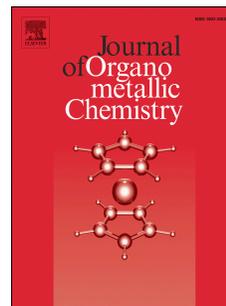


# Accepted Manuscript

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## Amidation of aldehydes using mono-cationic half-sandwich rhodium(III) complexes with functionalized phenylhydrazone ligands

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### Abstract

A series of mono-cationic half-sandwich rhodium(III) complexes have been synthesized in methanol using phenylhydrazone-derived ligands ( $L_1$ – $L_6$ ) and the starting precursor  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2]$  in a 2:1 molar ratio. The  $N,N'$ -phenylhydrazone complexes have been isolated as tetraphenylborate salts. All complexes were characterized by elemental analysis, FT-IR, UV-visible, NMR spectroscopy and mass spectrometry. The molecular structure of complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(L_1)\text{Cl}](\text{BPh}_4)$  (**1**) was confirmed by single-crystal X-ray structure analysis. Complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(L_3)\text{Cl}](\text{BPh}_4)$  (**3**) was used as an efficient catalyst for the amide formation reaction, with up to 99% conversion after 2 hours in toluene at 110°C in the presence of hydroxyl amine hydrochloride and sodium bicarbonate.

**Keywords:** Phenylhydrazone-based ligands; Half-sandwich complexes; Homogenous catalysis; Pentamethylcyclopentadienyl rhodium complexes; Amidation reaction.

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## Introduction

Organometallic compounds are powerful catalytic agents in synthetic organic chemistry [1]. Rhodium based complexes are very important for different catalytic reactions like the transfer hydrogenation [2], hydroformylation [3], hydrosilylation [4], coupling reactions [5], ring opening [6], ring closing [7], polymerisation [8], oxidation [9], isomerization [10], and others. Both oxidative addition and reductive elimination reactions are readily accessible, and accordingly, rhodium complexes have been widely used in the design of catalytic systems [11].

In parallel, ligand design is vital for the development of catalysts [12]. The structure of the ligand dictates the environment of the metal centers and subsequently the catalytic activity. Hydrazone-derived ligands possess distinct features that make them interesting for the design of metal-based catalysts. The tri-atomic C=N–N structure of hydrazone introduces electrophilic and nucleophilic characters to the ligand, which also offers great functional diversity. The structural properties of the hydrazone group enable its use in various applications [13]. Furthermore, chemical functionalization of the hydrazone group can increase its stability, modify its coordination ability, and generate higher modularity, thus overall fine-tuning the steric and electronic properties of the complex for optimization of the catalytic process [14].

The amide bond is present in many natural and synthetic polymers, as well as in peptides and proteins [15]. Amide bonds are typically synthesized by acylation of amines with carboxylic acid derivatives such as acid chloride, anhydride, active esters, etc... However, these methods have the inconvenience of producing a stoichiometric amount of side products and of using highly hazardous reagents [16]. Therefore, alternative methods for amide synthesis have been developed, such as the Beckmann rearrangement [17], the Staudinger reaction [18], the Schmidt reaction [19], the amino carbonylation of halo arenes [20], the iodonium-promoted alkyl halo

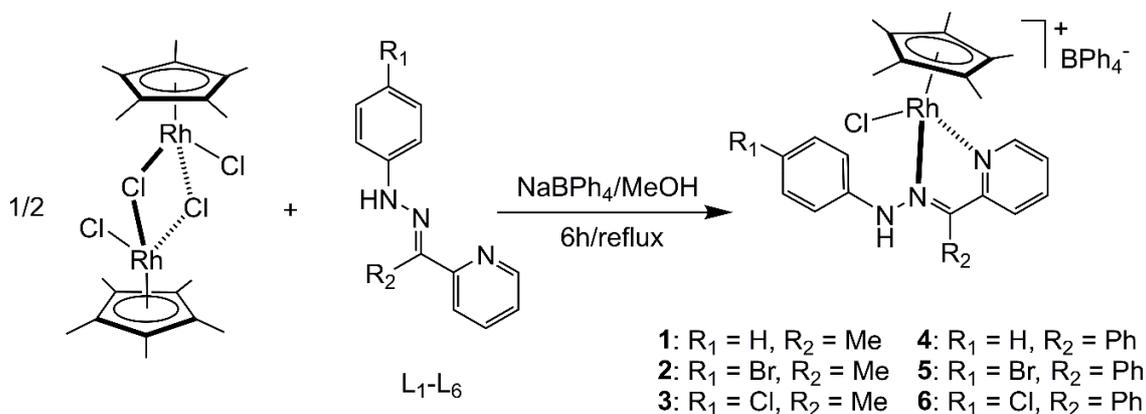
nitro alkane amine coupling [21], the direct amide synthesis from alcohols with amines or nitroarenes [22,23], the hydro amination of alkynes [24], the amidation of thioacids with azides [25], as well as the *trans*-amidation of primary amides [26]. An elegant alternative pathway, which is more atom economic and makes use of cheap and abundant starting materials, is the oxidative amidation of aldehyde with amines [27], using metal-based catalysts [28-37]. These catalytic reactions require large amount of catalysts and are generally performed at high temperature [38-40].

In contrast to the considerable growth of literature on the chemistry of hydrazone complexes, to the best of our knowledge, there are no reports available concerning the catalytic transformation of aldehyde to amides by half-sandwich rhodium(III) phenylhydrazone complexes containing *N,N'*-hydrazine-based donors. In view of the interest to understand the behavior of these simple and inexpensive ligands towards rhodium, six half-sandwich rhodium metal complexes containing hydrazine-derived ligands were synthesized. All complexes were fully characterized by spectroscopic and spectrometric methods, and one complex was tested as catalyst for the conversion of aldehydes to amides in the presence of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and  $\text{NaHCO}_3$ .

## Results and discussion

Six half-sandwich rhodium(III) complexes have been synthesized from the rhodium starting precursor  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2]$ , the phenyl hydrazone ligands ( $\text{L}_1\text{--}\text{L}_6$ ) and sodium tetraphenylborate in a 1:2:2 molar ratio in dry methanol under reflux for 6 hours (Scheme 1). The complexes were isolated as tetraphenylborate salts. All complexes are air-stable, non-hygroscopic in nature, partially soluble in water and highly soluble in common solvents such as chloroform, dichloromethane, acetonitrile and dimethyl sulfoxide. The complexes were found to

be diamagnetic, low spin in nature and characterized by elemental analysis, infrared, UV-visible,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectroscopy and ESI mass spectrometry (see experimental part).



Scheme 1. Synthesis of half-sandwich rhodium complexes **1-6**.

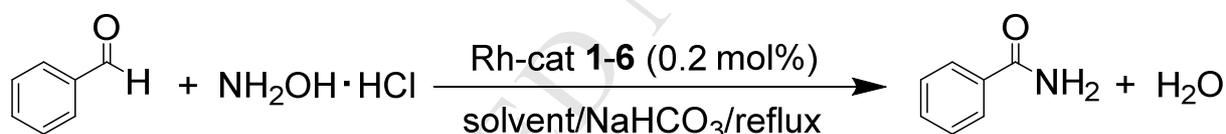
The coordination mode of the phenylhydrazone ligand to the rhodium metal center was first investigated by infrared spectroscopy. The spectra of the ligands were compared to those of the corresponding half-sandwich rhodium complexes. The phenylhydrazone ligands showed a very strong absorption around  $1600\text{--}1620\text{ cm}^{-1}$ , corresponding to the azomethine ( $\text{C}=\text{N}$ ) group. After coordination, the azomethine frequency is shifted to lower frequency at around  $1565\text{--}1600\text{ cm}^{-1}$ . This is due to the reduction of the electron density upon coordination of the azomethine group. Thus the infrared data confirmed the coordination of the nitrogen atom to the metal. In addition, a medium intensity band in the  $1015\text{--}1030\text{ cm}^{-1}$  region, which corresponds to coordinated pyridyl groups, is observed in all complexes, together with the  $\text{Rh}\text{--Cl}$  stretching frequency around  $320\text{ cm}^{-1}$ . The electronic spectra of the complexes were recorded between 800 and 200 nm in dichloromethane solution ( $10^{-4}\text{ M}$ ). All complexes show two to three absorption bands: An intense absorption band centered at 390 nm, which is assigned to MLCT transitions, and a band around 290–230 nm, which is attributed to  $n\text{-}\pi^*$  or  $\pi\text{-}\pi^*$  transitions.

$^1\text{H}$  NMR spectra were recorded in  $\text{CD}_3\text{CN}$ , and they confirm the proposed structure of the complexes. The aromatic protons of the complexes appear as one doublet of triplet and one triplet of doublet in the range of 8.82–8.79 ppm and 8.20–8.03 ppm, while the remaining aromatic protons appeared as a multiplet in the range of 8.03–7.08 ppm. The protons of the tetraphenyl borate counter ion appear as a multiplet ( $\sim 7.30$  ppm) and two triplets at  $\sim 7.03$  and  $\sim 6.88$  ppm, respectively. The complexes show a broad singlet in the range of 9.21–8.94 ppm corresponding to the uncoordinated NH proton. The acetyl methyl proton of complexes **1**, **2** and **3** appears as a sharp singlet at 2.60 ppm. Finally, the methyl protons of the pentamethylcyclopentadienyl ring ( $\text{Cp}^*$ ) are observed as a sharp singlet at  $\sim 1.47$  ppm. The electrospray ionization mass spectra of **1-6** display a molecular ion peak, which corresponds, after the loss of the  $\text{BPh}_4$  counter anion, to the cationic complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{Cl}]^+$ .

The molecular structure of **1** was unambiguously confirmed by single-crystal X-ray structure analysis. The ortep diagram of the mono-cationic complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{Cl}]^+$  is presented in Figure S1, together with selected bond lengths and angles. The complex is chiral, but crystallizes in the centrosymmetric space group  $P -1$ , thus displaying in the crystal both enantiomers. The complex shows a typical pseudo-tetrahedral geometry (piano-stool) around the metal center with an  $\eta^5$ -coordinated  $\text{Cp}^*$ , a chloride, and the  $N,N'$ -hydrazone ligand ( $\text{L}_1$ ). The bond length between the rhodium and the chloride is 2.4160(6) Å, while the two Rh-N bond lengths are almost identical at 2.099(2) Å ( $\text{Rh-N}_{\text{pyridyl}}$ ) and 2.101(2) Å ( $\text{Rh-N}_{\text{imine}}$ ). Upon coordination, the phenyl group of the hydrazine ligand is out of the pyridyl-azomethine plane by  $-69.3(3)^\circ$ . Overall, these geometrical parameters are consistent with those found in analogous  $N,N'$ -coordinated rhodium pentamethylcyclopentadienyl compounds [41].

In the crystal packing of **1**, two mono-cationic complexes are facing each other, thus forming dimers in the solid state. In these dimers (Figure S2), strong hydrogen bonds are observed, involving both the N-H and the chloride. The N-H...Cl contact shows a N...Cl distance of 3.328(2) Å, with a N-H...Cl angle of 157(2)°, while the C-H...Cl contact possesses a C...Cl distance of 3.642(3) Å and a C-H...Cl angle of 141°. The separation between the two cationic complexes is only 6.2120(8) Å (Rh...Rh distance).

Rhodium mediated amide formation is a very useful reaction in which an amide derivative is formed by hydroxyl amine hydrochloride and an aldehyde [42]. Therefore, the rhodium-based complexes **1-6** were tested as catalysts for this reaction. The initial conditions used for the transformation of benzaldehyde to benzamide (Scheme 2) were based on our previous studies dealing with analogous piano-stool catalysts [43].



Scheme 2: Organic transformation of aldehyde to amide with rhodium-based catalysts **1-6**.

Even so, the nature of the solvent, the choice of the base, and the catalysts/substrate ratio (see supporting information), were evaluated to confirm the initial catalytic conditions. The best solvent was toluene, with a 90% conversion of benzaldehyde to benzamide (Table S1). Among the following bases, NaHCO<sub>3</sub>, KHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, LiOH, K<sub>2</sub>CO<sub>3</sub>, Et<sub>3</sub>N and <sup>t</sup>BuOK, sodium bicarbonate gave the best conversion (Table S2). Is it worth mentioning here that in the absence of a base, the conversion of benzaldehyde to benzamide was not observed. Finally, by decreasing the catalyst/substrate ratio below 1:500, the formation of side products

(nitrile, carboxylic acid) appears, while above 1:500, the overall yield was reduced. Therefore, 1:500 seems to be the best compromise in term of catalyst/substrate ratio. Then, under these conditions, the effect of complexes **1-6** on the amidation of benzaldehyde as a function of time has been determined (Table 1).

Table 1. Effect of complexes **1-6** on the amidation of benzaldehyde (yields of benzamide as a function of time).<sup>a</sup>

Complex	1h	2h	4h	6h	8h
<b>1</b>	45	52	65	70	72
<b>2</b>	63	64	70	79	81
<b>3</b>	80	90	92	92	93
<b>4</b>	55	60	69	73	76
<b>5</b>	61	72	79	81	82
<b>6</b>	68	75	85	86	88

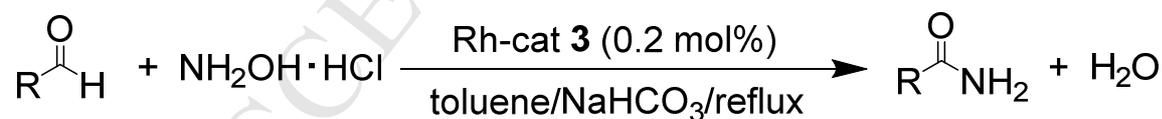
<sup>a</sup>Conditions: Reactions were carried out at 110°C using 1 mmol of benzaldehyde, 1 mmol of NH<sub>2</sub>OH·HCl, 1 mmol of NaHCO<sub>3</sub>, 0.002 mmol of catalyst in 2 ml of toluene. <sup>b</sup>Conversions were determined using <sup>1</sup>H NMR (integrations of H<sub>aldehyde</sub> vs H<sub>amide</sub>).

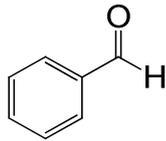
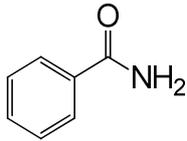
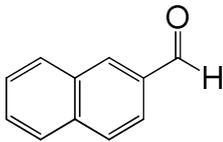
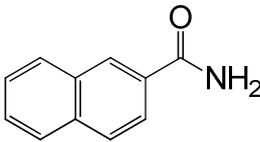
The time-conversion profiles of complexes **1-6** under standard conditions show that complex **3** is the best catalyst, reaching 93% formation of benzamide after 8 hours (Table 1). However, we can also observed that extending the reaction time does not increase significantly the yield, 90% conversion being already reached after 2 hours. The second best catalyst is complex **6**, which gives an 88% conversion after 8 hours. Then complexes **2** and **5** show similar profiles, which are better than complexes **1** and **4**. Interestingly, complexes **3** and **6** are the chloro derivatives (see Scheme 1), while complexes **2** and **5** are the bromo derivatives. These results

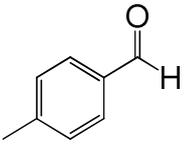
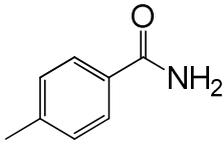
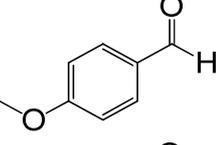
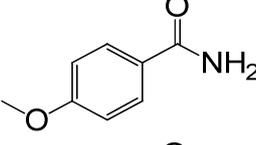
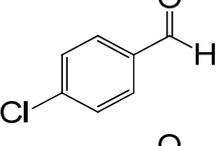
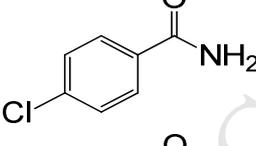
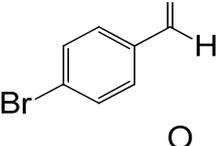
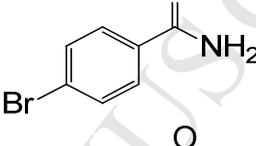
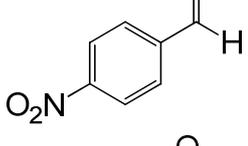
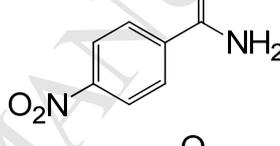
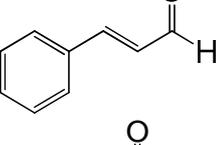
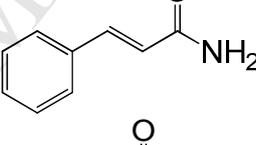
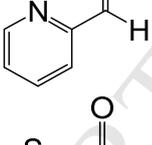
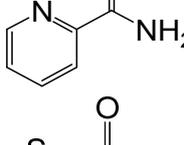
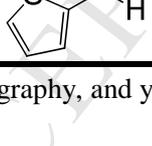
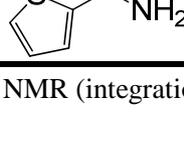
suggest that ligand optimizations is important for such *N,N'*-hydrazine-based complexes, and functionalization of the ligand can play an important role on the catalytic activity.

Having now confirmed the reaction conditions for the amide formation (toluene at reflux, 2 hours, NaHCO<sub>3</sub> as the base, and a catalyst/substrate ratio of 1:500) and identified the best catalyst among the six complexes, we tested the catalytic activity of complex **3** on various aldehydes: benzaldehyde, 2-naphthaldehyde, 4-chloro-benzaldehyde, 4-bromo-benzaldehyde, 4-methyl-benzaldehyde, 4-methoxy-benzaldehyde, *trans*-cinnamaldehyde, and 2-thiophene carboxaldehyde. The rates of conversion are listed in Table 2. As previously mentioned, benzaldehyde gives benzamide with a 90% yield (entry 1). Introduction of additional aromaticity to the aldehyde benzene ring (entry 2) decreases the yield to 85%, probably due to steric constraints or electronic effects. Similarly when electron donating groups (methyl, methoxy) are introduced at the *para*-position of benzaldehyde (entries 3 & 4) the yield decreases, while the presence of electron withdrawing groups (Br, Cl, NO<sub>2</sub>) at the same position (entries 5–7) increases the yields. High yields are also observed for cinnamaldehyde (entry 8), 2-pyridimide (entry 9) and with 2-thiophene carboxamide (entry 10).

Table 2: One pot conversion of aldehydes to amides using catalyst **3**.<sup>a</sup>



Entry	Aldehyde	Amide	Yield <sup>b</sup>
1			90
2			85

3			80	<sup>a</sup> Aldehyde (1 mmol), NH <sub>2</sub> OH·HCl (1 mmol), NaHCO <sub>3</sub> (1 mmol), catalyst (0.002 mmol) and toluene (2 ml), 2 hours at 110 °C. <sup>b</sup> Isolated yield
4			76	
5			94	
6			99	
7			90	
8			92	
9			95	
10			98	

ds after column chromatography, and yields obtained by <sup>1</sup>H NMR (integrations of H<sub>aldehyde</sub> vs H<sub>amide</sub>).

Complex **3** shows good to excellent yields for the transformation of aldehydes to amides under relatively mild conditions, low catalysts loading, and fast reaction time. In general, such catalytic reactions require large amount of catalysts and high temperatures. The Wilkinson's complex has been found to catalyze the one-pot transformation of aldoximes to the corresponding amides with a 5 mol% catalyst loading and a reaction temperature of 150 °C [38].

Similarly, Mizuno reported that aluminum supported rhodium hydroxide ( $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$ ) can act as an effective catalyst for the synthesis of primary amides with a 4 mol% catalyst loading and  $160^\circ\text{C}$  [39]. Recently, Hull reported a rhodium complex for amide formation reaction with good yield and similar catalyst loading in the presence of styrene as the base [40]. Overall, complex **3** compares well with previously reported rhodium-based catalysts for the formation of amides.

## Conclusion

Six half-sandwich rhodium catalysts incorporating *N,N'*-hydrazine-based ligands have been synthesized and characterized. Complex **3**,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_3)\text{Cl}]\text{BPh}_4$ , is an efficient catalyst for the formation of amides from aldehydes in the presence of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and  $\text{NaHCO}_3$  in toluene at reflux. This study confirms the versatility of rhodium-based catalysts in organic reactions.

## Experimental section

### Materials and methods

$\text{RhCl}_3\cdot n\text{H}_2\text{O}$ , 1,2,3,4,5-pentamethylcyclopentadiene, hydroxylamine hydrochloride, phenylhydrazone, acetyl pyridine, benzoyl pyridine, benzaldehyde, 1-naphthaldehyde, 4-anisaldehyde, *trans*-cinnamaldehyde, 2-thiophenecarboxaldehyde and sodium bicarbonate were obtained from Sigma Aldrich, while 4-nitrobenzaldehyde and 4-tolylaldehyde were purchased from Fluka and 4-bromobenzaldehyde from Acros. All reagents were of analytical reagent grade and used as received. The starting materials  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2]$  and the ligands were

prepared according to published methods [44,45]. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance II 400 MHz spectrometer. Infrared spectra were recorded in the range of 4000-400  $\text{cm}^{-1}$  with a Perkin-Elmer FTIR 1720 X-spectrometer. Electrospray mass spectra were obtained in positive mode with a LCQ Finnigan mass spectrometer. Microanalyses were carried out at the sophisticated analytical instrument facility Cochin (India), on a VarioEL III CHNS analyzer (Table S4). UV-visible absorption spectra were recorded on an Uvikon 930 spectrophotometer.

### General procedure for the synthesis of complexes 1-6.

One equivalent of the dimeric starting precursor  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2]$  was treated with two equivalents of phenylhydrazone ( $\text{L}_1\text{-L}_6$ ) in methanol (25ml). The mixture obtained was refluxed for 6 hours. In all cases, the solution turned from yellow to dark red. Then,  $\text{NaBPh}_4$  was added the hot solution to obtain the corresponding complex (**1-6**). On cooling, reddish brown colored precipitates were obtained, and the products were isolated by filtration, and washed with diethyl ether. The purity of the complexes was checked by TLC.

Complex **1**, brown solid; Yield: 65%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1597 (C=N), 1021 (py).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  (ppm) = 8.92 (br s, 1H, NH), 8.79 (dt,  $^3J_{\text{H-H}} = 5.6$  Hz, 1H,  $\text{H}_{\text{ar}}$ ), 8.19 (td,  $^3J_{\text{H-H}} = 8$  Hz, 1H,  $\text{H}_{\text{ar}}$ ), 8.01 (d,  $^3J_{\text{H-H}} = 7.6$  Hz, 1H,  $\text{H}_{\text{ar}}$ ), 7.81-7.77 (m, 1H,  $\text{H}_{\text{ar}}$ ), 7.47 (dd,  $^3J_{\text{H-H}} = 7.6$  Hz, 2H,  $\text{H}_{\text{ar}}$ ), 7.41-7.36 (m, 2H,  $\text{H}_{\text{ar}}$ ), 7.32-7.28 (m, 8H,  $\text{H}_{\text{Bar}}$ ), 7.12-7.08 (m, 1H,  $\text{H}_{\text{ar}}$ ), 7.03 (t,  $^3J_{\text{H-H}} = 7.6$  Hz, 8H,  $\text{H}_{\text{Bar}}$ ), 6.87 (t,  $^3J_{\text{H-H}} = 7.2$  Hz, 4H,  $\text{H}_{\text{Bar}}$ ), 2.59 (s, 3H,  $\text{H}_{\text{Me}}$ ), 1.45 (s, 15H,  $\text{H}_{\text{Cp}^*}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  (ppm) = 153.7 (C=N), 152.0 ( $\text{C}_{\text{ar}}$ ), 142.8 ( $\text{C}_{\text{ar}}$ ), 139.7 ( $\text{C}_{\text{ar}}$ ), 135.4 ( $\text{C}_{\text{ar}}$ ), 128.7 ( $\text{C}_{\text{ar}}$ ), 127.8 ( $\text{C}_{\text{ar}}$ ), 125.3 ( $\text{C}_{\text{Bar}}$ ), 122.1 ( $\text{C}_{\text{ar}}$ ), 121.4 ( $\text{C}_{\text{ar}}$ ), 116.4 ( $\text{C}_{\text{ar}}$ ), 97.4 (d,  $^2J_{\text{Rh-C}} = 8.2$  Hz,  $\text{C}_{\text{Cp}^*}$ ), 15.0 ( $\text{CH}_3$ ), 7.7 ( $\text{C}_{\text{Cp}^*}$ ). MS (ESI positive mode):  $m/z$

484 [M-BPh<sub>4</sub>]<sup>+</sup>. UV-vis (10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm): 385 (ε = 2050 cm<sup>-1</sup> mol<sup>-1</sup> L), 266 (ε = 19230 cm<sup>-1</sup> mol<sup>-1</sup> L), 231 (ε = 29450 cm<sup>-1</sup> mol<sup>-1</sup> L). Anal. Calcd for C<sub>47</sub>H<sub>48</sub>BClN<sub>3</sub>Rh: C, 70.21; H, 6.02; N, 5.23. Found: C, 70.19; H, 6.01; N, 5.15.

Complex **2**, brown solid; Yield: 60%. IR (KBr, ν, cm<sup>-1</sup>): 1592 (C=N), 1021 (py). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 9.03 (br s, 1H, NH), 8.79 (dt, <sup>3</sup>J<sub>H-H</sub> = 5.6 Hz, 1H, H<sub>ar</sub>), 8.20 (td, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, 1H, H<sub>ar</sub>), 8.03(d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 1H, H<sub>ar</sub>), 7.83-7.79 (m, 1H, H<sub>ar</sub>), 7.53-7.50 (m, 2H, H<sub>ar</sub>), 7.44-7.40 (m, 2H, H<sub>ar</sub>), 7.32-7.28 (m, 8H, H<sub>Bar</sub>), 7.02 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 8H, H<sub>Bar</sub>), 6.87 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 4H, H<sub>Bar</sub>), 2.60 (s, 3H, H<sub>Me</sub>), 1.46 (s, 15H, H<sub>Cp\*</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 153.5 (C=N), 152.1 (C<sub>ar</sub>), 142.1 (C<sub>ar</sub>), 139.8 (C<sub>ar</sub>), 135.4 (C<sub>ar</sub>), 131.5 (C<sub>ar</sub>), 128.1 (C<sub>ar</sub>), 125.5 (C<sub>ar</sub>), 125.3 (C<sub>Bar</sub>), 121.4 (C<sub>ar</sub>), 118.1 (C<sub>ar</sub>), 97.5 (d, <sup>2</sup>J<sub>Rh-C</sub> = 8.1 Hz, C<sub>Cp\*</sub>), 15.1 (CH<sub>3</sub>), 7.8 (C<sub>Cp\*</sub>). MS (ESI positive mode): m/z 564 [M-BPh<sub>4</sub>]<sup>+</sup>. UV-vis (10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm): 390 (ε = 860 cm<sup>-1</sup> mol<sup>-1</sup> L), 278 (ε = 8090 cm<sup>-1</sup> mol<sup>-1</sup> L), 232 (ε = 17650 cm<sup>-1</sup> mol<sup>-1</sup> L). Anal. Calcd for C<sub>47</sub>H<sub>47</sub>BBrClN<sub>3</sub>Rh: C, 63.93; H, 5.37; N, 4.76. Found: C, 63.95; H, 5.35; N, 4.75.

Complex **3**, brown solid; Yield: 80%. IR (KBr, ν, cm<sup>-1</sup>): 1596 (C=N), 1019 (py). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 9.01 (br s, 1H, NH), 8.79 (dt, <sup>3</sup>J<sub>H-H</sub> = 5.6 Hz, 1H, H<sub>ar</sub>), 8.19 (td, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, 1H, H<sub>ar</sub>), 8.02-8.00 (m, 1H, H<sub>ar</sub>), 7.81-7.78 (m, 1H, H<sub>ar</sub>), 7.50-7.47 (m, 2H, H<sub>ar</sub>), 7.40-7.37 (m, 2H, H<sub>ar</sub>), 7.33-7.28 (m, 8H, H<sub>Bar</sub>), 7.02 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 8H, H<sub>Bar</sub>), 6.87 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 4H, H<sub>Bar</sub>), 2.59 (s, 3H, H<sub>Me</sub>), 1.45 (s, 15H, H<sub>Cp\*</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 153.5 (C=N), 152.1 (C<sub>ar</sub>), 142.8 (C<sub>ar</sub>), 139.8 (C<sub>ar</sub>), 135.5 (C<sub>ar</sub>), 128.6 (C<sub>ar</sub>), 128.0 (C<sub>ar</sub>), 126.6 (C<sub>ar</sub>), 125.5 (C<sub>Bar</sub>), 121.4 (C<sub>ar</sub>), 117.8 (C<sub>ar</sub>), 116.9 (C<sub>ar</sub>), 97.5 (d, <sup>2</sup>J<sub>Rh-C</sub> = 8.2

Hz, C<sub>cp</sub>\*), 15.1 (CH<sub>3</sub>), 7.8 (C<sub>cp</sub>\*). MS (ESI positive mode): m/z 518 [M-BPh<sub>4</sub>]<sup>+</sup>. UV-vis (10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm): 383 (ε = 660 cm<sup>-1</sup> mol<sup>-1</sup> L), 292 (ε = 6800 cm<sup>-1</sup> mol<sup>-1</sup> L), 245 (ε = 15870 cm<sup>-1</sup> mol<sup>-1</sup> L). Anal. Calcd for C<sub>47</sub>H<sub>47</sub>BCl<sub>2</sub>N<sub>3</sub>Rh: C, 67.32; H, 5.65; N, 5.01. Found: C, 67.30; H, 5.60; N, 5.02.

Complex **4**, brown solid; Yield: 68%. IR (KBr, ν, cm<sup>-1</sup>): 1596 (C=N), 1030 (py). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 8.91 (br s, 1H, NH), 8.81 (dt, <sup>3</sup>J<sub>H-H</sub> = 5.6 Hz, 1H, H<sub>ar</sub>), 8.02 (td, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, 1H, H<sub>ar</sub>), 7.79-7.35 (m, 10H, H<sub>ar</sub>), 7.33-7.28 (m, 8H, H<sub>Bar</sub>), 7.24 (m, 2H, H<sub>ar</sub>), 7.15 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 1H, H<sub>ar</sub>), 7.02 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 8H, H<sub>Bar</sub>), 6.87 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 4H, H<sub>Bar</sub>), 1.47 (s, 15H, H<sub>Cp</sub>\*). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 154.0 (C=N), 152.2 (C<sub>ar</sub>), 142.8 (C<sub>ar</sub>), 139.6 (C<sub>ar</sub>), 135.4 (C<sub>ar</sub>), 131.4 (C<sub>ar</sub>), 130.8 (C<sub>ar</sub>), 130.1 (C<sub>ar</sub>), 130.0 (C<sub>ar</sub>), 129.9 (C<sub>ar</sub>), 128.7 (C<sub>ar</sub>), 128.6 (C<sub>ar</sub>), 128.5 (C<sub>ar</sub>), 127.6 (C<sub>ar</sub>), 126.6 (C<sub>ar</sub>), 125.3 (C<sub>Bar</sub>), 123.0 (C<sub>ar</sub>), 121.4 (C<sub>ar</sub>), 117.7 (C<sub>ar</sub>), 97.6 (d, <sup>2</sup>J<sub>Rh-C</sub> = 8.2 Hz, C<sub>cp</sub>\*), 7.6 (C<sub>cp</sub>\*). MS (ESI positive mode): m/z 546 [M-BPh<sub>4</sub>]<sup>+</sup>. UV-vis (10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm): 389 (ε = 820 cm<sup>-1</sup> mol<sup>-1</sup> L), 287 (ε = 9870 cm<sup>-1</sup> mol<sup>-1</sup> L), 232 (ε = 19350 cm<sup>-1</sup> mol<sup>-1</sup> L). Anal. Calcd for C<sub>52</sub>H<sub>50</sub>BCIN<sub>3</sub>Rh: C, 72.11; H, 5.82; N, 4.85. Found: C, 72.15; H, 5.80; N, 4.86.

Complex **5**, brown solid; Yield: 62%. IR (KBr, ν, cm<sup>-1</sup>): 1564 (C=N), 1030 (py). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 8.93 (br s, 1H, NH), 8.82 (dt, <sup>3</sup>J<sub>H-H</sub> = 5.6 Hz, 1H, H<sub>ar</sub>), 8.02 (td, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, 1H, H<sub>ar</sub>), 7.80-7.49 (m, 9H, H<sub>ar</sub>), 7.32-7.28 (m, 8H, H<sub>Bar</sub>), 7.27-7.24 (m, 2H, H<sub>ar</sub>), 7.02 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 8H, H<sub>Bar</sub>), 6.87 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 4H, H<sub>Bar</sub>), 1.49 (s, 15H, H<sub>Cp</sub>\*). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN, 25°C): δ (ppm) = 153.8 (C=N), 152.2 (C<sub>ar</sub>), 142.1 (C<sub>ar</sub>), 139.7 (C<sub>ar</sub>), 135.4 (C<sub>ar</sub>), 131.5 (C<sub>ar</sub>), 128.0 (C<sub>ar</sub>), 127.0 (C<sub>ar</sub>), 125.3 (C<sub>Bar</sub>), 121.4 (C<sub>ar</sub>), 119.3 (C<sub>ar</sub>), 115.1

(C<sub>ar</sub>), 97.7 (d,  $^2J_{\text{Rh-C}} = 8.2$  Hz, C<sub>cp\*</sub>), 7.7 (C<sub>cp\*</sub>). MS (ESI positive mode): m/z 626 [M-BPh<sub>4</sub>]<sup>+</sup>. UV-vis (10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$  (nm): 398 ( $\epsilon = 1620$  cm<sup>-1</sup> mol<sup>-1</sup> L), 289 ( $\epsilon = 16580$  cm<sup>-1</sup> mol<sup>-1</sup> L), 235 ( $\epsilon = 26240$  cm<sup>-1</sup> mol<sup>-1</sup> L). Anal. Calcd for C<sub>52</sub>H<sub>49</sub>BBrClN<sub>3</sub>Rh: C, 66.09; H, 5.23; N, 4.45. Found: C, 66.01; H, 5.20; N, 4.40.

Complex **6**, brown solid; Yield: 69%. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 1590 (C=N), 1018 (py). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25°C):  $\delta$  (ppm) = 8.94 (br s, 1H, NH), 8.82 (dt,  $^3J_{\text{H-H}} = 5.6$  Hz, 1H, H<sub>ar</sub>), 8.03 (td,  $^3J_{\text{H-H}} = 8.0$  Hz, 1H, H<sub>ar</sub>), 7.80-7.54 (m, 7H, H<sub>ar</sub>), 7.38-7.36 (m, 2H, H<sub>ar</sub>), 7.32-7.28 (m, 8H, H<sub>Bar</sub>), 7.25 (m, 2H, H<sub>ar</sub>), 7.02 (t,  $^3J_{\text{H-H}} = 7.6$  Hz, 8H, H<sub>Bar</sub>), 6.87 (t,  $^3J_{\text{H-H}} = 7.2$  Hz, 4H, H<sub>Bar</sub>), 1.49 (s, 15H, H<sub>Cp\*</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN, 25°C):  $\delta$  (ppm) = 153.8 (C=N), 152.2 (C<sub>ar</sub>), 141.7 (C<sub>ar</sub>), 139.7 (C<sub>ar</sub>), 135.4 (C<sub>ar</sub>), 131.5 (C<sub>ar</sub>), 129.9 (C<sub>ar</sub>), 128.4 (C<sub>ar</sub>), 127.9 (C<sub>ar</sub>), 125.3 (C<sub>Bar</sub>), 121.4 (C<sub>ar</sub>), 119.1 (C<sub>ar</sub>), 97.7 (d,  $^2J_{\text{Rh-C}} = 8.2$  Hz, C<sub>cp\*</sub>), 7.7 (C<sub>cp\*</sub>). MS (ESI positive mode): m/z 580 [M-BPh<sub>4</sub>]<sup>+</sup>. UV-vis (10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$  (nm): 390 ( $\epsilon = 990$  cm<sup>-1</sup> mol<sup>-1</sup> L), 292 ( $\epsilon = 10090$  cm<sup>-1</sup> mol<sup>-1</sup> L), 242 ( $\epsilon = 19340$  cm<sup>-1</sup> mol<sup>-1</sup> L). Anal. Calcd for C<sub>52</sub>H<sub>49</sub>BCl<sub>2</sub>N<sub>3</sub>Rh: C, 69.35; H, 5.48; N, 4.67. Found: C, 69.45; H, 5.41; N, 4.60.

### General procedure for the catalytic transformation of aldehyde to amide

Compound **3** (0.002 mmol), the aldehyde (1 mmol), NH<sub>2</sub>OH·HCl (1 mmol) and NaHCO<sub>3</sub> (1 mmol) were introduced in a dried schlenk tube and purged with N<sub>2</sub>. Then, to the mixture, dried and degassed toluene (2 ml) was added and the mixture was stirred for about 10 minutes at room temperature, before the solution was refluxed under stirring for 2 hours. The mixture was cooled and the products were extracted with methanol and dichloromethane before being filtered

through celite to remove the remaining catalyst and NaHCO<sub>3</sub>. The crude amide was purified using column chromatography, and dried under vacuum.

### Single-crystal X-ray structure analysis

Crystals of compound **1** were obtained at room temperature by the diffusion of pentane in a dichloromethane solution (1:3). A crystal was mounted on a Stoe Image Plate Diffraction system equipped with a  $\phi$  circle goniometer, using Mo-K $\alpha$  graphite monochromated radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with  $\phi$  range 0-200°. The structure was solved by direct methods using the program SHELXS-97, while the refinement and all further calculations were carried out using SHELXL-97 [46]. The H-atoms were found on Fourier difference map or included in calculated positions and treated as riding atoms using the SHELXL default parameters. Examination of the structure with PLATON [47] reveals voids corresponding to highly disordered solvent molecules, and accordingly, a new data set was generated with the SQUEEZE algorithm [48]. Then, the structure was refined to convergence. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on  $F^2$ . Crystallographic details are summarized in Table S5. Figure S1 was drawn with ORTEP [49] and Figure S2 with Mercury [50].

### Supplementary material

Figures S1 and S2, Tables S1-S5.

CCDC-1876101 complex **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from

the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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**HIGHLIGHTS**

- The synthesis of half-sandwich phenylhydrazone-based catalysts is presented.
- A rhodium complex was characterized by single-crystal X-ray analysis.
- The complexes are active catalysts for the formation of amides from aldehydes.