

## 2-Diphenylphosphanyl-4-pyridyl(dimethyl)amine as an Effective Ligand for the Ruthenium(II) Complex Catalyzed Homogeneous Hydration of Nitriles under Neutral Conditions

Makoto Muranaka, Isao Hyodo, Wataru Okumura, Toshiyuki Oshiki\*

Division of Chemistry and Biochemistry,  
Graduate School of Natural Science and Technology,  
Okayama University, Okayama 700-8530, Japan

\*Corresponding author. Tel.: +81-86-286-8035; fax: +81-86-286-8035.

E-mail address: oshiki@cc.okayama-u.ac.jp (T. Oshiki)

### Abstract

New homogeneous catalyst comprised of  $[\text{Ru}(\text{methallyl})_2(\text{cod})]$  (cod = 1,5-cyclooctadiene) (**1**) and 2-diphenylphosphanyl-4-pyridyl(dimethyl)amine (**2**) is shown to efficiently catalyze the hydration of various nitriles under neutral conditions. The hydration proceeds in the presence of 0.5 mol% of the ruthenium catalyst at 80 °C in 1,2-dimethoxyethane solution and the corresponding amide is obtained within few hours without the formation of byproducts. Comparison of some phosphine ligands for the hydration reveals that the dimethylamino moiety of **2** improves the catalytic performance dramatically.

*Keywords:* Hydration; Nitrile; Amides; Homogeneous catalysis; Ruthenium; Phosphine

## 1. Introduction

The catalytic hydration of nitriles to amides is an ideal atom-economical reaction and important reaction in commercial production of amides [1] (Scheme 1). The reaction is catalyzed by metalloenzymes [2], heterogeneous transition-metals [3] and homogeneous transition-metals [4]. Some of metalloenzymes and heterogeneous catalysts have been employed in the industrial production of amides. For example,  $5 \times 10^5$  tons of acrylamide per year has been produced from acrylonitrile. In a laboratory, a variety of homogeneous catalysts composed of transition-metal complexes such as chromium [5], molybdenum [6], ruthenium [7], cobalt [8], rhodium [9], iridium [10], nickel [11], palladium [12], platinum [13], gold [14] and zinc [15] have been investigated.

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Scheme 1

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A bifunctional catalysis is one of the recent trends in a homogeneous catalytic hydration of an unsaturated bond [7c-f 16]. A nitrogen-containing organophosphorus ligand (P,N ligand) have been used in the hydrations. We have reported that the ruthenium(II) complexes, [*cis*-Ru(acac)<sub>2</sub>(PPh<sub>2</sub>py)<sub>2</sub>] (acac = acetylacetonate; PPh<sub>2</sub>py = diphenyl-2-pyridylphosphine (**3**)) was an excellent bifunctional catalysts for hydration of nitriles to amides under neutral conditions [17]. The high turnover frequency of up to 20900 (mol of amide)/(mol of catalyst) h probably caused by the promotion of nucleophilic addition of water by the PPh<sub>2</sub>py ligand. The bifunctional ruthenium(II) catalyst affords various nitriles in almost quantitative yields. However, the reactions required high temperature (180 °C), and the yields of amides were reduced significantly

by decreasing the reaction temperature. In the catalyst system, it is difficult to generate a vacant coordination site for coordination of nitriles, because the site would be generated by the dissociation of an oxygen atom of the anionic bidentate acac ligand.

To achieve the catalytic hydration under more mild conditions, we turned our attention to [Ru(methallyl)<sub>2</sub>(cod)] (cod = 1,5-cyclooctadiene) (**1**) [18]. Complex **1** is a ruthenium(II) complex and a fluxionality of the methallyl fragment forms  $\eta^3$ - and  $\eta^1$ -methallyl species under mild conditions [19]. The generated  $\eta^1$ -species is a coordinatively unsaturated ruthenium(II) complexes and would exhibit a high performance as a catalyst. [20]

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Scheme 2

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Here we describe a new ruthenium(II) catalyst comprised of **1** and 2-diphenylphosphanyl-4-pyridyl(dimethyl)amine (**2**). Preparation of pyridylphosphine **2** was first reported by Fort and coworkers in 2002 [21]. They mentioned that electron-rich **2** is a potentially interesting ligand for a transition-metal complex. However, there are no reports using **2** as a ligand in fields of coordination and catalytic chemistry. Thus, here is a first example of that **2** acts as an effective ligand for a homogeneous catalytic reaction. The hydration of various nitriles proceeded at 80 °C under neutral conditions.

## 2. Results and discussion

Initially catalytic hydration of nitriles was investigated using benzonitrile as a substrate. Catalytic performances of the combination of **1** and pyridylphosphine derivatives **2–4** and **5** were summarized in Table 1.

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### Scheme 3

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Quantitative formation of benzamide was observed when using a mixture of **1** and **3** at 180 °C for 10 min (entry 1). The effect of ligand **3** was demonstrated by comparison with the hydration catalyzed by **1** and PPh<sub>3</sub>. When using PPh<sub>3</sub> as a ligand, no benzamide was detected in the reaction. These preliminary results provide the evidence that **1** is suitable ruthenium(II) complex and ligand **3** enhances the catalytic hydration. Thus, **3** behaves as an effective P,N ligand like our previously reported ruthenium(II) complexes for the hydration.[17a] Interestingly, sole complex **1** afforded benzamide in 8% yield.

At 80 °C for 3.5 h, the yield of benzamide was very low using **3** as a ligand (entry 2). The combination of **1** and **2** dramatically improved the rate of the reaction and benzamide was obtained in 61% yield (entry 3). On the contrary, **4** [16b] and **5** were slightly effective (entries 4 and 5). These results suggested that the electron-donating dimethylamino group of **2** increased the electron density of a nitrogen atom in the pyridine ring and water was more activated via a hydrogen bond [17a] than in the case of using **3** as a catalyst component. The rate of the reaction was accelerated with an increasing amount of **2** (entries 6–8). It was estimated that the ratio of **1** to **2** was three for the catalytic preparation of benzamide. Attempts to identify the ruthenium

species generated by the reaction of **1** and **2** failed. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the mixture of **1** and **2** showed complex signals from  $-22$  to  $17$  ppm under various conditions.

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Table 1

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Table 2 shows the results obtained for the hydration of benzonitrile under different conditions. 1,2-Dimethoxyethane is the best solvent for the hydration catalyzed by the mixture of **1** and **2**. The hydration in 1,2-dimethoxyethane proceeded at  $60$  °C. After 48 h, benzamide was obtained in 99% isolated yield (Scheme 4). THF and 1,4-dioxane were suitable solvent for the hydrations. No reactions proceeded in highly polar ionic liquids (entries 14 and 15). The hydration under solvent-free conditions also examined. Benzamide was only obtained in 9% yield (entry 10).

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Table 2

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Scheme 4

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The results of the catalytic hydration of various kinds of nitriles are summarized in Table 3. The para substituted aromatic nitriles, 4-tolunitrile, 4-methoxybenzonitrile and 4-chlorobenzonitrile were smoothly converted to the corresponding amides in high

yields (entries 1, 3 and 4). The electron withdrawing Cl group did not interrupt the hydration. The reaction of 2-tolunitrile is sluggish compare to that of 4-tolunitrile due to the sterically crowded nitrile group (entry 2). The low reactivity of 2-tolunitrile is quite different from those observed using our reported catalysts [17a]. The catalytic hydration proved to be affected by the presence of carbonyl groups. For example, the hydration of 4-cyanobenzaldehyde gave the corresponding amide only 1% yield (entry 5). In spite of longer reaction time (12 h), the yield of 4-cyanobenzoic acid methyl ester was very low (10%) (entry 6). These carbonyl moieties of the starting materials did not hydrolyzed in the reactions. Commercially useful nicotinamide could be obtained from 3-cyanopyridine (entry 7). The catalyst also hydrolyzed less reactive aliphatic nitriles. Phenylacetoneitrile was smoothly hydrated to give the desired amide in excellent yield (entry 9). The catalytic hydration of phenoxyacetoneitrile and *trans*-cinnamoneitrile afforded the corresponding amides in moderate yields (entries 10 and 11). Nonanamide was obtained from nonanoneitrile in almost quantitative yield under conditions similar to those for aromatic nitriles as a substrate (entry 12). In this type of aliphatic nitrile, the nitrile group is less electrophilic than that of an aromatic nitrile. Contrary to the reported hydration catalysts,[3a, 17a] the catalyst comprised of **1** and **2** is suitable for the hydration of less reactive aliphatic nitriles. In all catalytic hydrations examined, no byproduct was observed.

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Table 3

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### 3. Conclusion

In summary, we have presented new ruthenium(II) catalysts for the hydration of nitriles. The combination of **1** and **2** exhibited the best catalytic efficiency. Complex **1** is accessible and **2** can be prepared from readily available organic reagents. In addition, **2** is robust tertiary phosphine ligand and can be stored under ambient conditions. Owing to the strongly electron-donating dimethylamino group of **2**, the catalyst acted under 80 °C to give various amides in high yield. The protocol using **2** as a ligand would promise the broad application for a homogeneous catalytic reaction in organic synthesis. Continuing studies on the effect of the structure-efficiency relationships of ruthenium catalysts will allow us to further the usefulness of homogeneous hydration catalyst under neutral conditions.

#### 4. Experimental

All manipulations involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under argon. Anhydrous hexane, THF, and toluene were purchased from Wako Pure Chemical Industries, Ltd. and stored on 4Å molecular sieves under argon. Anhydrous 1,2-Dimethoxyethane was purchased from Kanto Chemicals and stored on 4A molecular sieves under argon. [Ru(methallyl)<sub>2</sub>(cod)] and **4** were purchased from Strem and used as received. Diphenyl-2-pyridylphosphine (**3**) and 4-(Dimethylamino)-phenyldiphenylphosphine (**5**) were purchased from Aldrich and used as received. <sup>1</sup>H, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 399.65 and 161.70 MHz, respectively, on a JEOL JNM-LA400 spectrometer. The <sup>1</sup>H NMR chemical shift is relative to tetramethylsilane; the resonance of the residual protons of CDCl<sub>3</sub> was used as an internal standard (δ 7.26 ppm chloroform for <sup>1</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts were relative to 85% H<sub>3</sub>PO<sub>4</sub> at δ 0.00 (external reference). Melting point was measured in a sealed tube on a Yanaco MP-S3 apparatus and was uncorrected.

#### 4.1. Preparation of **2**

Phosphine Ligand **2** was prepared according to the previously described procedure [21], with some modifications as follows. A solution of 2-(dimethylamino)ethanol (5 mL, 40 mmol) in hexane (50 mL) was cooled to 0 °C, and *n*-BuLi (2 M hexane solution, 50 mL, 80 mmol) was added as a droplet under argon-atmosphere. After 1.5 h of stirring at 0 °C, 4-dimethylaminopyridine (2.4 g, 20 mmol) was added as a solid. After 1 h of stirring at 0 °C, the reaction mixture was cooled to -78 °C, and a hexane (100 mL) solution of chlorodiphenylphosphine (9.0 mL, 50 mmol) was slowly added as a droplet. After 1.5 h for stirring at -78 °C, the resulting reaction mixture was filtered. Obtained solid was dried in desiccator overnight. Ethyl acetate and water were added to the dried solid, and then organic materials were extracted with ethyl acetate. Combined organic solution was dried over anhydrous NaSO<sub>4</sub>. The crude solid was recrystallized from ethyl acetate and hexane to give **2** in 53% yield as a pale yellow powder. The product was identified spectroscopically by comparison to the reported data. Mp 89–91 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.84 (s, 6H), 6.33–6.38 (m, 2H), 7.32–7.42(m, 10H), 8.32(d, *J*=5.8 Hz, 1H); <sup>31</sup>P{<sup>1</sup>H} NMR(CDCl<sub>3</sub>): δ -2.3(s).

#### 4.2. A typical procedure is described for the hydration of benzonitrile catalyzed by the combination of **1** and **2**.

Complex **1** and ligand **2** were placed in a 5 mL test tube equipped with a screw cap. 1,2-Dimethoxyethane (0.5 mL), benzonitrile (102 μl, 1.0 mmol), and water (72 μL, 4.0 mmol) were added, and then, the tube was sealed by the screw cap. The tube was heated in an oil bath. After the reaction, the reaction mixture was subjected to gas chromatography (Shimadzu GC-14A, column: RESTEK RTX-1 (15 m x 0.32 mm)). In Tables 1 and 2, the yields of benzamide were calculated from response factors



relative to an internal naphthalene standard. In Table 3, amides were isolated by a silica-gel short column using ethyl acetate as an eluent. The amides were identified spectroscopically by comparison to authentic samples.

### **Acknowledgement**

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Table 1. Catalytic hydration of benzonitrile using **2–5** as a ligand<sup>a</sup>

entry	ligand	amt of ligand <sup>b</sup>	temp (°C)	time (h)	yield (%)
1	<b>3</b>	2	180	0.17	>99
2	<b>3</b>	2	80	3.5	3
3	<b>2</b>	2	80	3.5	61
4	<b>4</b>	2	80	3.5	7
5	<b>5</b>	2	80	3.5	1
6	<b>2</b>	3	80	3.5	>99
7	<b>2</b>	4	80	3.5	91
8	<b>2</b>	0.5	80	3.5	10

<sup>a</sup> Experimental conditions: benzonitrile (1.0 mmol), water (4.0 mmol), **1** (0.005 mmol, 0.5 mol% per benzonitrile), 1,2-dimethoxyethane (0.5 mL), 80 °C, 3.5 h. <sup>b</sup> Molar ratio between ligand and **1**.

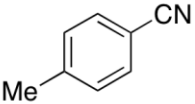
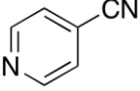
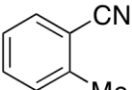
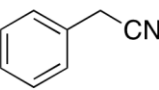
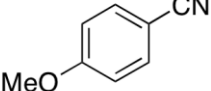
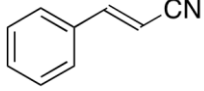
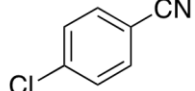
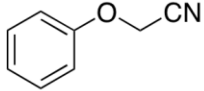
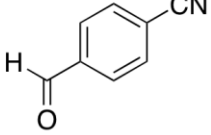
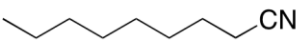
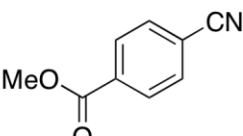
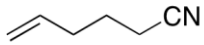
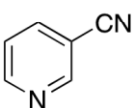
Table 2. Catalytic hydration of benzonitrile under various conditions<sup>a</sup>

entry	solvent	temp (°C)	time (h)	yield (%)
1	1,2-dimethoxyethane	80	3.5	>99
2	1,2-dimethoxyethane	60	3.5	30
3	THF	80	3.5	90
4	THF	60	3.5	2
5	THF	60	24	37
6	1,4-dioxane	80	3.5	>99
7	1,4-dioxane	60	3.5	11
8	1,4-dioxane	60	24	46
9	triglyme	60	3.5	0
10	cyclopentyl methyl ether	60	3.5	3
11	EtOH	80	3.5	23
12	EtOH	60	3.5	9
13	H <sub>2</sub> O	60	3.5	1
14	[BMIM]N(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	60	3.5	0
15	[BMIM]BF <sub>4</sub> <sup>b</sup>	60	3.5	0
16	none	60	3.5	9

<sup>a</sup> Experimental conditions: benzonitrile (1.0 mmol), water (4.0 mmol), **1** (0.005 mmol, 0.5 mol% per benzonitrile), **2** (0.015 mmol), solvent (0.5 mL). <sup>b</sup> BMIM = 1-butyl-3-methyl-imidazolinium.

Table 3

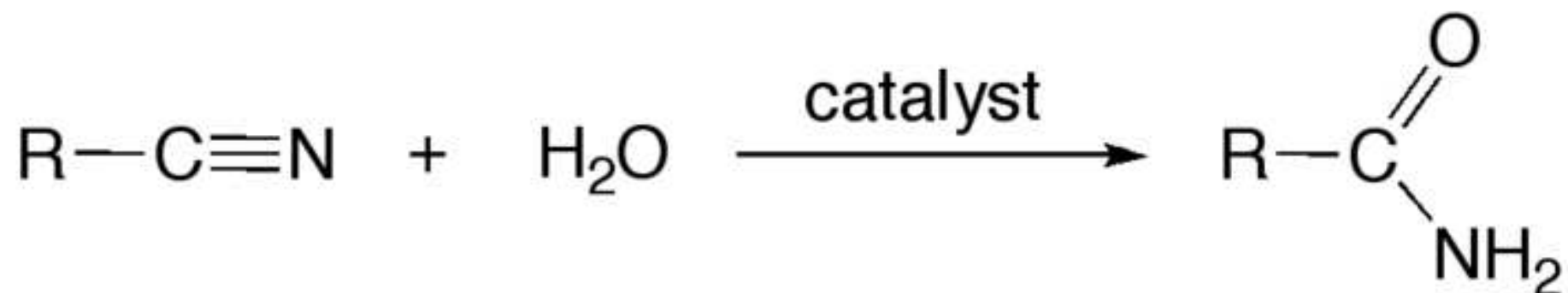
Catalytic hydration of various nitriles at 80 °C for 5 h <sup>a</sup>

entry	nitrile	yield (%)	entry	nitrile	yield (%)
1		96	8 <sup>b</sup>		41
2		38	9 <sup>b</sup>		91
3		99	10 <sup>b</sup>		60
4		95	11 <sup>b</sup>		63
5		1	12		99
6		6	13 <sup>b</sup>		45
7 <sup>b</sup>		38			

<sup>a</sup> Experimental conditions: nitrile (1.0 mmol), water (4.0 mmol), **1** (0.01 mmol, 1.0 mol% per nitrile), **2** (0.03 mmol), 1,2-dimethoxyethane (0.5 mL),. <sup>b</sup> 0.02 mmol of **1** (2.0 mol% per nitrile) and 0.06 mmol of **2** were used.

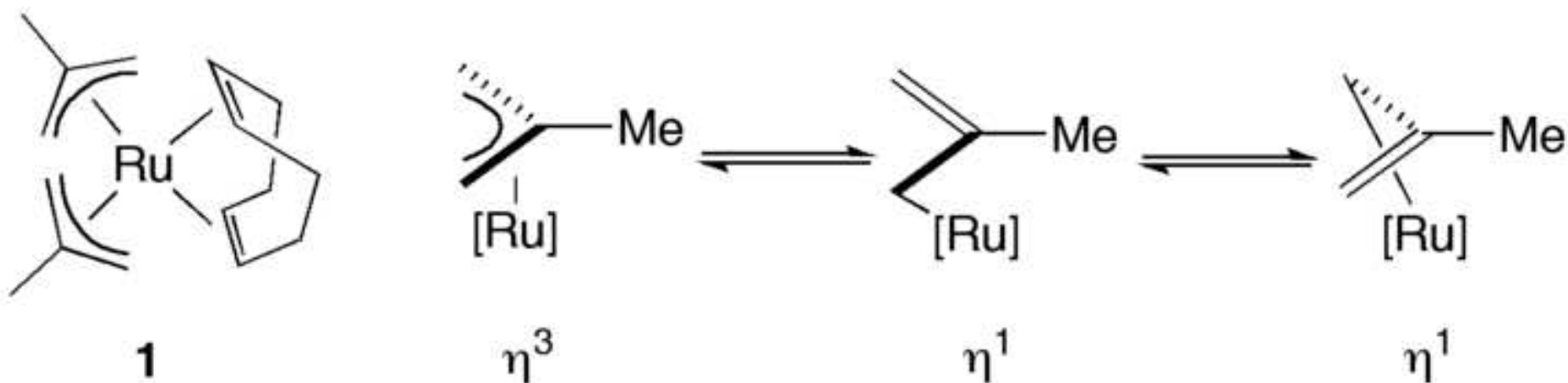
## Scheme 1

## Catalytic Hydration of a nitrile to an amide

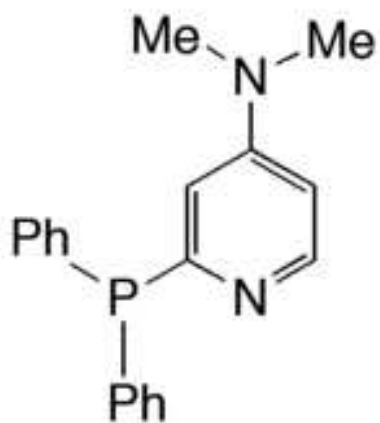
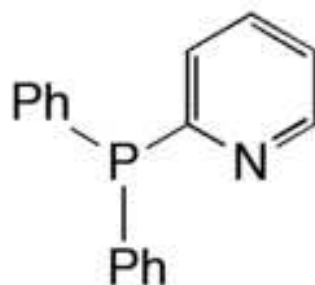
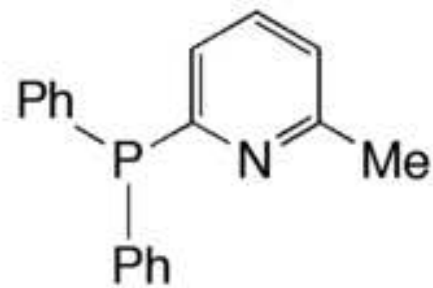
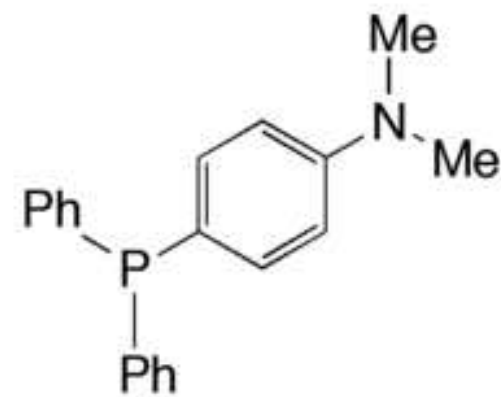




## Scheme 2

Complex **1** and schematic equation of its fluxional character

Scheme 3  
Structures of nitrogen containing phosphine ligands **2–5**

**2****3****4****5**

Scheme 4  
Catalytic Hydration at 60 °C

