>2</sub>CO<sub>3</sub>, 24 h, yield of **4**: A) 400 mg (0.627 mmol) 70%, B) 386 mg (0.605 mmol) 68%. <sup>1</sup>H NMR (360 MHz, C<sub>6</sub>D<sub>6</sub>) δ/ppm: 7.31–7.24 (m, 4H, H<sub>Ar</sub>), 7.15 (d, *J* = 6.8 Hz, 2H, H<sub>Ar</sub>), 4.99 (br, 2H, H<sub>cod</sub>), 4.43–3.36 (m, 4H, NCH<sub>2</sub>), 3.73–3.68 (m, 2H, H<sub>cod</sub>), 3.43–3.39 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.10–3.03 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.82–1.70 (m, 10H, H<sub>cod</sub>), 1.45–1.18 (m, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.05 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (90 MHz, CDCl<sub>2</sub>), δ/ppm: 214.9 (d, <sup>1</sup>J<sub>Rh-C</sub> = 47.7 Hz); 149.3; 146.4; 136.9; 128.8; 124.8; 123.3; 96.4 (d, <sup>1</sup>J<sub>Rh-C</sub> = 7.1 Hz); 67.8 (d, <sup>1</sup>J<sub>Rh-C</sub> = 13.9 Hz); 53.4; 32.4; 28.9; 28.6; 27.9; 26.6; 24.0; 22.7. MS(ESI), positive mode, in MeOH, *m/z* for **4**, [M]<sup>+</sup> (C<sub>35</sub>H<sub>50</sub>N<sub>2</sub>Rh), calculated: 601.3024, found: 601.3025.

### 3.3. General Methods

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance 360 MHz spectrometer (Bruker, Billerica, MA, USA) and were referenced to residual solvent peaks. Single crystal X-ray diffraction (SCXRD) measurements were performed using a Bruker D8 Venture diffractometer and the methods and software were described in [64–70]. Gas chromatographic measurements were done with the use of an Agilent Technologies 7890 A instrument (HP-5, 0.25 μm × 30 m × 0.32 mm, FID 300 °C (Agilent Technologies, Santa Clara, CA, USA); carrier gas: Nitrogen 1.9 mL/min). ESI-TOF-MS measurements were carried out on a Bruker maXis II MicroTOF-Q type Qq-TOF-MS instrument (Bruker Daltonik, Bremen, Germany) in positive ion mode. The mass spectra were calibrated internally using the exact masses of sodium formate clusters. The spectra were evaluated using the Compass Data Analysis 4.4 software from Bruker.

All catalytic reactions were carried out under air. The reaction temperatures were kept constant either by using a thermostated circulator (set e.g., to 80.0 ± 0.1 °C), or by running the reactions under reflux (lit. b.p. of 50% aqueous 2-propanol: 81.1 °C [71]). The products were identified by comparison of their retention time with known standard compounds.

#### a) Hydration of Benzonitrile without Product Isolation

100 μL (1.0 mmol) benzonitrile, 5.5 mg (0.01 mmol) [RhCl(cod)(IMes)] (**1**), 0.4 mg (0.01 mmol) NaOH, and 12.8 mg (0.1 mmol, 10 mol% of the substrate) naphthalene (internal standard) were dissolved in a mixture of 1.5 mL 2-propanol and 1.5 mL deionized water. This reaction mixture was placed into a temperature-controlled bath and stirred at 80 °C for 2 h. A 0.10 mL part of the resulting hot solution was extracted with 2 mL CH<sub>2</sub>Cl<sub>2</sub>, passed through a short MgSO<sub>4</sub> column and subjected to gas chromatography. Conversion of benzonitrile: 98%.

#### b) Hydration of Benzonitrile with Product Isolation

200 μL (2.0 mmol) benzonitrile, 11 mg (0.02 mmol) [RhCl(cod)(IMes)] (**1**), and 0.8 mg (0.02 mmol) NaOH were stirred in a mixture of 1.5 mL 2-PrOH and 1.5 mL deionized water, at 80 °C. After 3 h reaction time, the resulting solution was evaporated to dryness on a rotary evaporator and the residue was chromatographed on a short silica gel column using ethyl acetate as the eluent. Yield of benzamide: 217.3 mg (89%).

## 4. Conclusions

We have realized one-step syntheses of the [RhCl(cod)(NHC)] complexes 1–4 without generation of the free carbene ligands or the silver-NHC complexes. The metal precursor [RhCl(cod)]<sub>2</sub> and the

respective imidazolium/imidazolinium salt was stirred overnight in toluene at 70 °C, and the desired complexes were produced in good to excellent yields. An efficient catalytic system for the selective hydration of nitriles to the corresponding amides in a water/2-propanol solvent, with tolerance of air and several functional groups, is also described. The suggested reaction mechanism considers the nucleophilic attack of a Rh(I)-coordinated OH<sup>-</sup> onto the nitrile carbon atom activated by the N-coordination of nitrile group to the metal ion.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/10/1/125/s1>. Table S1. Retention times of nitriles and amides used in this study; Table S2. Experimental conditions of X-ray diffraction measurements of Rh(I)-complexes; Table S3. Unit cell data of [RhCl(cod)(IPr)] [54] and [IrCl(cod)(IPr)] [57]; Figure S1. Time course of the conversion of benzonitrile with 1 mol% of catalyst 1; Figure S2 and S3. GC separation of benzonitrile/benzamide and 2-pyridinecarbonitrile/2-pyridin-carboxamide; Figures S4–S11. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of [RhCl(cod)(IMes)] (1), [RhCl(cod)(SIMes)] (2), [RhCl(cod)(IPr)] (3), [RhCl(cod)(SIPr)] (4); Figure S12 and S13. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of benzamide obtained by hydration of benzonitrile with catalyst 1; Figures S14 and S15. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of isonicotinamide obtained by hydration of 4-pyridinecarbonitrile with catalyst 1; Figures S16 and S17. HR ESI-MS spectra of benzamide and isonicotinamide; Figures S18–S21. HR ESI-MS spectra of catalysts 1–4; Figure S22. ORTEP view of [RhCl(cod)(SIPr)] (4) (50% ellipsoid level); Figure S23. ORTEP view of [RhCl(cod)(IPr)]\_benzene\_3 (50% ellipsoid level); Figure S24. ORTEP view of [RhCl(cod)(SIPr)]\_benzene\_4 (50% ellipsoid level).

**Author Contributions:** Conceptualization, C.E.C. and F.J.; Methodology, G.P. (Gábor Papp) and A.U.; Synthesis and characterization of catalysts, C.E.C., N.J.D., G.P. (Gergely Papp), and S.D.; Catalysis experiments, C.E.C., N.J.D., G.P. (Gergely Papp), and S.D.; Discussion of experimental results, all authors; Writing—Original Draft Preparation, all authors; Writing—Review and Editing, C.E.C., F.J., S.D., and A.U. All authors have read and agreed to the published version of the manuscript

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**Conflicts of Interest:** The authors declare no conflict of interest.

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