

# Transfer hydrogenation of ketones catalyzed by new rhodium and iridium complexes of aminophosphine containing cyclohexyl moiety and photosensing behaviors of rhodium and iridium based devices

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## ABSTRACT

The reaction of  $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$  and  $\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-Cl})\text{Cl}_2$  with aminophosphine ligands  $\text{Cy}_2\text{PNHCH}_2\text{-C}_4\text{H}_3\text{X}$  (X: O; S) gave a range of new monodentate  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{-C}_4\text{H}_3\text{O})(\text{cod})\text{Cl}]$ , (**1**),  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{-C}_4\text{H}_3\text{S})(\text{cod})\text{Cl}]$ , (**2**),  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{-C}_4\text{H}_3\text{O})(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]$ , (**3**) and  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{-C}_4\text{H}_3\text{S})(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]$ , (**4**) complexes, which were characterized by analytical and spectroscopic methods. The new rhodium(I) and iridium(III) catalysts were applied to transfer hydrogenation of acetophenone derivatives using 2-propanol as a hydrogen source. The results showed that the corresponding alcohols could be obtained with high activity (up to 99%) under mild conditions. Notably,  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{-C}_4\text{H}_3\text{O})(\text{cod})\text{Cl}]$  complex (**1**) is much more active than the other analogous complexes in the transfer hydrogenation. Moreover, organic–inorganic rectifying contacts were fabricated forming rhodium(I) and iridium(III) complex thin films on *n*-Si semiconductors and evaporating Au metal on the structures. Electrical properties of the contacts including ideality factor, barrier height and series resistance were determined using their current–voltage (*I*–*V*) data. The photoelectrical characteristics of the devices were examined under the light with 40–100 mW/cm<sup>2</sup> illumination conditions. It was seen that light had strong effects on *I*–*V* characteristics of the devices and the ones fabricated using **3** and **4** complexes had unusually forward and reverse bias photoconducting behavior.

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## 1. Introduction

Transition metal complexes are powerful catalysts for organic transformations and when suitable ligands are bound to a metal center, they can offer chemio, regio or stereo selectivity under mild conditions [1]. However, the appropriate choice of metal precursors and the reaction conditions are crucial for catalytic properties [2]. A number of transition metal complexes are known to catalyze hydrogen transfer from an alcohol to a ketone [3–5]. Over the last three decades, most effort on hydrogenation has been focused on

the use of ruthenium, rhodium and iridium catalysts [6–10]. Rhodium and iridium complexes have been proven to lead to very efficient processes along with potential industrial applications [11–14].

To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored [15–17]. Phosphorus–nitrogen containing ligands have particular use in catalysis where it is necessary for part of ligand to dissociate to allow an organic fragment to coordinate and undergo transformations [18,19]. The presence of P–N ligands enables many different and important catalytic processes to occur [7,20,21]. Especially, aminophosphines are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful transformations. Synthesis of new aminophosphines to stabilize transition metals in

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low valent states is considered to be a most challenging task in view of their potential utility in a variety of metal-mediated organic transformations [22].

Hydrogen transfer reactions are mild methodologies for reduction of ketones or imines and oxidation of alcohols or amines in which a substrate-selective catalyst transfers hydrogen between the substrate and a hydrogen donor or acceptor, respectively [23–25]. From an industrial point of view, catalytic transfer hydrogenation is an attractive alternative for high pressure catalytic hydrogenations with molecular hydrogen [26]. Here, hydrogen donors such as secondary alcohols (e.g., 2-propanol) are applied to convert carbonyl compounds to alcohols. The risk associated with the use of molecular hydrogen at high pressures is thereby eliminated [27,28]. Furthermore, there are several other advantages for use of 2-propanol such as, it is inexpensive, readily available and has an appropriate boiling point. It is also a good solvent for many organic compounds. Upon dehydrogenation, 2-propanol is converted to acetone, which can be easily removed from the reaction mixture, and thus simplifies the reaction process [29,30].

Organic materials have obtained an important place in the fields of electrical and optical device industry. They have been preferred in device applications because of their key advantages including large area coating, using on flexible substrates and low cost [31,32]. Among the other organic compounds, there is a growing interest on metal complexes because of their mechanical and chemical stabilities [33]. While some studies have concentrated on finding suitable metal complexes for device technology [34,35], others have focused on the usage of these compounds in the fabrication of devices including solar cells, Schottky diodes and light emitting diodes [36–39]. Studies on metal–semiconductor (MS) devices with organic semiconductor have shown that these structures presented photovoltaic and photoconductivity influences when they are exposed to light because of electron and hole production at the interface [40].

To the best our knowledge, there is no report on the use of these complexes including aminophosphines having cyclohexyl moiety on phosphorus atom in rhodium and iridium catalyzed transfer hydrogenation reaction. As part of our research program, we report here the synthesis and full characterization of four new aminophosphine complexes  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{O})(\text{cod})\text{Cl}]$  (**1**),  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{S})(\text{cod})\text{Cl}]$  (**2**),  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{O})(\eta^5\text{—C}_5\text{Me}_5)\text{Cl}_2]$  (**3**) and  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{S})(\eta^5\text{—C}_5\text{Me}_5)\text{Cl}_2]$  (**4**). We also report their catalytic activity in transfer hydrogenation reactions of ketones with *iso*-PrOH. Furthermore, up to now, studies have reported to reverse bias photosensing properties of organic based devices [38,41,42]. In this study, fabrication of organic–inorganic heterojunction devices, their electrical properties including ideality factor, barrier height and series resistance values and photoelectrical properties are presented. It is also reported that the devices obtained using **3** and **4** complexes have reverse and current bias photoconduction behavior which have not reported up to now for organic based devices.

## 2. Results and discussion

### 2.1. Synthesis and characterization of the metal complexes

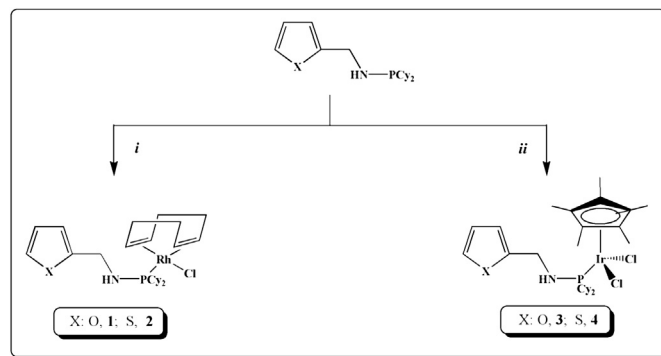
Synthesis and characterization of the ligands, furfuryl-2-(*N*-dicyclohexylphosphino)methylamine and thiophene-2-(*N*-dicyclohexylphosphino)methylamine, were mentioned elsewhere [43]. We examined various coordination chemistry of these aminophosphines with  $[\text{Rh}(\mu\text{—Cl})(\text{cod})_2]$  precursor. Reaction of furfuryl-2-(*N*-dicyclohexylphosphino)methylamine or thiophene-2-(*N*-dicyclohexylphosphino)methylamine with  $[\text{Rh}(\mu\text{—Cl})(\text{cod})_2]$  in a

molar ratio of 2/1 at room temperature for 45 min afforded  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{O})(\text{cod})\text{Cl}]$  (**1**) and  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{S})(\text{cod})\text{Cl}]$  (**2**), respectively as crystalline yellow powders (Scheme 1). The complexes of **1** and **2** were isolated as indicated by doublets in the  $^{31}\text{P}\text{—}\{^1\text{H}\}$  NMR spectra at  $\delta$  71.98 (d,  $^1J_{\text{RhP}}$ : 156.5 Hz) and 74.39 (d,  $^1J_{\text{RhP}}$ : 154.1 Hz) ppm, respectively, (Fig. 1). In their  $^1\text{H}$  NMR spectra, **1** and **2** are characterized by CH resonances of cod at  $\delta$  ~ 5.35 and 3.55 ppm, whereas in the  $^{13}\text{C}\text{—}\{^1\text{H}\}$  NMR spectra, resonances at  $\delta$  ~ 70 and 104 ppm correspond to CH resonances of cod (for details see Experimental Section). Furthermore, other  $^1\text{H}$  and  $^{13}\text{C}\text{—}\{^1\text{H}\}$  NMR data are in agreement with the proposed structures. The complexes were also characterized by IR and microanalysis.

We studied coordination chemistry of aminophosphines including cyclohexyl moiety with  $[\text{Ir}(\eta^5\text{—C}_5\text{Me}_5)(\mu\text{—Cl})\text{Cl}]_2$  precursor as well.  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{O})(\eta^5\text{—C}_5\text{Me}_5)\text{Cl}_2]$ , **3** and  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{S})(\eta^5\text{—C}_5\text{Me}_5)\text{Cl}_2]$ , **4** were obtained by the reaction of ligands with  $[\text{Ir}(\eta^5\text{—C}_5\text{Me}_5)(\mu\text{—Cl})\text{Cl}]_2$  in a molar ratio of 2/1 at room temperature for 1 h (Scheme 1). In the  $^{31}\text{P}\text{—}\{^1\text{H}\}$  NMR spectra, resonances at  $\delta$  ~ 43 ppm may be attributed to complexes of **3** and **4** (Fig. 1).  $^{13}\text{C}$  NMR spectra of the complexes display singlets at  $\delta$  ~ 10 ppm attributable to methyl carbons of Cp\* and doublets at  $\delta$  ~ 92 due to carbons of Cp\* ring. The  $^1\text{H}$  NMR spectra are consistent with the anticipated structures. The structural compositions of the complexes **3** and **4** were further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values (for details see Experimental section).

### 2.2. Catalytic transfer hydrogenation of ketones

The brilliant catalytic performance of aminophosphine-based transition metal complexes [44], and references therein] prompted us to develop new Rh(I) and Ir(III) complexes with well-shaped ligands, since NH unit forms a hydrogen bond with the carbonyl oxygen atom to stabilize the transition state. Therefore, the presence of an NH moiety in the ligands is crucially important to determine the catalytic performance of the bifunctional catalysts [45–47]. An important and unprecedented aspect is that the carbonyl compound does not interact directly with the metal center for its own activation [48]. To this end, we observed the catalytic activation of complexes **1–4** in the transfer hydrogenation of ketones to the corresponding alcohols. In a typical experiment, 0.005 mmol of the complex and 0.5 mmol of ketone were added to a solution of NaOH in *iso*-PrOH (0.025 mmol of NaOH in 5 mL *iso*-PrOH) and refluxed at 82 °C, the reaction being monitored by GC. In all reactions, these complexes catalyzed the



**Scheme 1.** Synthesis of the  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{O})(\text{cod})\text{Cl}]$  (**1**),  $[\text{Rh}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{S})(\text{cod})\text{Cl}]$  (**2**),  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{O})(\eta^5\text{—C}_5\text{Me}_5)\text{Cl}_2]$  (**3**) and  $[\text{Ir}(\text{Cy}_2\text{PNHCH}_2\text{—C}_4\text{H}_3\text{S})(\eta^5\text{—C}_5\text{Me}_5)\text{Cl}_2]$  (**4**) complexes (i) 1/2 equiv.  $[\text{Rh}(\mu\text{—Cl})(\text{cod})_2]$ , thf; (ii) 1/2 equiv.  $[\text{Ir}(\eta^5\text{—C}_5\text{Me}_5)(\mu\text{—Cl})\text{Cl}]_2$ , thf.

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