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RESEARCH HIGHLIGHTS

- ✓ For the first time complexes of aminophosphine carrying cyclohexyl moiety were synthesized and characterized.

- ✓ [Rh(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(cod)Cl] was a more efficient catalyst in the transfer hydrogenation.

- ✓ Fabrication of organic-inorganic heterojunction devices, their electrical properties including ideality factor, barrier height and series resistance values and photoelectrical properties are presented.

- ✓ The devices obtained using Ir(III)-aminophosphine complexes have reverse and current bias photoconduction behavior which have not reported up to now for organic based devices.

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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Novel Rh(I) and Ir(III) complexes containing aminophosphine ligands including cyclohexyl moiety have been synthesized. The use of the new complexes for the reduction of the ketonic C=O bond under hydrogen transfer conditions was investigated. Surprisingly, [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl] was a more efficient catalyst in the transfer hydrogenation than the other complexes. In addition, the electrical properties of the devices were analyzed in dark and under a solar simulator with various illumination conditions. The results showed excellent reverse and forward bias photosensing behaviors for [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2] and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2] complexes.

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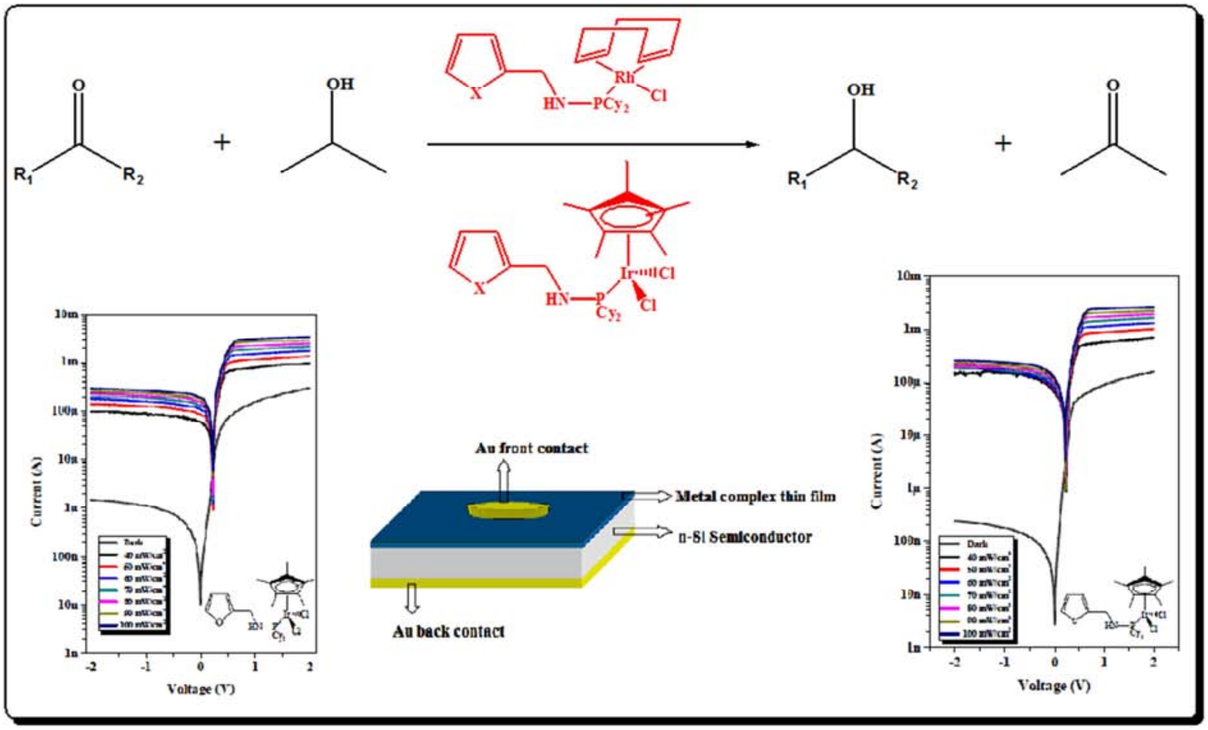
O
R1
R2
+
OH
X
HN
PCy2
Rh
Cl
OH
R1
R2
+
O
X
HN
P
Cy2
Ir
Cl
Cl
Au front contact
Metal complex thin film
n-Si Semiconductor
Au back contact
Current (A)
Voltage (V)
10m
1m
100µ
10µ
1µ
100n
10n
1n
-2
-1
0
1
2
Dark
40 mW/cm²
50 mW/cm²
60 mW/cm²
70 mW/cm²
80 mW/cm²
90 mW/cm²
100 mW/cm²

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ABSTRACT

The reaction of $[Rh(\mu\text{-}Cl)(cod)]_2$ and $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ with aminophosphine ligands $Cy_2PNHCH_2\text{-}C_4H_3X$ (X: O; S) gave a range of new monodendate $[Rh(Cy_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$, (**1**), $[Rh(Cy_2PNHCH_2\text{-}C_4H_3S)(cod)Cl]$, (**2**), $[Ir(Cy_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$, (**3**) and $[Ir(Cy_2PNHCH_2\text{-}C_4H_3S)(\eta^5\text{-}C_5Me_5)Cl_2]$, (**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, $[Rh(Cy_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ 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

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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^2 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.

Keywords: Aminophosphine; Iridium; Transfer Hydrogenation; Rectifying contact; Electrical properties; Photoconductor

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 [3,4,5]. Over the last three decades, most effort on hydrogenation has been focused on the use of ruthenium, rhodium and iridium catalysts [6,7,8,9,10]. Rhodium and iridium complexes have been proven to lead to very efficient processes along with potential industrial applications [11,12,13,14].

To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored [15,16,17]. 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 [20,21,22]. 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 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 [23].

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 [24,25,26]. From an industrial point of view, catalytic transfer hydrogenation is an attractive alternative for high pressure catalytic hydrogenations with molecular hydrogen [27]. 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 [28,29]. 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 [30,31].

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 [32,33]. Among the other organic compounds, there is a growing interest on metal complexes because of their mechanical and chemical stabilities [34]. While some studies have concentrated on finding suitable metal complexes for device technology [35,36], others have focused on the usage of these compounds in the fabrication of devices including solar cells, Schottky diodes and light emitting diodes [37,38,39,40]. 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 [41].

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 $[Rh(Cy_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ (**1**), $[Rh(Cy_2PNHCH_2\text{-}C_4H_3S)(cod)Cl]$, (**2**), $[Ir(Cy_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$, (**3**) and $[Ir(Cy_2PNHCH_2\text{-}C_4H_3S)(\eta^5\text{-}C_5Me_5)Cl_2]$, (**4**). We also report their catalytic activity in transfer hydrogenation reactions of ketones with iso-PrOH. Furthermore, up to know, studies have reported to reverse bias photosensing properties of organic based devices [39,42,43]. 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.

3. Results and discussion

3.1. 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 [44]. We examined various coordination chemistry of these aminophosphines with $[Rh(\mu\text{-}Cl)(cod)]_2$ precursor. Reaction of furfuryl-2-(*N*-dicyclohexylphosphino)methylamine or thiophene-2-(*N*-dicyclohexylphosphino) methylamine with $[Rh(\mu\text{-}Cl)(cod)]_2$ in a molar ratio of 2/1 at room temperature for 45 min afforded $[Rh(Cy_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$, (**1**) and $[Rh(Cy_2PNHCH_2\text{-}C_4H_3S)(cod)Cl]$ (**2**), respectively as crystalline yellow powders (Scheme 1). The complexes of **1** and **2** were isolated as indicated by doublets in the $^{31}P\text{-}\{^1H\}$ NMR spectra at δ 71.98 (d, $^1J_{RhP}$: 156.5 Hz) and 74.39 (d, $^1J_{RhP}$: 154.1 Hz) ppm, respectively, (Figure 1). In their ^1H NMR spectra, **1** and **2** are characterized by CH resonances of cod at δ ~5.35 and 3.55 ppm, whereas in the $^{13}C\text{-}\{^1H\}$ NMR spectra, resonances at δ ~70 and 104 ppm correspond to CH resonances of cod (for details see Experimental Section). Furthermore, other ^1H and $^{13}C\text{-}\{^1H\}$ NMR data are in agreement with the proposed structures. The complexes were also characterized by IR and microanalysis.

Insert Scheme 1 Here

We studied coordination chemistry of aminophosphines including cyclohexyl moiety with $[Ir(\eta^5-C_5Me_5)(\mu-Cl)Cl]_2$ precursor as well. $[Ir(Cy_2PNHCH_2-C_4H_3O)(\eta^5-C_5Me_5)Cl_2]$, **3** and $[Ir(Cy_2PNHCH_2-C_4H_3S)(\eta^5-C_5Me_5)Cl_2]$, **4** were obtained by the reaction of ligands with $[Ir(\eta^5-C_5Me_5)(\mu-Cl)Cl]_2$ in a molar ratio of 2/1 at room temperature for 1 h (Scheme 1). In the $^{31}P-\{^1H\}$ NMR spectra, resonances at $\delta \sim 43$ ppm may be attributed to complexes of **3** and **4** (Figure 1). ^{13}C NMR spectra of the complexes display singlets at $\delta \sim 10$ ppm attributable to methyl carbons of Cp* and doublets at $\delta \sim 92$ due to carbons of Cp* ring. The ^1H 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).

Insert Figure 1 Here

3.2. Catalytic transfer hydrogenation of ketones

The brilliant catalytic performance of aminophosphine-based transition metal complexes [45, 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 [46,47,48]. An important and unprecedented aspect is that the carbonyl compound does not interact directly with the metal center for its own activation [49]. 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 ºC, the reaction being monitored by GC. In all reactions, these complexes catalyzed the reduction of ketones to the corresponding alcohols via hydrogen transfer from *iso*-PrOH.

These complexes as catalyst precursors for the transfer hydrogenation of acetophenone have been tested and typical results are summarized in Table 1. As seen, high conversions can be achieved with the **1-4** catalytic systems. Conversions of transfer hydrogenation of acetophenone were negligible either at room temperature with a base and at reflux temperature in the absence of base in all the reactions (see Table 1). Thus, one can conclude that high temperature as well as presence of base is necessary to obtain considerable conversions. Results obtained from the optimization studies indicated clearly that the excellent conversions were achieved in the reduction of acetophenone to 1-phenylethanol when **1-4** were used as the catalytic precursor, with a substrate-catalyst molar ratio (100:1) in *iso*-PrOH at 82 °C (Table 1, entries 1, 8, 15 and 22). Furthermore, it should be pointed out that complex [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (**1**), is more active than [Rh(Cy_2PNHCH_2-C_4H_3S)(cod)Cl], (**2**), [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2], (**3**) and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**) complexes, because, conversion of acetophenone occurred in 15 min and 8 h by **1** and **2-4**, respectively. In addition, the yields gradually decreased on by increasing the mole ratios of [acetophenone]/[Ru] from 100/1 to 500/1 or 1000/1. Furthermore, performing the reaction in the presence of small amount of water did not change reaction time, while that in air slowed down the reaction (Table 1, entries 4, 5, 11, 12, 18, 19, 25 and 26).

Insert Table 1 Here

The complexes [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (**1**), [Rh(Cy_2PNHCH_2-C_4H_3S)(cod)Cl], (**2**), [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2], (**3**) and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**) were also extensively investigated with a variety of substrates. As expected, electronic properties (the nature and position) of the substituents on the phenyl ring of the ketone caused significant changes in the reduction rate. To ensure that the observed results could be attributed to purely electronic effects [50], substrates involving *para*- and *orto*- substituted acetophenone derivatives were investigated. The results indicated that strong electron withdrawing substituents, such as F, Cl and Br were capable of higher conversion (Table 2). Conversely, the most electron-donor substituents, (2-methoxy or 4-methoxy) led to lower conversion. It is well-known that the presence of an electron withdrawing group has generally been found to facilitate the hydrogen transfer reaction [51,52] which has been attributed to the hydridic nature of the reducing species involved. As such, reactions with fluoro proceeded to higher conversion owing to rapid hydride transfer, while reactions with electron-donating substituents methoxy proceeded in a slower and more controlled manner [53,54].

Insert Table 2 Here

Encouraged by the high catalytic activities gained in these preliminary studies, we next extended our investigations to include hydrogenation of various simple ketones. A variety of simple ketones (S/C=100/1) can be transformed to the corresponding secondary alcohols with high conversion, as exemplified in Table 3. The cyclic substrates are convertible to the corresponding alcohols with a moderate conversion. Furthermore, under identical conditions, transfer hydrogenation of methyl isobutyl ketone led to 99 % conversion within 1.5 h, while that of diethyl ketone occurred in 3 h with the same conversion by [Rh(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(cod)Cl], **1**.

Insert Table 3 Here

We also carried out further experiments to examine the effect of bulkiness of the alkyl groups on the catalytic activity and the results were given in Table 4 (Entries 1–16). As the steric hindrance of the alkyl group growths from ethyl to isopropyl, the extent of the time is increasing. Reaction of *tert*-butyl phenyl ketone possessing a bulky alkyl substituent proceeded rather slowly and in somewhat increasing time. Hence, it was found that the activity is highly dependent on the steric bulk of the alkyl group [55] and the reactivity gradually decreased by increasing the bulkiness of them [56].

Insert Table 4 Here

3.3. Electrical and photoelectrical properties of Au/metal complex/n-Si devices

I-*V* measurements of a structure give important information about electrical characteristics of the device. Main electrical parameters of a diode such as ideality factor, barrier height and series resistance can be determined using its *I*-*V* data in dark. In addition, photoelectrical parameters of a structure including open circuit voltage (V_{OC}) closed circuit current (I_{SC}) can be extracted using its *I*-*V* data under light. Figure 2 presents *I*-*V* measurements of Au/metal complex/n-Si structures in dark and under a solar simulator with various illumination conditions. As seen from the figures, all structures have excellent rectification behavior. When a rectifying diode is taken into account, *I*-*V* can be analyzed using thermionic emission theory.

Insert Figure 2 Here

According to the theory, the ideality factor and the barrier height values of a device can be extracted from the slope and the current axis intercept of the linear regions of the forward bias

I-V plots, respectively. The calculated ideality factor and the barrier height values are given in Table 5. As seen from the table, the ideality factors of the junctions are greater than unity. According to the theory, ideality factor should be very close to unity (1.03) when image force lowering is considered. The deviation from ideal diode can be attributed the effects of series resistance of the structure, existence of interface states at organic-inorganic interface, recombination-generation at the interface and tunneling [57,58]. The barrier height values of the structures are very close to each other and vary between 0.76 and 0.80 ev. Up to now, many kinds of molecules including small organic compounds, metal complexes, polymers and biological compounds have been used in the fabrication of organic-inorganic devices. For instance, several researchers [40] have synthesized and characterized Cu(II), Co(III), Ni(II) and Pd(II) complexes of $N_2S_2O_2$ thio Schiff base ligand and showed their usage in the fabrication of organic–inorganic hybrid devices. The calculated barrier heights of the devices were between 0.75 and 0.88 eV. Other researchers [59] have reported the *I-V* and capacitance-voltage (*C-V*) characteristics of an Al/p-Si/organic semiconductor formed using CoPc thin film on p-Si semiconductor. They have showed the strong effects of CoPc interlayer on electrical properties of metal/semiconductor (MS) contact. Therefore, it can be easily said that the organic thin films have strong impacts on the electrical performance of the organic-inorganic devices and they behave as an active layer.

Insert Table 5 Here

The curvature in the higher voltage values of the *I-V* measurements are because of the series resistance of the structures. The series resistance of the devices may be caused by contact wires or bulk resistance of the organic material and semiconductor [60]. Series resistance of a diode can be calculated by the help of Norde functions [61]. It is also possible to determine barrier height values using Norde Functions. The obtained barrier height and series resistance values are also given in Table 5. As seen from the table, the devices obtained using [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(η^5-C$_5$Me$_5$)Cl$_2$], (**3**), and [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$S)(η^5-C$_5$Me$_5$)Cl$_2$], (**4**), have lower series resistance compared with ones fabricated using [Rh(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(cod)Cl], (**1**) and [Rh(Cy$_2$PNHCH$_2$-C$_4$H$_3$S)(cod)Cl], (**2**). The large differences in series resistance between the compounds can be attributed to the higher conductivity values of compounds **3** and **4**. As it is well known, conjugation is one of the most important properties increasing the conductivity of organic compounds. Thus, the obtained results are in consistent with the theory.

Figure 2 also presents the influences of light intensity on *I-V* properties of the structures. Although all structures have sensitivity to the light, the devices obtained using **3** and **4** have reverse bias and forward bias photosensing properties. As seen from the figures, current values of Au/**3**/n-Si and Au/**4**/n-Si are nearly fixed after the series resistance curvatures in forward bias. The reverse and forward bias photosensing properties of the structures imply the photoconductivity of [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(η^5-C$_5$Me$_5$)Cl$_2$] and [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$S)(η^5-C$_5$Me$_5$)Cl$_2$], compounds. There are many papers on the increase of reverse bias current with the increase of light intensity [39,43,44]. To the best our knowledge, there is no report on the forward bias photosensing properties of a device. The photovoltaic parameters of all structures determined under the light with 100 mW/cm^2 illumination intensity called one sun are given in Table 6. The table presents the superior photovoltaic properties of the junctions formed using compounds **3** and **4**. By taking Figure 1 and Table 6 into account, one can easily say that the [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(η^5-C$_5$Me$_5$)Cl$_2$] and [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$S)(η^5-C$_5$Me$_5$)Cl$_2$] might be used in the fabrication reverse bias or forward bias photosensor applications.

Insert Table 6 Here

3. Conclusion

In conclusion, new rhodium(I) and iridium(III) complexes containing furfuryl-2-(*N*-dicyclohexylphosphino)methylamine and thiophene-2-(*N*-dicyclohexylphosphino)methyl amine ligands have been synthesized with high yield. All complexes were characterized using multi nuclear NMR, IR and microanalysis. The use of the new complexes for the reduction of the ketonic C=O bond of acetophenone derivatives under hydrogen transfer conditions was investigated. Surprisingly, $[Rh(Cy_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ was a more efficient catalyst in the transfer hydrogenation reaction than the other complexes. It was also found that these catalysts containing cyclohexyl moiety exhibited promising catalytic activity compared to those of containing phenyl moiety. The construction of the catalysts containing cyclohexyl moiety and their flexibility toward transfer hydrogenation make these encouraging systems to follow. In addition, organic-inorganic rectifying contacts were formed by spin coating of complexes on n-Si semiconductor and evaporating Au metal on thin films. The electrical properties of the devices were analyzed in dark and under a solar simulator with various illumination conditions and the results showed excellent reverse and forward bias photosensing behaviors for $[Ir(Cy_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$ and $[Ir(Cy_2PNHCH_2\text{-}C_4H_3S)(\eta^5\text{-}C_5Me_5)Cl_2]$ complexes, which were attributed the photoconducting properties of the complexes.

4. Experimental

4.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware, solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. $[Rh(\mu\text{-}Cl)(cod)]_2$ and $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ are purchased from Fluka and were used as received. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. ^1H (400.1 MHz), ^{13}C NMR (100.6 MHz) and

^{31}P-{^{1}H} NMR spectra (162.0 MHz) were recorded on a Bruker AV400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4 respectively. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by Gallenkamp Model apparatus with open capillaries. GC analyses were performed on a Shimadzu 2010 Plus Gas Chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30m x 0.32mm x 0.25μm). The GC parameters for transfer hydrogenation of ketones were as follows; initial temperature, 110 ºC; initial time, 1 min; solvent delay, 4.48 min; temperature ramp 80 ºC/min; final temperature, 200 ºC, 19 min; final time, 21.13 min; injector port temperature, 200 ºC; detector temperature, 200 ºC, injection volume, 2.0 μL.

4.2. General procedure for the transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a solution of complexes [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (**1**), [Rh(Cy_2PNHCH_2-C_4H_3S)(cod)Cl], (**2**), [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2], (**3**) and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**) (0.005 mmol), NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*-PrOH (5 mL) were refluxed until the reactions were completed. After this period a sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC. Conversions obtained are related to the residual unreacted ketone.

4.3. Synthesis of rhodium and iridium complexes

4.3.1. [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (1)

A mixture of [Rh(μ-Cl)(cod)]$_2$ (0.235 g, 0.48 mmol) and [Cy_2PNHCH_2-C_4H_3O] (0.279 g, 0.95 mmol) in 15 mL of tetrahydrofuran was stirred at room temperature for 45 min. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **1** as a yellow microcrystalline solid. Yield 0.472 g, 91.8 %, m.p. = 148-150°C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.36 (d, 1H, ^{3}J = 1.9 Hz, **H**-5), 6.32 (dd, 1H, ^{3}J = 1.9 and 3.0 Hz, **H**-4), 6.19 (d, 1H, ^3J = 3.0 Hz, **H**-3), 5.34 (br, 2H, C**H** of cod), 4.03 (dd, 2H, ^3J = 5.7 and 5.8 Hz, C**H**$_2$-), 3.55 (br, 2H, C**H** of cod), 2.78 (dt, 1H, ^3J(HH) = 5.7 and ^2J(HP) = 12.6 Hz), N**H**-), 1.23-2.42 (m, 30H, C**H**$_2$ of cod + protons of cyclohexyl); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ (26.43, 27.14, 27.23, 27.27, 27.33, 27.86, 28.38, 28.81, 29.01, 29.05) (**C**H$_2$ of cyclohexyl + cod), 35.69 (d, ^1J = 25.2 Hz, **C**H of cyclohexyl), 40.49 (d, ^2J = 11.1 Hz, **C**H$_2$), 68.79 (d, ^1J = 15.1 Hz, **C**H of cod (a)), 103.88 (d, ^1J = 6.4 Hz**,** **C**H of cod (b)), 106.23 (**C**-3), 110.26 (**C**-4), 141.86 (**C**-5), 153.80 (d, ^3J = 5.0 Hz, **C**-2); assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ 71.98 (d, ^1J (^{103}Rh-^{31}P) = 156.5 Hz); IR, (KBr): υ 3320 (N-H), 1076 (P-N), cm^{-1}. $C_{25}H_{40}NOPRhCl$ (539.9 g/mol): calcd. C 55.61, H 7.47, N 2.59; found C 55.42, H 7.31, N 2.45.

4.3.2. [Rh(Cy$_2$PNHCH$_2$-C$_4$H$_3$S)(cod)Cl], (2)

A mixture of [Rh(μ-Cl)(cod)]$_2$ (0.208 g, 0.42 mmol) and [Cy$_2$PNHCH$_2$-C$_4$H$_3$S] (0.261 g, 0.84 mmol) in 15 mL of tetrahydrofuran was stirred at room temperature for 45 min. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **2** as a yellow microcrystalline solid. Yield 0.418 g, 89.1 %, m.p. = 150-152 °C. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ 7.23 (dd, 1H, ^3J = 1.2, 4.9 Hz, **H**-5), 6.94-6.97 (m, 2H, **H**-3 + **H**-4), 5.35 (br, 2H, C**H** of cod), 4.25 (dd, 2H, ^3J = 6.7 and 6.8 Hz, C**H**$_2$-), 3.56 (br, 2H, C**H** of cod), 3.08 (dt, 1H, ^3J HH) = 6.7 and ^2J HP) = 12.8 Hz, N**H**), 1.39-2.46 (m, 30H, protons of cyclohexyl + C**H**$_2$ of cod); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ (25.98, 26.43, 27.14, 27.23, 27.27, 27.33, 28.03, 28.40, 29.01, 29.10) (**C**H$_2$ of cyclohexyls + cod), 35.89 (d, ^1J = 25.2 Hz, **C**H of cyclohexyls), 42.75 (d, ^2J = 9.1 Hz, **C**H$_2$-), 68.88 (d, ^1J = 13.1 Hz, **C**H of cod, (a)), 104.04 (d, ^1J = 9.1 Hz**,** **C**H of cod, (b)), 126.81, 124.55, 124.38 (**C**-3, **C**-4 and **C**-5), 144.40 (d, ^3J = 5.0 Hz, **C**-2); assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ 74.39 (d, ^1J (^{103}Rh-^{31}P) = 154.1 Hz); IR, (KBr): υ 3322 (N-H), 849 (P-N) cm^{-1}.

$C_{25}H_{40}NSPRhCl$ (556.0 g/mol): calcd. C 54.00, H 7.25, N 2.52; found C 53.82, H 7.19, N 2.41.

4.3.3. $[Ir(Cy_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$, (3)

A mixture of $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ (0.379 g, 0.48 mmol) and $[Cy_2PNHCH_2\text{-}C_4H_3O]$ (0.279 g, 0.95 mmol) in 15 mL of tetrahydrofuran was stirred at room temperature for 1 h. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (20 mL). The precipitated product was filtered and dried in vacuo yielding **3** as an orange microcrystalline solid. Yield 0.583 g, 88.6 %, m.p. = 189-191°C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.31 (d, 1H, ^3J = 2.6 Hz **H**-5), 6.43 (dd, 1H, ^3J = 1,7 and 2.6 Hz, **H**-4), 6.30 (d, 1H, ^3J = 1.7 Hz, **H**-3), 4.15 (dd, 2H, ^3J = 6.2 and 6.4 Hz, C**H**$_2$-), 3.30 (dt, 1H, ^3J(HH) = 6.2 and ^2J(HP) = 12.2 Hz, N**H**), 1.19-2.24 (m, 37H, protons of cyclohexyls + C**H$_3$** of Cp* (C_5Me_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 9.58 (C_5**Me**$_5$), 26.44, 27.20, 27.32, 27.41, 27.97, 28.37 (**C**H$_2$ of cyclohexyls), 39.07 (d, ^1J = 34.2 Hz, **C**H of cyclohexyls), 41.48 (d, ^2J = 7.0 Hz, **C**H$_2$-), 91.92 (d, ^2J = 12.0 Hz, **C**$_5$Me$_5$), 106.53 (**C**-4), 110.40 (**C**-3), 141.21 (**C**-5), 154.51 (**C**-2); assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 43.98 (s); IR, (KBr): υ 3341 (N-H), 852 (P-N) cm^{-1}; $C_{27}H_{43}NOPIrCl_2$ (691.7 g/mol): calcd. C 46.88, H 6.27, N 2.02; found C 46.73, H 6.21, N 1.98.

4.3.4. $[Ir(Cy_2PNHCH_2\text{-}C_4H_3S)(\eta^5\text{-}C_5Me_5)Cl_2]$, 4

A mixture of $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ (0.336 g, 0.42 mmol) and $[Cy_2PNHCH_2\text{-}C_4H_3S]$ (0.261 g, 0.84 mmol) in 15 mL of tetrahydrofuran was stirred at room temperature for 1 h. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **4** as an orange microcrystalline solid. Yield 0.539 g, 90.3 %, m.p. = 169-171°C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.15 (d, 1H, ^3J = 2.0 Hz, **H**-5), 7.12 (dd, 1H, ^3J = 2.0 and 3.2 Hz, **H**-4), 6.93 (d, 1H, ^3J = 3.2 Hz, **H**-3), 4.36 (dd, 2H, ^3J = 5.6 and 5.7 Hz, C**H**$_2$-), 3.39 (dt, 1H, ^3J HH) = 5.6

and ^2J (HP) = 12.8 Hz, N**H**,), 1.20-2.26 (m, 37H, protons of cyclohexyls + C**H**$_3$ of Cp*); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 9.61 (C$_5$**Me**$_5$), (26.43, 27.21, 27.30, 27.40, 28.05, 28.42) (**C**H$_2$- of cyclohexyls), 39.06 (d, ^1J = 34.2 Hz, **C**H of cyclohexyls), 43.50 (d, ^2J = 8.0 Hz, **C**H$_2$-), 91.89 (d, ^2J = 2.0 Hz, **C**$_5$Me$_5$), 124.45, 123.74 (**C**-4and **C**-5), 126.80 (**C**-3), 144.79 (**C**-2); assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ 43.34 (s). IR, (KBr): υ 3332 (N-H), 1070 (P-N) cm^{-1}; $C_{27}H_{43}NSPIrCl_2$ (707.8 g/mol): calcd. C 45.82, H 6.12, N 1.98; found C 45.71, H 6.03, N 1.85.

4.4. Fabrication and characterization of Au/metal complex/n-Si devices

An n-Si semiconductor with (100) orientation and 1-10 Ωcm resistivity was used in this study to fabricate Au/metal complex/n-Si devices. The semiconductor was cleaned by boiling in trichloroethylene and ultrasonically vibrating in acetone and methanol. The native oxide on n-Si wafer was removed using 0.4 % HF:H$_2$O solution. The wafer was dipped in deionized water and dried under N$_2$ flow. Au ohmic back contact was formed by evaporation of Au on n-Si in high vacuum and annealing the n-Si/Au contact in N$_2$ atmosphere at 420 °C. The thin films of metal complexes were formed on n-Si wafer by means of a SCS G3P-8 spin coater. Finally, Au metal was evaporated on the structure to obtain the front contact of the devices. Current-voltage (*I-V*) measurements were carried out using Keithley 2400 sourcemeter in dark and under a solar simulator with AM1.5 global filter for various light intensities.

References

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[1] M.T. Miller, P.K. Gantzel, T.B. Karpishin. Effects of Sterics and Electronic Delocalization on the Photophysical, Structural, and Electrochemical Properties of 2,9-Disubstituted 1,10-Phenanthroline Copper(I) Complexes. Inorg. Chem. 38 (1999) 3414-3422.

[2] G. Venkatachalam, R. Ramesh. Ruthenium(III) bis-bidendate Schiff base complexes mediated Transfer hydrogenations of imines. Inorg. Chem. Commun. 9(2006) 703-707.

[3] O. Pamies, J.-E. Backvall. Studies on the mechanism of metal-catalyzed hydrogen transfer from alcohols to ketones**.** Chem. Eur. J. 23 (2001) 5052-5058.

[4] N. Meriç, C. Kayan, M. Aydemir, Y. S. Ocak, A. Baysal, H. Temel. Application of dinuclear ruthenium (II) arene complexes in transfer hydrogenation of ketones. Dicle Univ. J. Inst. Sci.

Tech. 2 (2013) 1-8.

[5] C. Kayan, N. Meriç, M. Aydemir, A. Baysal, H. Temel. Aniline based aminophosphine and cationic bis(phosphino) amine Ru(II) complexes: investigation of catalytic activity in transfer hydrogenation of ketones. Dicle Univ. J. Inst. Sci. Tech. 2 (2013) 20-27.

[6] M. Aydemir, A. Baysal, N. Meric, B.Gümgüm. New active ruthenium(II) complexes based N3,N3'-bis(diphenylphosphino)-2,2'-bipyridine-3,3-diamine and P,P'-diphenylphosphinous acid P,P'-[2,2'-bipyridine]-3,3'-diamine and P-P'-diphenylphosphinous acid P,P'-[2,2'-bipyridine]-3,3'-diyl ester ligands for transfer hydrogenation of aromatic ketones by propan-2-ol. J. Organometal. Chem. 694 (2009) 2488-2492.

[7] M. Aydemir, A. Baysal. Ruthenium-catalyzed transfer hydrogenation of aromatic ketones with aminophosphine or bis(phosphino)amine ligands derived from isopropyl substituted anilines. Polyhedron 29 (2010) 1219-1224.

[8] M. Aydemir, N. Meriç, C. Kayan, F. Ok, A. Baysal. Rhodium-catalyzed transfer hydrogenation with functionalized bis(phosphino)amine ligands. Inorg. Chim. Acta. 398 (2013) 1-10.

[9] A.N. Ajjou, J.-L. Pinet. The biphastic transfer hydrogenation of aldehydes and ketones with isopropanol catalyzed by water-soluble rhodium complexes. J. Mol. Catal. A Chem. 214 (2004) 203-206.

[10] Y.-Y. Li, H. Zhang, J.-S. Chen, X.-L. Liao, Z.-R. Dong, J.-X. Gao. An efficient chiral iridium catalyst for asymmetric transfer hydrogenation of ketones. J. Mol. Catal. A Chem. 218 (2004) 153-156.

[11] R. Noyori, T. Ohkuma. Asymmetric Catalysis by Architectural and Functional Molecular Engineering: Practical Chemo- and Stereoselective Hydrogenation of Ketones. Angew. Chem. Int. Ed. 40 (2001) 40-73.

[12] H.U. Blaser, F. Spindler, M. Studer. Enantioselective catalysis in fine chemicals production. Appl. Catal. A: Gen. 221 (2001) 119-143.

[13] S.C. Stinson. Chiral drugs interactions. Chem. Eng. News. 77 (1999) 101-120.

[14] V. Turcry, C. Pasquier, F. Agbossou-Niedercorn. Aminophosphine phosphinite (AMMP) and enantioselective hydrogenation of ketones: further developments. C.R. Chimie 6 (2003) 179–184.

[15] a) J.T. Mague, J. Krinsky. Synthetic and structural studies of the coordination behavior of 2-pyridylbis(diphenylphosphino) methane. Inorg. Chem. 40 (2001) 1962-1971; b) A.M.Z Slawin, M.B.Smith, J. D. Woollins. Synthesis and characterization of the first E-unidentate [Ph2P(O)NP(E)Ph2]- metal complexes. [Au{Ph2P(O)NP(E)Ph2-*E*}{Ph2P(O)NHPPh2}] and [Pd{Ph2P(O)NP(E)Ph2-2(H2NCH2CH2NH2)] (E = S or Se), J. Chem. Soc. Dalton. Trans. (1998) 1537-1539; c) K.V. Katti, V.S. Reddy, P.R. Singh. Coordination Chemistry of

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Phosphorus(III) and Phosphorus(V) Hydrazides. Chem. Soc. Rev. 24 (1995) 97-107; d) M.S. Balakrishna, P.P. George, S.M. Mobin. New diphosphinite derived from cyclohexane-1,4-diol. Synthesis, oxidation reactions and X-ray crystal structure of $Ph_2P(S)O(C_6H_{10})OP(S)Ph_2$. Polyhedron 24 (2005) 475-480.

[16] M. Aydemir, A. Baysal, F. Durap, B. Gümgüm, S. Özkar, L.-T. Yıldırım. Synthesis and characterization of transition metal complexes of thiophene-2-methylamine: X-ray crystal structure of palladium (II) and platinum (II) complexes and use of palladium(II) complexes as pre-catalyst in Heck and Suzuki cross-coupling reactions Appl. Organometal. Chem. 23 (2009) 467–475.

[17] A. Kılıç, F. Durap, M. Aydemir, A. Baysal, E. Taş. Ru(II) with chelating containing N4-type donor quadridentate Pd-oxime metal complexes: Syntheses, spectral characterization, thermal and catalytic properties. J. Organomet. Chem. 693 (2008) 2835-2842.

[18] P. Bhattacharyya, J.D. Woollins. Polyhedron report number-56-bis(diphenylphosphino) amine and related chemistry. Polyhedron 14 (1995) 3367-3388.

[19] M. Aydemir, A. Baysal, E. Şahin, B. Gümgüm, S. Özkar. Aminophosphine-Palladium(II) Complexes: Synthesis, Structure and Applications in Suzuki and Heck Cross-Coupling Reactions. Inorg. Chim. Acta 378 (2011) 10–18.

[20] M. Aydemir, A. Baysal, N. Gürbüz, İ. Özdemir, B. Gümgüm, S. Özkar, N. Çaylak, L.-T. Yıldırım. Synthesis and characterization of new (*N*-diphenylphosphino)-isopropylanilines and their complexes: crystal structure of $(Ph_2P{=}S)NH\text{-}C_6H_4\text{-}4\text{-}CH(CH_3)_2$ and catalytic activity of palladium(II) complexes in the Heck and Suzuki cross-coupling reactions Appl. Organometal. Chem. 24 (2010) 17-24.

[21] M. Aydemir, A. Baysal. Ruthenium-catalyzed transfer hydrogenation of aromatic ketones with aminophosphine or bis(phosphino)amine ligands derived from isopropyl substituted anilines Polyhedron 29 (2010) 1219–1224.

[22] M. Aydemir, N. Meriç, A. Baysal. Applications of transition metal complexes containing 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine ligand to transfer hydrogenation of ketones J. Organomet. Chem. 720 (2012) 38-45.

[23] a) A. Buhling, P.C.J. Kamer, P.W.N.M. van Leeuwen. Novel amphiphilic diphosphines-synthesis, X-Ray structure, rhodium complexes, use in hydroformulation, and rhodium recycling. Organometallics 16 (1997) 3027- 3037; b) T.J. Kwok, D.J. Wink. Characterization and application of catalytic regioselective hydroformylation with a cationic bis (dioxaphospholane) rhodium catalyst precursor. Organometallics 12 (1993) 1954-1959; c) H. Bricout, J.-F Carpentier, A. Mortreuz. Bis(aminophosphine)-nickel complexes as efficient catalysts for alkylation of allylic acetates with stabilized nucleophiles. Tetrahedron Lett. 37 (1996) 6105-6108; d) I. Suisse, H. Bricout, A. Mortreux. Highly selective synthesis of 4-

vinylcyclohexene by cyclodimerization of Butadiene catalysed by aminophosphinephosphinite and bis(aminophosphine) chiral ligands nickel complexes. Tetrahedron Lett. 35 (1994) 413-416; e) D. Gleich, R. Schmid, W.A.Herrmann. A molecular-model to explain and predict the stereoselectivity in rhodium-catalyzed hydroformulation. Organometallics 17 (1998) 2141-2143.

[24] S. Gladiali, E. Alberico, in: M. Beller, C. Bolm, (Eds.), Transition Metals for Organic Synthesis, Wiley-VCH., Weinheim, 2004, Vol. 2, pp. 145-166.

[25] S.E. Clapham, A. Hadzovic, R.H. Morris. Mechanisms of the H_2-Hydrogenation and Transfer Hydrogenation of Polar Bonds Catalyzed by Ruthenium Hydride Complexes. Coord. Chem. Rev. 248 (2004) 2201-2237.

[26] J.E. Backvall. Transition metal hydrides as active intermediates in hydrogen transfer reactions J. Organomet. Chem. 652 (2002) 105-111.

[27] G. Zassinovich, G. Mestroni, S. Gladiali. Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts. Chem. Rev. 92 (1992) 1051-1069.

[28] R.V. Wisman, J.G. de Vries, B.-J. Deelman, H.J. Heeres. Kinetic Studies on the Asymmetric Transfer Hydrogenation of Acetophenone Using a Homogeneous Ruthenium Catalyst with a Chiral Amino-Alcohol Ligand. Org. Process Res. Dev. 10 (2006) 423-429.

[29] M. Aydemir, F. Durap, A. Baysal, N. Meric, A. Buldağ, B. Gümgüm, S. Özkar, L.T. Yıldırım. Novel Neutral Bis(phosphinite) Bridged Dinuclear Ruthenium(II) arene Complexes and Their Application in Transfer Hydrogenation of Aromatic Ketones: X-ray Structure of a New Schiff Base, N3,N3′-di-2-hydroxybenzylidene-[2,2']bipyridinyl-3,3′-diamine. J. Mol. Catal A: Chemical 326 (2010) 75-81.

[30] Y.X. Chen, Syntheses and applications of novel chiral ligands, Polytechnic University, Hong Kong, 1999: Ph.D. Thesis.

[31] M. Aydemir, N. Meric, F. Durap, A. Baysal, M. Toğrul. Asymmetric transfer hydrogenation of aromatic ketones with the ruthenium(II) catalyst derived from C_2 symmetric *N,N′*-bis[(1*S*)-1-benzyl-2-*O*-(diphenylphosphinite)ethyl]ethanediamide. J. Organomet. Chem. 695 (2010) 1392-1398.

[32] S.E. Habas, H.A.S. Platt, M.F.A.M. van Hest, D.S. Ginley. Low-Cost Inorganic Solar Cells: From Ink to Printed Device. Chem. Rev. 110 (2010) 6571–6594.

[33] R.V. Salvatierra, C.E. Cava, L.S. Roman, A.J.G. Zarbin. ITO-Free and Flexible Organic Photovoltaic Device Based on High Transparent and Conductive Polyaniline/Carbon Nanotube Thin Films Adv. Funct. Mater. 23 (2013) 1490–1499.

[34] N. Sekar, V.Y. Gehlot. Metal complex dyes for dye-sensitized solar cells: Recent developments Resonance, 15 (2010) 819.

[35] U. Olgun, M. Gulfen. Synthesis and spectroscopic–voltammetric behaviors of silver(I) 2,5-diphenylthiazolo[5,4-*d*]thiazole. Dyes Pigm. 99 (2013) 1004-1009.

[36] L. Giribabu, V.K. Singh, T. Jella, Y. Soujanya, A. Amat, F. De Angelis, A. Yella, P. Gao, M. K. Nazeeruddin. Sterically demanded unsymmetrical zinc phthalocyanines for dye-sensitized solar cells. Dyes Pigm. 98 (2013) 518-529.

[37] C. Dragonetti, A. Valore, A. Colombo, M. Magni, P. Mussini, D. Roberto, R. Ugo, A. Valsecchi, V. Trifiletti, N. Manfredi, A. Abbotto. Ruthenium oxyquinolate complexes for dye-sensitized solar cells. Inorg. Chim. Acta 405 (2013) 98–104.

[38] S. Pasa, Y.S. Ocak, H. Temel, T. Kilicoglu. Synthesis, characterization and catalytic behavior in the Suzuki reaction of Schiff base and its complexes and the optical properties of nickel complex used in the fabrication of a photodiode. Inorg. Chim. Acta, 405 (2013) 493-504.

[39] H. Temel, S. Pasa, Y.S. Ocak, I. Yilmaz, S. Demir, I. Ozdemir. Synthesis, characterization, electrochemical behaviors and applications in the Suzuki–Miyaura cross-coupling reactions of $N_2S_2O_2$ thio Schiff base ligand and its Cu(II), Co(III), Ni(II), Pd(II) complexes and their usage in the fabrication of organic–inorganic hybrid devices. Synth. Met. 161 (2012) 2765–2775.

[40] H. Tang, Y. Li, Q. Chen, B. Chen, Q. Qiao, W. Yang, H. Wu, Y. Cao. Efficient yellow–green light-emitting cationic iridium complexes based on 1,10-phenanthroline derivatives containing oxadiazole-triphenylamine unit. Dyes Pigm. 100 (2013) 79-86.

[41] M. El-Nahass, K. Abd-El-Rahman, A. Darwish. Fabrication and electrical characterization of p-NiPc/n-Si heterojunction. Microelectron. J. 38 (2007) 91-95.

[42] T. Kılıcoglu, Y.S. Ocak. Electrical and photovoltaic properties of an organic–inorganic heterojunction based on a BODIPY dye. Microelectron. Eng. 88 (2011) 150–154.

[43] R.K. Gupta, M. Cavas, A.A. Al-Ghamdi, Z.H. Gafer, F. El-Tantawy, F. Yakuphanoglu. Electrical and photoresponse properties of Al/p-CuFeO2/p-Si/Al MTCOS photodiode. Sol. Energy 92 (2013) 1–6.

[44] Furfuryl-(N-dicyclohexylphosphino)amine: Yield 0.279 g, 93.3 %. ^{1}H NMR (400.1 Hz, $CDCl_3$): δ 7.33 (d, 1H, H-5, ^{3}J = 1.6 Hz), 6.29 (dd, 1H, H-4, ^{3}J = 1.6 and 3.0 Hz), 6.13 (d, 1H, H-3, ^{3}J = 3.0 Hz), 4.04 (dd, 2H, CH_2-, ^{3}J(HP) = 7.7 and ^{3}J(HH) = 7.6 Hz), 2.42 (dt, -NH-, 1H, ^{3}J(HH) = 7.6 and ^{2}J(HP) = 7.7 Hz), 1.16-1.77 (m, 22 H, protons of cyclohexyls); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 26.55, 27.03, 27.16, 27.28, 29.12, 29.30 (CH_2- of cyclohexyls), 36.40 (d, CH- of cyclohexyls, ^{1}J = 11.1 Hz), 45.86 (d, CH_2-, ^{2}J = 27.2 Hz), 105.56 (C-3), 110.09 (C-4), 141.27 (C-5), 156.23 (d, C-2, ^{3}J= 3.0 Hz), assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 61.61 (s, NH-$P(Cy)_2$); IR, (KBr): υ 801 (P-N), 3257 (N-H) cm^{-1}; $C_{17}H_{28}NOP$ (293.39 g/mol): calcd. C 69.60, H 9.62, N 4.77; found C 69.49, H 9.54, N 4.61 %. Thiophene(N-dicyclohexylphosphino)amine: Yield 0.261 g, 95.6 %. ^{1}H NMR (400.1 Hz, $CDCl_3$): δ 7.18 (d, 1H, H-5, ^{3}J = 5.0 Hz), 6.90-6.94 (m, 2H, H-3 and H-4), 4.27 (dd, 2H, CH_2-, ^{3}J(HP) = 6.4 and ^{3}J(HH) = 6.3

Hz), 2.98 (m, 1H, N$\underline{H}$), 1.24-1.81 (m, 22H, protons of cyclohexyls); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 26.01, 26.57, 27.00, 27.70, 29.43, 29.62 ($\underline{C}$H$_2$ of cyclohexyls), 36.58 (d, $\underline{C}$H of cyclohexyls, ^{1}J = 10.1 Hz), 48.16 (d, $\underline{C}$H$_2$, ^{2}J = 4.0 Hz), 123.46 ($\underline{C}$-3), 123.67 ($\underline{C}$-5), 126.36 ($\underline{C}$-4), 147.40 ($\underline{C}$-2), assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ 61.69 (s, NH-$\underline{P}$(Cy)$_2$); IR, (KBr): υ 798 (P-N), 3253 (N-H) cm^{-1}; $C_{17}H_{28}NSP$ (309.45 g/mol): calcd. C 65.98, H 9.12, N 4.53; found C 65.87, H 8.99, N 4.35 %.

[45] M. Aydemir, A. Baysal, N. Meriç, B. Gümgüm. New active ruthenium(II) complexes based N3,N3′-bis(diphenylphosphino)-2,2′-bipyridine-3,3′-diamine and P,P′-diphenylphosphinous acid-P,P′-[2,2′-bipyridine]-3,3′-diyl ester ligands for transfer hydrogenation of aromatic ketones by propan-2-ol J. Organomet. Chem. 694 (2009) 2488-2492.

[46] a) S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori. Asymmetric Transfer Hydrogenation of Aromatic Ketones Catalyzed by Chiral Ruthenium(II) Complexes J. Am. Chem. Soc. 117 (1995) 7562–7563; b) J. Takehara, S. Hashiguchi, A. Fujii, S. Inoue, T. Ikariya, R. Noyori, J. Amino alcohol effects on the ruthenium(II)-catalysed asymmetric transfer hydrogenation of ketones in propan-2-ol Chem. Soc., Chem. Commun. (1996) 233–234.

[47] T. Ohkuma, R. Noyori. Asymmetric Catalysis by Architectural and Functional Molecular Engineering: Practical Chemo- and Stereoselective Hydrogenation of Ketones. Angew. Chem., Int. Ed. 40 (2001) 40–73.

[48] R. Noyori. Asymmetric Catalysis: Science and Opportunities. Angew. Chem., Int. Ed. 41 (2002) 2008–2022.

[49] T. Ikariya, A.J. Blacker. Asymmetric Transfer Hydrogenation of Ketones with Bifunctional Transition Metal-Based Molecular Catalysts. Acc. Chem. Res. 40 (2007) 1300–1308.

[50] H.L. Lowry, K.S. Richardson, in Harper Collins, Mechanism and Theory in Organic Chemistry, New York, 1987, Chapter 2.

[51] I. Yamada, R. Noyori. Assymetric Transfer Hydrogenation of Benzaldehydes. Org. Lett. 2 (2000) 3425-3427.

[52] M.J. Palmer, M. Wills. Asymmetric transfer hydrogenation of C=O and C=N bonds. Tetrahedron: Asymmetry 10 (1999) 2045-2061.

[53] D.H. McDaniel, H.C. Brown. An Extended Table of Hammett Substitutent Constants Based on the Ionization of Substituted Benzoic Acids. J. Org. Chem. 23 (1958) 420-427.

[54] J.W. Faller, A.R. Lavoie. Catalysts for the Asymmetric Transfer Hydrogenation of Ketones Derived from L-Prolinamide and (*p*-CymeneRuCl$_2$)$_2$ or (Cp*RhCl$_2$)$_2$. Organometallics 20 (2001) 5245-5247.

[55] J.–X. Gao, X.–D. Yi, P.–P. Xu, C.-L. Tang, H.–L. Wan, T. Ikariya. New chiral cationic rhodium–aminophosphine complexes for asymmetric transfer hydrogenation of aromatic ketones. J. Organometal. Chem. 592 (1999) 290-295.

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[56] J.–X. Gao, H. Zhang, X.–D. Yi, P.–P. Xu, C.–L. Tang, H.–L. Wan, K.–R.Tsai, T. Ikariya. New chiral catalysts for reduction of ketones. Chirality 12 (2000) 383-388.

[57] M. Campos, L.O.S. Bulhoes, C.A. Lindino. Gas-sensitive characteristics of metal/semiconductor polymer Schottky device. Sens. Actuators 87 (2000) 67-71.

[58] O. Gullu, A. Turut, S. Asubay. Electrical characterization of organic-on-inorganic Semiconductor Schottky structures. J. Phys. Condens. Matter. 20 (2008) 045215.

[59] F. Yakuphanoglu, M. Kandaz, B.F. Senkal. Al / p-type silicon/organic semiconductor based on phthalocyanine rectifier contact. Thin Solid Films 516 (2008) 8793-8796.

[60] O. Gullu, A. Turut. Photovoltaic And Electronic Properties Of Quercetin/P-Inp Solar Cells. Sol. Energy Mater. Sol. Cells. 92 (2008) 1205– 1210.

[61] H. Norde. A modified forward *I-V* plot for Schottky diodes with high series resistance. J. Appl. Phys. 50 (1979) 5052.

Captions

Scheme 1 Synthesis of the [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (**1**), [Rh(Cy_2PNHCH_2-C_4H_3S)(cod)Cl], (**2**), [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2], (**3**) and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**) complexes (*i*) 1/2 equiv. [Rh(μ-Cl)(cod)$]_2$, thf; (*ii*) 1/2 equiv. [Ir(η^5-C_5Me_5)(μ-Cl)Cl$]_2$, thf.

Figure 1 The ^{31}P-{^{1}H} NMR spectra of the complexes [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (**1**), [Rh(Cy_2PNHCH_2-C_4H_3S)(cod)Cl], (**2**), [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2], (**3**) and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**).

Figure 2 *I-V* measurements of Au/metal complex/n-Si structures fabricated using a) **1** b) **2** c) **3** and d) **4** compounds.

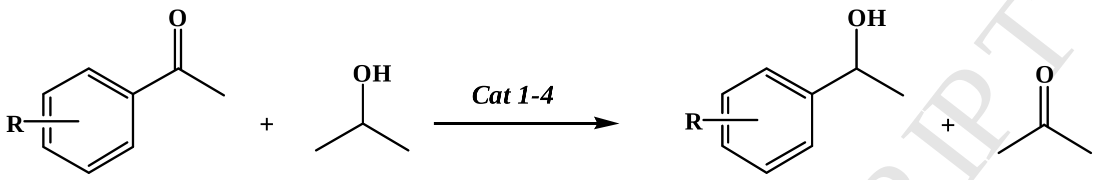
Table 1 Transfer hydrogenation of acetophenone with *iso-P*rOH catalyzed [Rh(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(cod)Cl], (**1**), [Rh(Cy$_2$PNHCH$_2$-C$_4$H$_3$S)(cod)Cl], (**2**), [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$O)(η^5-C$_5$Me$_5$)Cl$_2$], (**3**) and [Ir(Cy$_2$PNHCH$_2$-C$_4$H$_3$S)(η^5-C$_5$Me$_5$)Cl$_2$], (**4**).

Entry	*Catalyst*	*S/C/NaOH*	*Time*	*Conversion(%)*[i]	*TOF(h^{-1})*[k]
1	**1 [a]**	**100:1:5**	**15 min**	98	392
2	**1 [b]**	**100:1:5**	**24 h**	trace	....
3	**1 [c]**	**100:1**	**24 h**	trace	....
4	**1 [d]**	**100:1:5**	**15 min**	96	384
5	**1 [e]**	**100:1:5**	**3 h**	98	33
6	**1 [f]**	**500:1:5**	**45 min**	99	132
7	**1 [g]**	**1000:1:5**	**1.5 h**	97	65
8	**2 [a]**	**100:1:5**	**8 h**	98	12
9	**2 [b]**	**100:1:5**	**24 h**	trace	....
10	**2 [c]**	**100:1**	**24 h**	trace	....
11	**2 [d]**	**100:1:5**	**8 h**	96	12
12	**2 [e]**	**100:1:5**	**30 h**	97	<5
13	**2 [f]**	**500:1:5**	**20 h**	98	<5
14	**2 [g]**	**1000:1:5**	**40 h**	97	<5
15	**3 [a]**	**100:1:5**	**8 h**	97	12
16	**3 [b]**	**100:1:5**	**24 h**	trace	....
17	**3 [c]**	**100:1**	**24 h**	trace	....
18	**3 [d]**	**100:1:5**	**8 h**	97	12
19	**3 [e[**	**100:1:5**	**30 h**	98	<5
20	**3 [f]**	**500:1:5**	**20 h**	97	<5
21	**3 [g]**	**1000:1:5**	**40 h**	96	<5
22	**4 [a]**	**100:1:5**	**8 h**	96	12
23	**4 [b]**	**100:1:5**	**24 h**	trace	....
24	**4 [c]**	**100:1**	**24 h**	trace	....
25	**4 [d]**	**100:1:5**	**8 h**	98	12
26	**4 [e]**	**100:1:5**	**30 h**	98	<5
27	**4 [f]**	**500:1:5**	**20 h**	98	<5
28	**4 [g]**	**1000:1:5**	**40 h**	96	<5

Reaction conditions:

[a] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 100:1:5; [b] At room temperature; acetophenone/Ru/NaOH, 100:1:5; [c] Refluxing in *iso*-PrOH; acetophenone/Ru, 100:1, in the absence of base; [d] Added 0.1 mL of H$_2$O; [e] Refluxing the reaction in air; [f] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 500:1:5; [g] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 1000:1:5; [i] Determined by GC (three independent catalytic experiments); [k] Referred at the reaction time indicated in column; TOF= (mol product/mol Ru(II)Cat.)x h^{-1}.

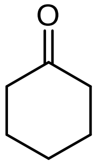
Table 2 Transfer hydrogenation results for substituted acetophenones with the catalyst systems, [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (**1**), [Rh(Cy_2PNHCH_2-C_4H_3S)(cod)Cl], (**2**), [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2], (**3**) and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**).[a]



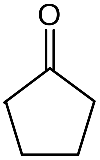
Entry	R	Time	Conversion(%)[b]	TOF(h^{-1})[c]
***Cat:Rh(I) complex* 1**				
1	**4-F**	**10 min**	**96**	**576**
2	**4-Cl**	**10 min**	**98**	**588**
3	**4-Br**	**15 min**	**98**	**392**
4	**2-MeO**	**25 min**	**97**	**233**
5	**4-MeO**	**20 min**	**96**	**288**
***Cat:Rh(I) complex* 2**				
6	**4-F**	**6 h**	**96**	**16**
7	**4-Cl**	**6 h**	**98**	**16**
8	**4-Br**	**8 h**	**97**	**12**
9	**2-MeO**	**12 h**	**98**	**8**
10	**4-MeO**	**10 h**	**98**	**10**
Cat:Ir(III) complex 3				
11	**4-F**	**6 h**	**96**	**16**
12	**4-Cl**	**6 h**	**95**	**16**
13	**4-Br**	**8 h**	**95**	**12**
14	**2-MeO**	**12 h**	**98**	**8**
15	**4-MeO**	**10 h**	**97**	**10**
***Cat:Ir(III) complex* 4**				
16	**4-F**	**6 h**	**97**	**16**
17	**4-Cl**	**6 h**	**97**	**16**
18	**4-Br**	**8 h**	**95**	**12**
19	**2-MeO**	**12 h**	**97**	**8**
20	**4-MeO**	**10 h**	**96**	**10**

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 °C, the concentration of acetophenone derivatives is 0.1 M; [b] Purity of compounds is checked by ^1H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone; [c] TOF = (mol product/mol Cat.) x h^{-1}.

Table 3 Transfer hydrogenation of various simple ketones with *iso*-*P*rOH catalyzed by [Rh(Cy_2PNHCH_2-C_4H_3O)(cod)Cl], (**1**), [Rh(Cy_2PNHCH_2-C_4H_3S)(cod)Cl], (**2**), [Ir(Cy_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2], (**3**) and [Ir(Cy_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**).[a]



a



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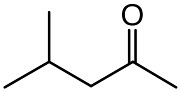

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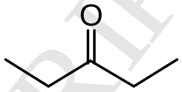
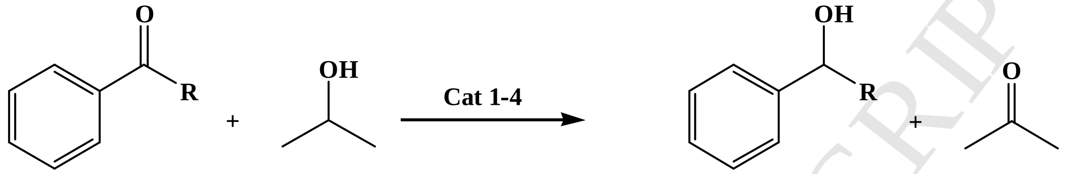


d

Entry	*Cat*	*Substrate*	*Time*	*Conversion(%)*[b]
1	1	a	30 min	96
2	2	b	10 h	98
3	3	c	10 h	97
4	4	d	10 h	98
5	1	a	30 min	96
6	2	b	10 h	98
7	3	c	10 h	95
8	4	d	10 h	97
9	1	a	3/2 h	99
10	2	b	20 h	97
11	3	c	20h	98
12	4	d	20 h	97
13	1	a	3h	99
14	2	b	30 h	96
15	3	c	30 h	99
16	4	d	30h	95

[a] Refluxing in *iso*-PrOH; ketone/Ru/NaOH, 100:1:5; [b] Determined by GC (three independent catalytic experiments); [b] Purity of compounds is checked by ^1H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.

Table 4 Transfer hydrogenation results for substituted alkyl phenyl ketones with the catalyst systems $[Rh(Cy_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$, (**1**), $[Rh(Cy_2PNHCH_2\text{-}C_4H_3S)(cod)Cl]$, (**2**), $[Ir(Cy_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$, (**3**) and $[Ir(Cy_2PNHCH_2\text{-}C_4H_3S)(\eta^5\text{-}C_5Me_5)Cl_2]$, (**4**).[a]



Entry	*R*	*Time*	*Conversion(%)*[b]	*TOF(h^{-1})*[c]
***Cat:Rh(I) complex* 1**				
1	**ethyl**	**20 min**	**97**	**291**
2	**propyl**	**30 min**	**96**	**192**
3	***iso*-propyl**	**40 min**	**96**	**144**
4	***ter*-butyl**	**1.5 h**	**95**	**63**
***Cat:Rh(I) complex* 2**				
5	**ethyl**	**16 h**	**96**	**<10**
6	**propyl**	**32 h**	**98**	**<5**
7	***iso*-propyl**	**40 h**	**95**	**<5**
8	***ter*-butyl**	**50 h**	**97**	**<5**
Cat:Ir(III) complex 3				
9	**ethyl**	**16 h**	**95**	**<10**
10	**propyl**	**32 h**	**97**	**<5**
11	***iso*-propyl**	**40 h**	**98**	**<5**
12	***ter*-butyl**	**50 h**	**97**	**<5**
***Cat:Ir(III) complex* 4**				
13	**ethyl**	**16 h**	**97**	**<10**
14	**propyl**	**32 h**	**97**	**<5**
15	***iso*-propyl**	**40 h**	**97**	**<5**
16	***ter*-butyl**	**50 h**	**96**	**<5**

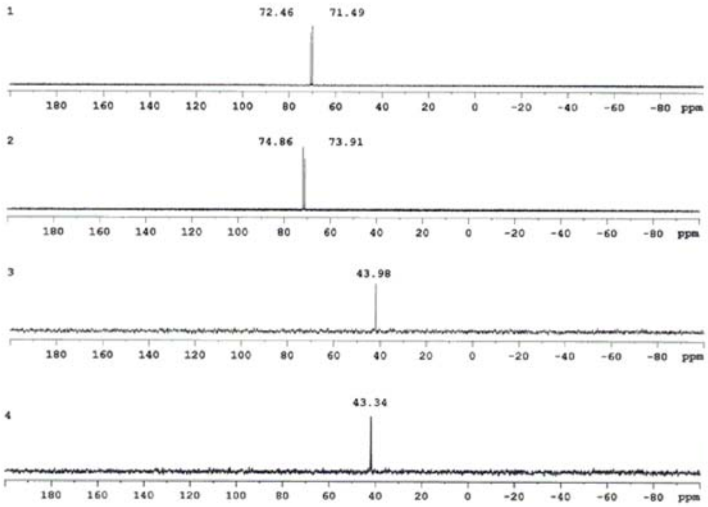
[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 °C, respectively, the concentration of alkyl phenyl ketones is 0.1 M; [b] Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone; [c] TOF = (mol product/mol Cat.) x h^{-1}.

Table 5 Electrical parameters of the devices obtained using metal complexes

	ln$I$-V		Norde	
Device	n	ϕ_b	ϕ_b	R_S
Au/1/n-Si	1.65	0.79	0.83	17080
Au/2/n-Si	1.67	0.80	0.83	165800
Au/3/n-Si	1.82	0.76	0.85	313
Au/4/n-Si	1.41	0.78	0.83	3518

Table 6 Photovoltaic parameters of the devices under the light with 100 mW/cm^2 illumination intensity

Device	I_{SC} (μA)	V_{OC} (mV)
Au/1/n-Si	5.40	125
Au/2/n-Si	0.16	95
Au/3/n-Si	196	226
Au/4/n-Si	114	206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71.49
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2
74.86
73.91
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3
43.98
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4
43.34
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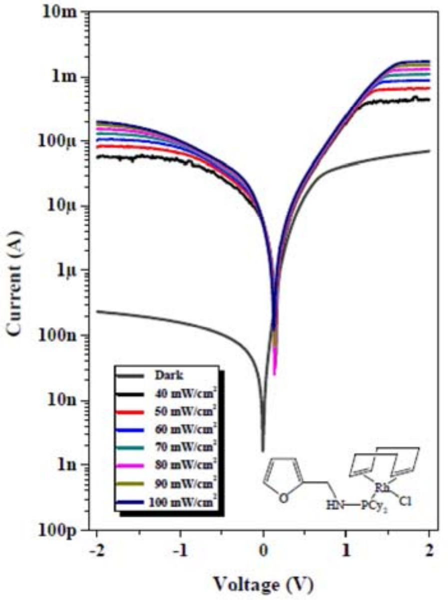
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1m
100µ
10µ
1µ
100n
10n
1n
100p
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-1
0
1
2
Voltage (V)
Dark
40 mW/cm2
50 mW/cm2
60 mW/cm2
70 mW/cm2
80 mW/cm2
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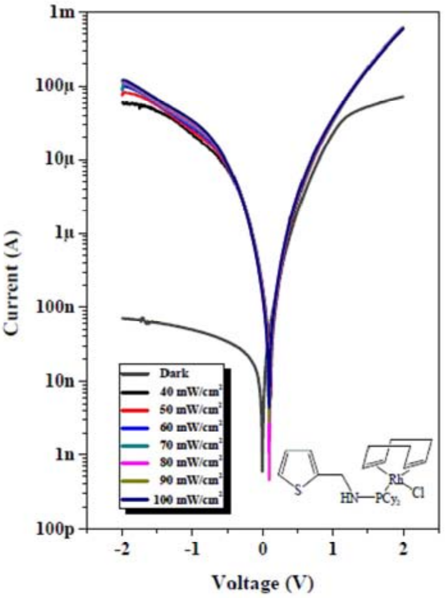
O
HN
PCy2
Rh
Cl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10n
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0
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2
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Dark
40 mW/cm2
50 mW/cm2
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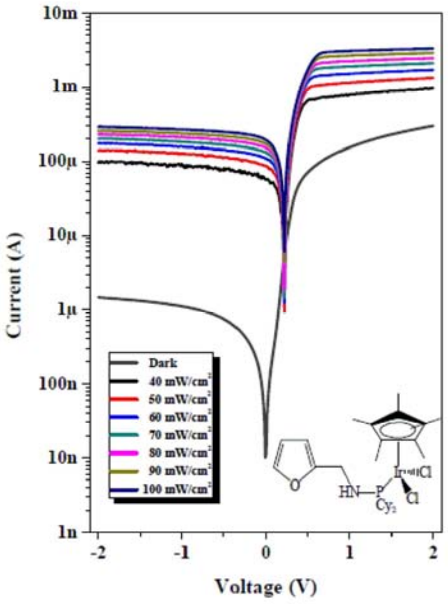
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1m
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10µ
1µ
100n
10n
1n
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0
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Dark
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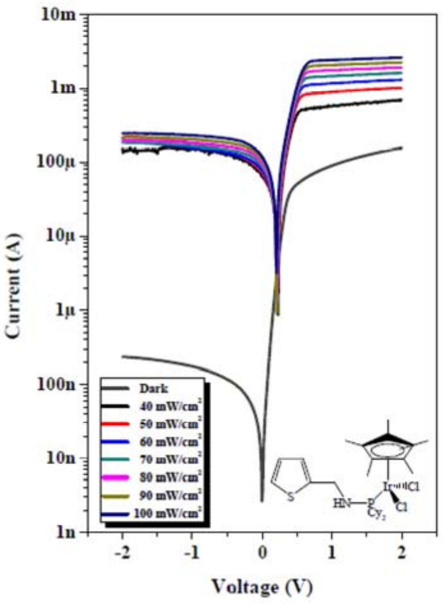
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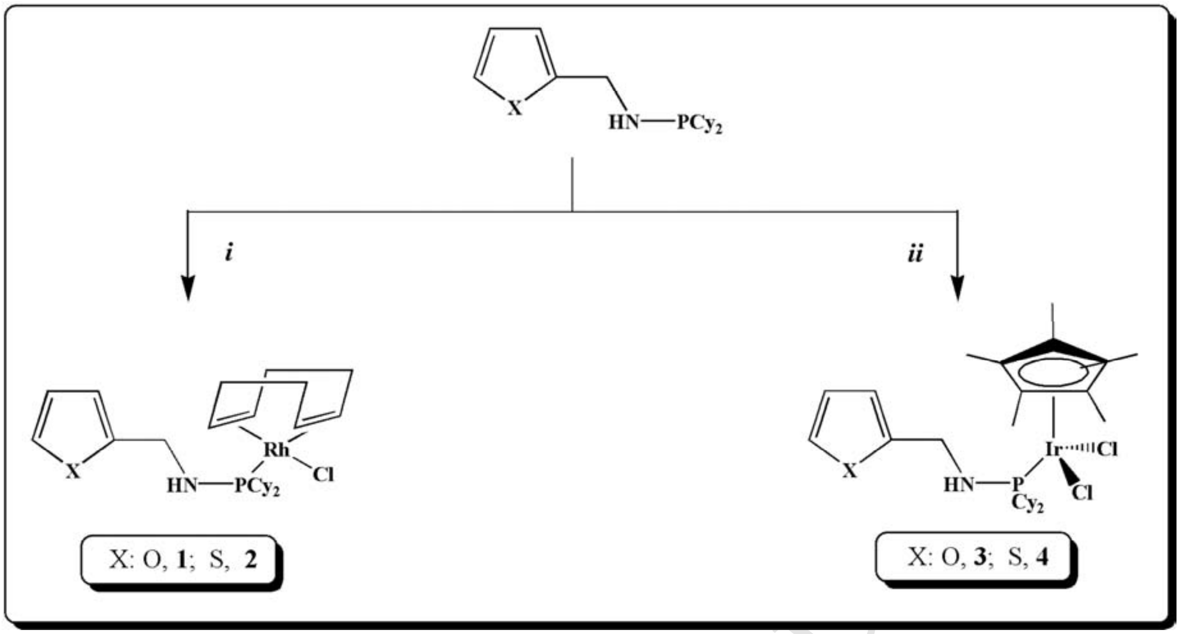
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