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# Rhodium-catalyzed transfer hydrogenation with aminophosphines and analysis of electrical characteristics of rhodium(I) complex/n-Si heterojunctions

**Murat Aydemir[a,b]*, Yusuf Selim Ocak[b,c], Khadichakhan Rafikova[d], Nurzhamal Kystaubayeva[d], Cezmi Kayan[a], Alexey Zazybin[d], Fatih Ok[a], Akın Baysal[a] and Hamdi Temel[b,e]**

**A series of novel neutral mononuclear rhodium(I) complexes of the P—NH ligands have been prepared starting from [Rh(cod)Cl]$_2$ complex. Structural elucidation of the complexes was carried out by elemental analysis, IR and multinuclear NMR spectroscopic data. The complexes were applied to the transfer hydrogenation of acetophenone derivatives to 1-phenylethanol derivatives in the presence of 2-propanol as the hydrogen source. Catalytic studies showed that all complexes are also excellent catalyst precursors for transfer hydrogenation of aryl alkyl ketones in 0.1 M iso-PrOH solution. In particular, [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] acts as an excellent catalyst, giving the corresponding alcohols in excellent conversion up to 99% (turnover frequency ≤ 588 h$^{-1}$). Furthermore, rhodium(I) complexes have been used in the formation of organic–inorganic heterojunction by forming their thin films on n-Si and evaporating Au on the films. It has been seen that the structures have rectifying properties. Their electrical properties have been analyzed with the help of current–voltage measurements. Finally, it has been shown that the complexes can be used in the fabrication of temperature and light sensors. Copyright © 2014 John Wiley & Sons, Ltd.**

**Keywords:** aminophosphine; rhodium; transfer hydrogenation; heterojunction; temperature sensor

## Introduction

Since the discovery that functional P-based ligands increase considerably the activity and/or selectivity of metal catalysts, the preparation of this type of ligand has been the subject of extensive investigations.[1–4] Small variations in these ligands can cause noteworthy changes in their coordination behavior and the structural features of the formed complexes.[5–9] Among these ligands, P—NH-containing ones have particular use in catalysis where it is necessary for part of the ligand to dissociate to allow an organic fragment to coordinate and undergo transformations. The presence of P—N ligands enables many different and important catalytic processes to occur including Heck[10,11] and Suzuki[12,13] reactions. A large number of complexes with aminophosphine ligands have also been evaluated in different catalytic reactions, including allylic alkylation,[14] amination,[15] Sonogashira,[16] hydroformylation,[17] hydrogenation[18] and polymerization[19] reactions.

Catalytic hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen.[20,21] In transfer hydrogenation, organic molecules such as primary and secondary alcohols[22] or formic acid and its salts[23] have been employed as the hydrogen source. In particular, transition-metal-catalyzed procedures for transfer hydrogenation of a wide variety of functional groups by different hydrogen donors are an interesting alternative to molecular hydrogenation.[24] The hydrogenation of ketones, which is one of the most exciting and powerful methods of synthesizing alcohols, has been receiving increased attention as well and has led to extraordinary success.[25] Specifically, the catalytic transfer hydrogenation[26] of ketones is one of the most attractive methods for synthesizing secondary alcohols, which form an important class of intermediates for fine chemicals and pharmaceuticals.[27,28]

There are several metal sources available that have to mediate the hydride transfer from the donor to the substrate. Even if main-group metals such as aluminum have historically been used in the transfer hydrogenation reactions,[29,30] today's catalysts of

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* Correspondence to: Murat Aydemir, Department of Chemistry, Faculty of Science, University of Dicle, 21280 Diyarbakir, Turkey. E-mail: aydemir@dicle.edu.tr

a Department of Chemistry, Faculty of Science, University of Dicle, 21280, Diyarbakir, Turkey

b Science and Technology Application and Research Center, University of Dicle, 21280, Diyarbakir, Turkey

c Department of Science, Faculty of Education, University of Dicle, 21280, Diyarbakir, Turkey

d Department of Chemical Engineering, Kazakh–British Technical University, 050000, Almaty, Kazakhstan

e Faculty of Pharmacy, University of Dicle, 21280, Diyarbakir, Turkey

choice are transition metal complexes predominantly of ruthenium, rhodium[31] or iridium.[32–34] Although very frequently ruthenium- or iridium-based catalysts have been applied in the hydrogenation of various ketones,[35] rhodium complexes have proven to lead very efficient processes along with potential industrial applications.[36–38] Furthermore, organic electronics have advanced in recent years because of the easy and low-cost application processes.[39] Organic compounds have been used in the fabrication of different kinds of electrical and optical devices, including organic field effect transistors,[40] organic light-emitting diodes,[41] Schottky diodes,[42] temperature and light sensors[43,44] and solar cells.[45,46] Interest in the devices formed by metal complexes has been increasing rapidly because of their high thermal and mechanical stability.[47] Many studies have been performed to use them with suitable structures and for synthesis of new compounds that can be used for this purpose.[45,48] Therefore, it can be said that both synthesis and usage of metal complexes in the formation of electrical and optical devices have great importance.

The design and synthesis of aminophosphine ligands[49–52] have played a significant role in the development of transition-metal-catalyzed reactions.[53–55] In recent years, we have reported upon the synthesis and applications of a number of modified rhodium(I)–aminophosphine catalysts containing the arene rings for transfer hydrogenation.[56–58] In view of the promising results, the rhodium complexes were shown to be efficient homogeneous hydrogenation catalysts toward various substrates.[59,60] By taking into account that the easily prepared aminophosphine ligands were also found to be effective ligands for the rhodium-catalyzed transfer hydrogenation, we thought that Rh(I)–aminophosphine catalysts would be valuable material for study. Herein we report the synthesis of novel [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**), [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] (**2**) and [Rh(cod)(PPh$_2$NH—C$_6$H$_3$—2,6-(CH(CH$_3$)$_2$))$_2$Cl] (**3**) complexes and their presentation in the transfer hydrogenation of various ketones. Another aim of this study was to show fabrication of organic–inorganic rectifying heterojunctions by novel rhodium(I) complexes, determine their electrical properties by current–voltage (*I–V*) measurements and present their temperature- and light-sensing properties.

## Experimental

### 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. PPh$_2$Cl, 2-isopropylaniline, 4-isopropylaniline and 2,6-diisopropylaniline were purchased from Fluka and used as received. The starting material [Rh(cod)(μ-Cl)]$_2$[61] was prepared according to the literature procedure. IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. $^1$H (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 $\delta$ referenced to external TMS and 85% H$_3$PO$_4$ 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

GC analyses were performed on a Shimadzu 2010 Plus gas chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). The GC parameters for transfer hydrogenation of ketones were as follows: initial temperature, 110°C; initial time, 1 min; solvent delay, 4.48 min; temperature ramp 80°C min$^{-1}$; final temperature, 200°C; final time, 21.13 min; injector port temperature, 200°C; detector temperature, 200°C, injection volume, 2.0 μl.

### General Procedure for the Transfer Hydrogenation of Ketones

A typical procedure for the catalytic hydrogen transfer reaction is as follows. A solution of rhodium complexes, [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**), [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] (**2**) or [Rh(cod)(PPh$_2$NH—C$_6$H$_3$—2,6-(CH(CH$_3$)$_2$))$_2$Cl] (**3**), NaOH (0.05 mmol) and the corresponding ketone (1.0 mmol) in degassed iso-PrOH (10 ml) were refluxed until the reactions were completed. After this period a sample of the reaction mixture was withdrawn, diluted with acetone and analyzed immediately by GC. The conversions are related to the residual unreacted ketone.

### Fabrication and Characterization of Heterojunctions

In the study, an n-Si semiconductor with (100) orientation and 1–10 Ω cm resistivity was used in the fabrication of devices. First, the wafer was degreased by boiling in trichloroethylene for 5 min and ultrasonically vibrated in 2-propanol and acetone for 5 min. The wafer was rinsed in 0.4% HF–H$_2$O solution to remove the native oxide of the wafer. After each step the wafer was cleaned by deionized water. The n-Si semiconductor was then dried under nitrogen atmosphere. An ohmic contact for n-Si was formed by evaporating an Au contact on the unpolished side of the semiconductor and annealing at 420°C for 3 min under nitrogen atmosphere. Before the formation of rhodium(I) complex thin films, the wafer was cut into several parts. The thin films of rhodium(I) complexes were formed by SCS G3P-8 spin coater. The thicknesses of the films were measured as 112, 120 and 116 nm for rhodium(I) complexes, respectively, with the help of a PHE-102 spectroscopic ellipsometer. The front contacts on thin films were also obtained by evaporating Au at high vacuum. The electrical properties of the devices were obtained and compared by means of *I–V* data obtained at room temperature in the dark using a Keithley 2400 source meter. Furthermore, the temperature-sensing properties of the Au/1/n-Si device were examined using *I–V* measurements between 300 and 380 K and light-sensing properties of the structure were tested under a solar simulator with AM1.5 global filter and 40–100 mW cm$^{-2}$ illumination intensity.

### Synthesis of Rhodium(I)–Aminophosphine Complexes

#### *Synthesis of [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**)*

A mixture of [Rh(cod)(μ-Cl)]$_2$ (0.1 g, 0.20 mmol) and [Ph$_2$PNH—(C$_6$H$_4$) —2-CH(CH$_3$)$_2$) ] (0.13 g, 0.41 mmol) in 20 ml THF 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–hexane (15 ml). The precipitated product was filtered and dried *in vacuo*, yielding **1** as a yellow microcrystalline powder. Yield 0.20 g, 89.1%; m.p. 180–182°C. $^1$H NMR ($\delta$ in ppm relative to TMS, *J* Hz, in CDCl$_3$): 7.85–7.81 (m, 4H, *o*-protons of phenyls), 7.46–7.39 (m, 6H, *m*- and *p*-protons of phenyls), 7.08 (d, 1H, $J_{H\text{–}H} = 7.6$ Hz, H-3), 6.85–6.80 (m, 1H, H-4), 6.72 (t, 1H, $J_{H\text{–}H} = 7.6$ Hz, H-5), 6.53 (d, 1H, H-6, $J = 7.6$ Hz), 5.59 (s, 2H, CH—cod), 3.77 (s, 1H, NH), 3.24–3.27 (m,1H, $CH(CH_3)_2$— aniline), 2.94 (s, 2H, —CH—cod), 2.43–1.86 (m, 8H, —$CH_2$—cod), 1.09 (d, 6H, $J_{H\text{–}H} = 6.7$ Hz, $CH(CH_3)_2$— aniline); $^{13}C$ NMR ($\delta$ in ppm relative to TMS, *J* Hz, in $CDCl_3$): 140.10 (C-1), 139.23 (C-2), 139.09 (*i*-carbons of phenyls),132.91 (*o*-carbons of phenyls), 130.56 (*p*-carbons of phenyls), 128.25 (*m*-carbons of phenyls), 125.66 (C-3), 125.19 (C-5), 121.92 (C-4), 120.37 (C-6), 104.70 (CH—cod), 72.03 (CH—cod), 32.67 ($CH_2$—cod), 28.61 ($CH_2$—cod), 27.13 ($CH(CH_3)_2$—aniline), 23.07 ($CH(CH_3)_2$—aniline); assignment was based on $^1H$–$^{13}C$ HETCOR and $^1H$–$^1H$ COSY spectra; $^{31}P\text{-}\{^1H\}$ NMR ($\delta$ in ppm relative to $H_3PO_4$, in $CDCl_3$): 56.68 (d, $J_{RhP} = 157.1$ Hz); selected IR (KBr pellet, in $cm^{-1}$): $\upsilon$ 917 (PN), $\upsilon$ 1434 (PPh), $\upsilon$ 3239 (NH); [$C_{29}H_{34}NPRhCl$] (565.91 g $mol^{-1}$): calcd C 61.55, H 6.06, N 2.47; found C 61.49, H 5.96, N 2.44%.

*Synthesis of [Rh(cod)($PPh_2NH$—$C_6H_3$—4-$CH(CH_3)_2$)Cl] (**2**)*

To a solution of [Rh(cod)(μ-Cl)]$_2$ (0.35 g, 0.70 mmol) in THF, a solution (THF, 30 ml) of [$Ph_2PNH$— ($C_6H_4$) —4-$CH(CH_3)_2$] (0.45 g, 1.40 mmol) was added. The reaction mixture was allowed to proceed with stirring at room temperature for 1 h. After this time, the solution was filtered and the solvent evaporated under vacuum. The solid residue thus obtained was washed with diethyl ether (3 × 10 ml) and then dried under vacuum. Following ecrystallization from petroleum ether–hexane (15 ml), a light crystalline powder was obtained. Yield 0.72 g, 90.1%; m.p. 153–156°C. $^1H$ NMR ($\delta$ in ppm relative to TMS, *J* Hz, in $CDCl_3$): 7.94–7.82 (m, 4H, *o*-protons of phenyls), 7.50–7.40 (m, 6H, *m- and p*-protons of phenyls), 6.84 (d, 2H, H-3 and H-5, $J_{H\text{–}H} = 8.4$ Hz), 6.53 (d, 2H, H-2 and H-6, $J = 8.4$ Hz), 5.64–5.54 (m, 2H, CH—cod), 4.60 (s, 1H, NH), 3.36–2.96 (m, 2H, CH—cod), 2.43-2.39 (m, 2H, $CH_2$—cod and 1H, $CH(CH_3)_2$), 2.33–1.88 (m, 6H, $CH_2$—cod), 1.12 (d, 6H, —$CH(CH_3)_2$ aniline, $J_{H\text{–}H} = 6.8$ Hz); $^{13}C$ NMR ($\delta$ in ppm relative to TMS, *J* Hz, in $CDCl_3$): 141.32 (C-1), 139.81 (C-4), 139.52 (*i*-carbons of phenyls),132.91 (*o*-carbons of phenyls), 130.60 (*p*-carbons of phenyls), 128.32 (*m*-carbons of phenyls), 127.20 (C-2), 126.51 (C-6), 119.15 (C-3), 118.52 (C-5), 104.78 (CH—cod), 71.61 (CH—cod), 33.12 ($CH_2$—cod), 28.60 (—$CH(CH_3)_2$—aniline), 28.03($CH_2$—cod), 23.97 (—$CH(CH_3)_2$—aniline); assignment was based on $^1H$–$^{13}C$ HETCOR and $^1H$–$^1H$ COSY spectra; $^{31}P\text{-}\{^1H\}$ NMR ($\delta$ in ppm relative to $H_3PO_4$, in $CDCl_3$): 55.20 (d, $J_{RhP} = 157.1$ Hz); selected IR (KBr pellet, in $cm^{-1}$): $\upsilon$ 921 (PN), $\upsilon$ 1435 (PPh), $\upsilon$ 3244 (NH); [$C_{29}H_{34}NPRhCl$] (565.91 g $mol^{-1}$): calcd C 61.55, H 6.06, N 2.47; found C 61.48, H 5.94, N 2.42%.

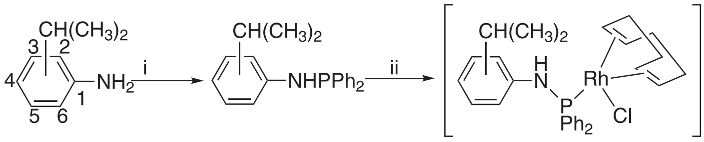
*Synthesis of [Rh(cod)($PPh_2NH$—$C_6H_3$—2,6-($CH(CH_3)_2$))$_2$Cl] (**3**)*

To a solution of [Rh(cod)(μ-Cl)]$_2$ (0.10 g, 0.20 mmol) in THF, a solution (THF, 30 ml) of [$Ph_2PNH$— ($C_6H_3$) —2,6-{$CH(CH_3)_2$}$_2$] (0.15 g, 0.41 mmol) was added. The reaction mixture was allowed to proceed with stirring at room temperature for 1 h. After this time, the solution was filtered and the solvent evaporated under vacuum. The solid residue thus obtained was washed with diethyl ether (3 × 10 ml) and then dried under vacuum. Following recrystallization from petroleum ether–hexane (15 ml), a light-brown crystalline powder was obtained. Yield 0.20 g, 82.2%; m. p. 190°C (dec). $^1H$ NMR ($\delta$ in ppm relative to TMS, *J* Hz, in $CDCl_3$): 7.62–7.58 (m, 4H, *o*-protons of phenyls), 7.41–7.33 (m, 6H, *m*- and *p*-protons of phenyls), 7.28 (m, 1H, H-3), 7.04 (t, 1H, H-4, $J_{H\text{–}H} = 7.6$ Hz), 6.89 (d, 1H, H-5, $J = 7.6$ Hz), 5.77 (s, 1H, $J = 9.0$ Hz, NH), 5.60 (s, 2H, CH—cod), 3.37–3.30 (m, 2H, $CH(CH_3)_2$, 2.82 (s, 2H, CH—cod), 2.45–2.33 (m, 4H, $CH_2$—cod), 2.09–2.07 (m, 2H, $CH_2$—cod), 1.91–1.87 (m, 2H, $CH_2$—cod), 0.78 (d, 12H, $J_{H\text{–}H} = 6.7$ Hz, $CH(CH_3)_2$, aniline); $^{13}C$ NMR ($\delta$ in ppm relative to TMS, *J* Hz, in $CDCl_3$): 146.90 (C-1), 136.29 (*i*-carbons of phenyls), 133.75 (*o*-carbons of phenyls), 131.54 (C-2), 131.07 (C-6), 130.31 (*p*-carbons of phenyls), 127.68 (*m*-carbons of phenyls), 125.86 (C-4), 123.17 (C-3), 123.15 (C-5), 104.66 (CH—cod), 71.80 (CH—cod), 32.63 ($CH_2$—cod), 28.87 ($CH(CH_3)_2$—aniline), 28.59 ($CH_2$—cod), 23.73 ($CH(CH_3)_2$—aniline); assignment was based on $^1H$–$^{13}C$ HETCOR and $^1H$–$^1H$ COSY spectra; $^{31}P\text{-}\{^1H\}$ NMR ($\delta$ in ppm relative to $H_3PO_4$, in $CDCl_3$): 65.63 (d, $J_{RhP} = 157.1$ Hz); selected IR data (KBr pellet, in $cm^{-1}$): $\upsilon$ 930 (PN), $\upsilon$ 1435 (PPh), $\upsilon$ 3250 (NH); [$C_{32}H_{40}NPRhCl$] (607.99 g $mol^{-1}$): calcd C 63.21, H 6.63, N 2.30; found C 63.12, H 6.56, N 2.28%.

## Results and Discussion

### Synthesis and Characterization of the Metal Complexes

As shown in Scheme 1, three (*N*-diphenylphosphino)-isopropylaniline ligands, having isopropyl substituent at carbon 2-, 4-, or 2,6-, were synthesized from the aminolysis[62] of chlorodiphenylphosphine with 2-isopropylaniline, 4-isopropylaniline or 2,6-diisopropylaniline, respectively, under anaerobic conditions It is well known that aminolysis[63,64] appears to be the most common method used for the synthesis of aminophosphines,[65,66] whereby the solvent has a significant influence on the rate and product of the aminolysis. (*N*-Diphenylphosphino)-isopropylanilines, having isopropyl substituent at the carbon 2- or 2,6-, were easily prepared from the aminolysis of $H_2N$—$C_6H_4$—2-$CH(CH_3)_2$ or $H_2N$—$C_6H_4$—2,6-{$CH(CH_3)_2$}$_2$, respectively, with 1 equiv. of chlorodiphenylphosphine in the presence of triethylamine using THF/$CH_2Cl_2$ (1/2) and $CH_2Cl_2$ as a solvent, respectively. Both compounds were isolated as viscous oily substances in high yield under anaerobic conditions. However, the attempt to synthesize (*N*-diphenylphosphino)-4-isoprophylaniline hardly succeeded, owing to the formation of *N,N*-bis(diphenylphosphino)-4-isopropylaniline. Therefore, preparation of (*N*-diphenylphosphino)-4-isopropylaniline was achieved only with 1 equiv. of $Ph_2PCl$, in the presence of *n*-BuLi at −78°C as a yellow, viscous oily compound (Scheme 1). These three aminophosphines were fully characterized by multinuclear NMR, IR spectroscopy and elemental analysis. The $^{31}P\text{-}\{^1H\}$ NMR spectra of ligands, 2-, 4- and 2,6- show single resonances at $\delta$ 29.0, 31.8 and 45.5 ppm, respectively, comparable to those of other aminophosphines.[67] Furthermore, characteristic $J_{(31P\text{–}13C)}$ coupling constants of the carbons of the phenyl rings were



R: 2-$CH(CH_3)_2$ **1**; 4-$CH(CH_3)_2$ **2**; 2,6-($CH(CH_3)_2$)$_2$ **3**

**Scheme 1.** Synthesis of aminophosphine ligands and their [Rh(cod)($PPh_2NH$—$C_6H_4$—2-$CH(CH_3)_2$)Cl] (**1**), [Rh(cod)($PPh_2NH$—$C_6H_4$—4-$CH(CH_3)_2$)Cl] (**2**) and [Rh(cod)($PPh_2NH$—$C_6H_3$—2,6-($CH(CH_3)_2$))$_2$Cl] (**3**) complexes: (i) 1 equiv. $Ph_2PCl$, 1 equiv. $Et_3N$, THF/$CH_2Cl_2$ (1/2) for **1**; 1 equiv. *n*-BuLi at −78°C, 1 equiv. $Ph_2PCl$, 1 equiv. $Et_3N$, $CH_2Cl_2$, for **2**; 1 equiv. $Ph_2PCl$, 1 equiv. $Et_3N$, $CH_2Cl_2$ for **3**; (ii) 1/2 equiv. [Rh(μ-Cl)(cod)]$_2$, THF, for **1–3**.

observed in the $^{13}$C NMR spectrum (including *i*-, *o*-, *m*-, *p*- carbons of phenyl rings; for details see Experimental section) which were consistent with literature values.[68] These compounds are unstable in solution toward oxidation when exposed to air or moisture. Solution of ligands in $CDCl_3$, prepared under anaerobic conditions, is oxidized gradually to give respective oxide and bis(diphenylphosphino) monoxide $[P(O)Ph_2PPh_2]$ derivatives.

We examined simple coordination chemistry of $[Rh(cod)(\mu\text{-}Cl)]_2$ with $[Ph_2PNH—(C_6H_4)—2\text{-}CH(CH_3)_2]$, $[Ph_2PNH—(C_6H_4)—4\text{-}CH(CH_3)_2]$ and $[Ph_2PNH—(C_6H_3)—2,6\text{-}\{CH(CH_3)_2\}_2]$ aminophosphine ligands. Reactions of $[Rh(cod)(\mu\text{-}Cl)]_2$ with (*N*-diphenylphosphino)-2-isopropylaniline, (*N*-diphenylphosphino)-4-isopropylaniline and (*N*-diphenylphosphino)-2,6-diisopropylaniline in THF in a ratio of 1/2:1 at room temperature for 1 h gave a microcrystalline precipitate of neutral complexes **1–3**, respectively. Complexation reactions were straightforward, with coordination to rhodium being carried out at room temperature. These ligands were expected to cleave the $[Rh(cod)(\mu\text{-}Cl)]_2$ dimer to give the corresponding complexes via monohapto coordination of the aminophosphine groups. Bridge cleavage of the dimer, $[Rh(cod)(\mu\text{-}Cl)]_2$ with aminophosphines gave the mononuclear complexes in high yields. These complexes are highly soluble in $CH_2Cl_2$ and slightly soluble in hexane, and they can be crystallized from petroleum ether–hexane solution. The coordination of the ligand through the P donor was confirmed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. Compounds **1–3** were isolated as indicated by doublets in the $^{31}P\text{-}\{^1H\}$ NMR spectra at $\delta$ 56.68 (d, $^1J_{RhP}$: 157.1 Hz), 55.20 (d, $^1J_{RhP}$: 157.1 Hz) and 65.63 (d, $^1J_{RhP}$: 157.1 Hz) ppm, respectively (Fig. 1),[69,70] indicating that aminophosphine ligands act as monodentate ligands. Analysis by $^1$H NMR reveals these compounds to be diamagnetic, exhibiting signals corresponding to the aromatic rings for **1–3** at approximately 7.94–7.33 ppm (for details see Experimental section). Furthermore, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **1**, $J(^{31}P–^{13}C)$ coupling constants of the carbons of the phenyl rings were observed which were consistent with literature values.[71] The structural compositions of complexes **1–3** were further confirmed by IR spectroscopy and microanalysis, and were found to be in good agreement with theoretical values.

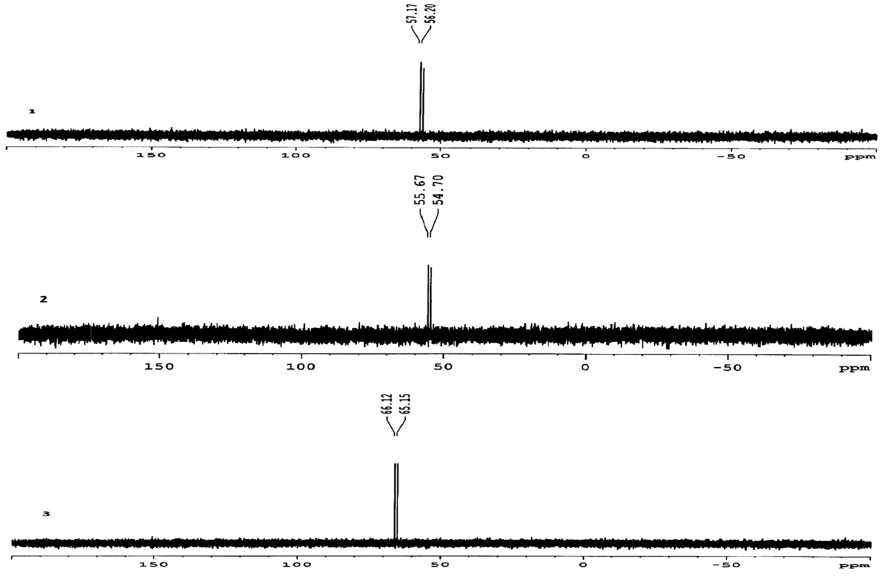


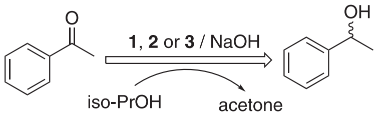
**Figure 1.** The $^{31}P\text{-}\{^1H\}$ NMR spectra of $[Rh(cod)(PPh_2NH\text{-}C_6H_4\text{-}2\text{-}CH(CH_3)_2)Cl]$ (**1**), $[Rh(cod)(PPh_2NH\text{-}C6H_4\text{-}4\text{-}CH(CH_3)_2)Cl]$ (**2**) and $[Rh(cod)(PPh_2NH\text{-}C_6H_4\text{-}2,6\text{-}(CH(CH_3)_2))_2Cl]$ (**3**) complexes.

## Catalytic Transfer Hydrogenation of Acetophenone Derivatives

Recently we reported that the novel half-sandwich metal complexes, based on the ligands with a P—NH backbone, are active catalysts in the reduction of aromatic ketones.[72–76] The complex with sp$^3$-hybribized nitrogen containing N—H bonds displays a higher reaction rate. On the other hand, the presence of an N—H group in the ligands makes it possible to stabilize a six-membered cyclic transition state by forming a hydrogen bond with the oxygen atom of ketones.[77–79] Therefore, these kinds of ligands are attractive and also widely used, especially in ruthenium, rhodium and iridium complexes, for catalytic transfer hydrogenation reactions.[80–83]

In a preliminary study, the catalytic activity of complexes **1–3** in transfer hydrogenation of aromatic ketones by iso-PrOH was investigated. In a typical experiment, 0.01 mmol of the complex and 1 mmol acetophenone were added to a solution of NaOH in iso-PrOH (0.05 mmol NaOH in 10 ml iso-PrOH), refluxed at 82°C and the reaction was monitored by GC. Complexes **1–3** were employed as a precursor for the catalytic transfer hydrogenation of the acetophenone by iso-PrOH /NaOH as a reducing system, and the results are summarized in Table 1. These three complexes catalyzed the reduction of ketones to the corresponding alcohols via hydrogen transfer from iso-PrOH in all reactions. At room temperature no appreciable formation of 1-phenylethanol was found (Table 1, entries 1–3). It is well known that the base facilitates the formation of ruthenium alkoxide by abstracting proton of the alcohol, and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several research groups on studies of rhodium-catalyzed transfer hydrogenation reaction by metal hydride intermediates.[84–91] The role of the base is to generate a more nucleophilic alkoxide ion which would rapidly attack the rhodium complex responsible for dehydrogenation of iso-PrOH. As can be seen from Table 1 (entries 4–6), the pre-catalysts as well as the presence of NaOH are necessary to observe appreciable conversions. As Table 1 shows, high conversions can be achieved with the **1–3** catalytic systems. As seen in Table 1, increasing the substrate–catalyst ratio does not lower conversion of the product in most cases, except for lengthening the time. Remarkably, transfer hydrogenation of acetophenone could achieve up to 99% conversion even when the substrate–catalyst ratio reached 1000:1 (Table 1, entries 7–9). In addition, the choice of base, such as KOH and NaOH, had little influence on the conversion (Table 1, entries 10–12). Outcomes obtained from optimization studies indicated clearly that excellent conversions were achieved in the reduction of acetophenone to 1-phenylethanol when Rh(I)–aminophosphine catalysts were used as the catalytic precursor, with a substrate–catalyst molar ratio (100:1) in iso-PrOH at 82°C (Table 1, entries 13–15). With a complex–NaOH ratio of 1/5, the catalyst systems are very active, leading to a quantitative transformation of the acetophenone, with a good turnover frequency (TOF) of $<396\ h^{-1}$.

**Table 1.** Transfer hydrogenation of acetophenone with iso-*Pr*OH catalyzed by [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**), [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] (**2**) and [Rh(cod)(PPh$_2$NH—C$_6$H$_3$—2,6-(CH(CH$_3$)$_2$))$_2$Cl] (**3**)



| Entry | Catalyst | S/C/NaOH | Time | Conversion(%)[f] | TOF (h$^{-1}$)[g] |
|---|---|---|---|---|---|
| 1 | 1[a] | 100:1:5 | 1 h | <5 | |
| 2 | 2[a] | 100:1:5 | 1 h | <5 | |
| 3 | 3[a] | 100:1:5 | 1 h | <5 | |
| 4 | 1[b] | 100:1 | 2 h | <5 | |
| 5[b] | | 100:1 | 2 h | <5 | |
| 6[b] | | 100:1 | 2 h | <5 | |
| 7[c] | | 1000:1:5 | 3 h | 99 | 33 |
| 8 | 2[c] | 1000:1:5 | 1 h | 99 | 99 |
| 9[c] | | 1000:1:5 | 5 h | 98 | 20 |
| 10 | 1[d] | 100:1:5 | 45 min | 98 | 33 |
| 11 | 2[d] | 100:1:5 | 15 min | 99 | 99 |
| 12 | 3[d] | 100:1:5 | 1 h | 99 | 20 |
| 13 | 1[e] | 100:1:5 | 45 min | 99 | 131 |
| 14 | 2[e] | 100:1:5 | 15 min | 99 | 396 |
| 15 | 3[e] | 100:1:5 | 1 h | 98 | 98 |

*Reaction conditions*:

[a] At room temperature; acetophenone/catalyst/NaOH, 100:1:5,

[b] Refluxing in *iso*-PrOH; acetophenone/catalyst, 100:1, in the absence of base,

[c] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 1000:1:5,

[d] Refluxing in *iso*-PrOH; acetophenone/catalyst/KOH, 100:1:5,

[e] Refluxing in *iso*-PrOH; acetophenone/catalyst/NaOH, 100:1:5,

[f] Determined by GC (three independent catalytic experiments),

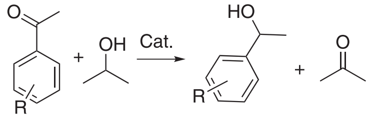
[g] Referred at the reaction time indicated in column; TOF = (moles product/moles catalyst) × h$^{-1}$.

As seen in Table 1, catalytic activities in the studied hydrogen transfer reactions were generally much higher for the [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] (**2**) than for the [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**) and [Rh(cod)(PPh$_2$NH—C$_6$H$_3$—2,6-(CH(CH$_3$)$_2$))$_2$Cl] (**3**). Under identical conditions, transfer hydrogenation of acetophenone derivatives with system **2** led to 99% conversion within 15 min whereas, with catalysts **1** and **3** as the auxiliary, similar (99% and 98%) conversions were achieved only after periods of 45 min and 1 h, respectively (Table 1).

Encouraged by the high catalytic activities obtained in these preliminary studies, we next extended our investigations to include hydrogenation of various simple ketones. First, the catalysts [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**), [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] (**2**) and [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2,6-(CH(CH$_3$)$_2$))$_2$Cl] (**3**) were extensively investigated with acetophenone derivatives (Table 2). The catalytic reduction of acetophenone derivatives was tested with the conditions optimized for acetophenone, and the results are given in Table 2, which illustrates conversions of the reduction performed in 0.1 M iso-PrOH solution containing complexes **1–3** and NaOH (ketone:catalyst:NaOH = 100:1:5). It is well known that the nature and position of the substituents on the phenyl ring of the ketone cause significant changes in the reduction rate.[92] For instance, the introduction of electron-withdrawing substituents, such as F, Cl and NO$_2$, to the *para* position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved, giving rise to easier hydrogenation (Table 2, entries 1–4, 7–10 and 13–16).[93,94] Conversely, an *ortho*- or *para*-substituted acetophenone with an electron donor substituent, i.e. 2-methoxy or 4-methoxy, is reduced more slowly than acetophenone (Table 2, entries 5, 6, 11, 12, 17 and 18). Extensive research indicates clearly that with each of the tested complexes the best yield was achieved in the reduction of acetophenone derivatives when [Rh(cod)(PPh$_2$NH–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl] (**2**) was used as the catalyst.

We also conducted further experiments to explore the effect of bulkiness of the alkyl groups on catalytic activity, and the

**Table 2.** Transfer hydrogenation results for substituted acetophenones with catalyst systems [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**), [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] (**2**) and [Rh(cod)(PPh$_2$NH—C$_6$H$_3$—2,6-(CH(CH$_3$)$_2$))$_2$Cl] (**3**)[a]



| Entry | R | Time | Conversion (%)[b] | TOF (h$^{-1}$)[c] |
|---|---|---|---|---|
| *Catalyst*: [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl], (**1**) | | | | |
| 1 | 4-F | 30 min | 98 | 198 |
| 2 | 4-Cl | 45 min | 99 | 132 |
| 3 | 4-Br | 45 min | 99 | 132 |
| 4 | 4-NO$_2$ | 30 min | 99 | 198 |
| 5 | 2-MeO | 1 h | 98 | 98 |
| 6 | 4-MeO | 2 h | 97 | 49 |
| *Catalyst*: [Rh(cod)(PPh$_2$NH—C$_6$H$_3$—4-CH(CH$_3$)$_2$)Cl], (**2**) | | | | |
| 7 | 4-F | 10 min | 98 | 588 |
| 8 | 4-Cl | 15 min | 99 | 396 |
| 9 | 4-Br | 20 min | 98 | 294 |
| 10 | 4-NO$_2$ | 10 min | 99 | 594 |
| 11 | 2-MeO | 30 min | 99 | 198 |
| 12 | 4-MeO | 1 h | 98 | 98 |
| *Catalyst*: [Rh(cod)(PPh$_2$NH—C$_6$H$_3$—2,6-(CH(CH$_3$)$_2$))$_2$Cl], (**3**) | | | | |
| 13 | 4-F | 30 min | 99 | 198 |
| 14 | 4-Cl | 45 min | 99 | 125 |
| 15 | 4-Br | 1 h | 98 | 98 |
| 16 | 4-NO$_2$ | 30 min | 98 | 196 |
| 17 | 2-MeO | 2 h | 99 | 50 |
| 18 | 4-MeO | 3 h | 98 | 33 |

*Reaction conditions*:

[a] Catalyst (0.01 mmol), substrate (1.0 mmol), iso-PrOH (10 ml), NaOH (0.05 mmol%), 82°C, respectively; concentration of acetophenone derivatives is 0.1 M.

[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments); yields are based on methyl aryl ketone.

[c] TOF = (moles product/moles catalyst) × h$^{-1}$.

results are given in Table 3 (entries 1–12). A variety of simple aryl alkyl ketones were transformed to the corresponding secondary alcohols, and it was found that catalytic activity was highly dependent on the steric hindrance of the alkyl group. The reactivity regularly decreased by increasing the bulkiness of the alkyl groups.[95–97]

### Determination of some Electrical Properties of Heterojunctions Formed Using Rhodium(I) Thin Films

*I–V* plots of Au/1/n-Si, Au/2/n-Si and Au/3/n-Si structures are presented in Fig. 2. The figure indicates that all structures have rectifying behavior which is limited by the properties of the inorganic semiconductor substrate and the magnitude of the energy barrier at the hetero interface, i.e. while the reverse current demonstrated excellent saturation, the forward current increased exponentially with voltage.[98] Therefore the *I–V* data can be analyzed by thermionic emission theory. According to the theory, the relationship between applied voltage and current may be written as[99]

$$I = AA^{*}T^{2}\exp\left(\frac{q\phi_{\mathrm{b}}}{kT}\right)\exp\left(\frac{q(V-IR_{\mathrm{s}})}{nkT}\right) \tag{1}$$

where

$$I_{0} = AA^{*}T^{2}\exp\left(\frac{q\phi_{\mathrm{b}}}{kT}\right) \tag{2}$$

is the saturation current, $A$ is the effective diode area, $A^{*}$ is the Richardson constant, $q$ is the electronic charge, $\phi_{\mathrm{b}}$ is the barrier height of the diode, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $R_{\mathrm{s}}$ is the series resistance and $n$ is the dimensionless ideality factor. The ideality factors of Au/1/n-Si, Au/2/n-Si and Au/3/n-Si were determined from the slope of the linear parts of the forward-bias *I–V* plots as 1.82, 1.37 and 1.88, respectively. According to the theory, the ideality factor of a diode should be close to unity. The deviation from unity for the structures can be attributed to effects of series resistance, existence of interface state densities and fabrication-induced defects. The barrier heights of the Au/1/n-Si, Au/2/n-Si and Au/3/n-Si heterojunctions were extracted from saturation current values as 0.76, 0.76 and 0.74 eV, respectively, which imply very similar band structures at organic–inorganic interface. The small difference between the values can be attributed to effects of natural oxide layers on n-Si formed during fabrication processes and interface states. Similar structures have also been reported with different metal complexes in the literature.[48,100,101] Temel *et al.*[48] synthesized $N_2S_2O_2$ thio Schiff base ligand and its Cu(II), Co(III), Ni(II) and Pd(II) complexes, and presented their usage in the fabrication of organic–inorganic hybrid devices. They showed that the structures had good rectifying properties and their barrier height values changed between 0.78 and 0.88 eV, which is remarkably higher than conventional Al/n-Si metal–semiconductor contact. El-Nahass *et al.*[102] fabricated an Au/NiPc/n-Si heterojunction by forming NiPc thin films on n-Si using an evaporation technique. They calculated the ideality factor and barrier height values of the Au/NiPc/n-Si diode as 1.68 and 0.55 eV, respectively.

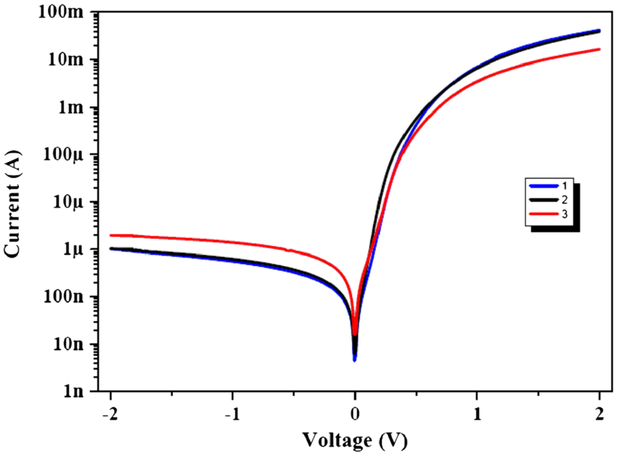


**Figure 2.** ln *I–V* plots of the diodes formed using rhodium(I) complex thin films.

**Table 3.** Transfer hydrogenation results for substituted alkyl phenyl ketones with the catalyst systems [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2-CH(CH$_3$)$_2$)Cl] (**1**), [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—4-CH(CH$_3$)$_2$)Cl] (**2**) and [Rh(cod)(PPh$_2$NH—C$_6$H$_4$—2,6-(CH(CH$_3$)$_2$))$_2$Cl] (**3**)[a]

| Entry | Catalyst | Time | Substrate | Product | Conversion (%)[b] | TOF (h$^{-1}$)[c] |
|---|---|---|---|---|---|---|
| 1 | **1** | 1 h | Substrate 1 | Product 1 | 99 | 99 |
| 2 | **2** | 1/3 h | | | 98 | 294 |
| 3 | **3** | 3/2 h | | | 99 | 149 |
| 4 | **1** | 3/2 h | Substrate 2 | Product 2 | 99 | 149 |
| 5 | **2** | 1/2 h | | | 98 | 196 |
| 6 | **3** | 2 h | | | 98 | 49 |
| 7 | **1** | 2 h | Substrate 3 | Product 3 | 99 | 50 |
| 8 | **2** | 1 h | | | 99 | 99 |
| 9 | **3** | 3 h | | | 98 | 33 |
| 10 | **1** | 4 h | Substrate 4 | Product 4 | 98 | 25 |
| 11 | **2** | 2 h | | | 98 | 49 |
| 12 | **3** | 5 h | | | 98 | 20 |

[a] Catalyst (0.01 mmol), substrate (1.0 mmol), iso-PrOH (5 ml), NaOH (0.05 mmol%), 82°C, respectively; concentration of alkyl phenyl ketones is 0.1 M.

[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments); yields are based on methyl aryl ketone.

[c] TOF = (moles product/moles catalyst) × h$^{-1}$.

The deviations from linearity in ln *I–V* plots in Fig. 2 show the effect of series resistance. The series resistance of the diodes can be calculated using one of the common equations proposed by Norde:[103]

$$F(V) = \frac{V}{2} - \frac{1}{\beta}\left(\frac{I(V)}{AA^{*}T^{2}}\right) \tag{3}$$

where $I(V)$ is the current obtained from *I–V* data. The barrier height value is calculated using the following equation, with the help of the minimum value of $F$ vs. $V$ plot:

$$\phi_{\mathrm{b}} = F(V_{0}) + \frac{V_{0}}{2} - \frac{kT}{q} \tag{4}$$

where $F(V_0)$ is the minimum $F(V)$ value and $V_0$ is the corresponding voltage value. $F(V)$–$V$ plots of the structures obtained using the rhodium(I) complexes are presented in Fig. 3. The series resistance ($R_s$) of a diode is defined by the relation

$$R_s = \frac{kT(2-n)}{qI_{\min}} \tag{5}$$

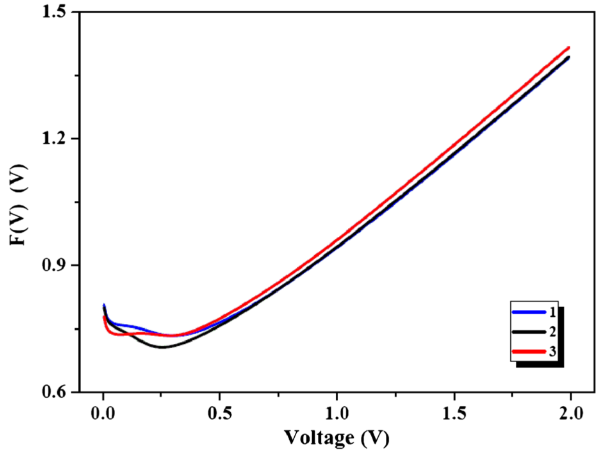


**Figure 3.** *F-V* plots of the diodes formed using rhodium(I) complex thin films.

where $I_{\min}$ is the corresponding current value at $V_0$. The barrier height values and series resistance values of Au/1/n-Si, Au/2/n-Si and Au/3/n-Si heterostructures were calculated as 0.87, 0.81 and 0.85 eV and 138, 434 and 132 Ω, respectively.

## Temperature- and Light-Sensing Properties of a Heterojunction Formed Using Rhodium(I) Thin Film

The temperature-dependent *I*–*V* plot of Au/1/n-Si heterojunction between 300 and 380 K in the dark is presented in Fig. 4(a). As clearly seen from the figure, temperature has a strong effect, especially on reverse-bias *I*–*V* characteristics of the diode. When the temperature was increased at the same time, the reverse current increased for fixed voltage. This shows that the structure can be used as a temperature sensor. The temperature dependence of ideality factor and barrier height values was executed with the help of equations (1) and (2). As presented in Fig. 4(b), the ideality factor value of the device decreased from 1.82 to 1.16 and the barrier height value of the structure increased from 0.76 to 0.85 eV with increase in temperature. When the thermionic emission theory is considered, it can be seen that the current transport has strong temperature dependence. Electrons at low temperatures are able to overcome the lower barriers and the current transport will be dominated by current flow through the patches of lower Schottky barrier height and a larger ideality factor.[104–106] When the temperature increases, more electrons have sufficient energy to surmount the higher barrier. The sensitivity of organic–inorganic diodes to temperature has been

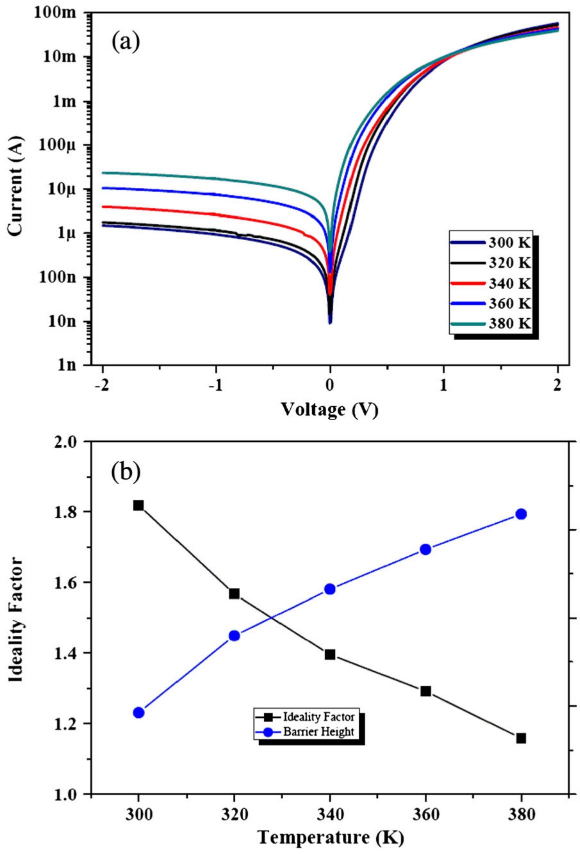


**Figure 4.** (a) The temperature dependent *I-V* plot of Au/1/n-Si heterojunction between 300 and 380 K. (b) The temperature dependence of ideality factor and barrier height values of Au/1/n-Si heterojunction.

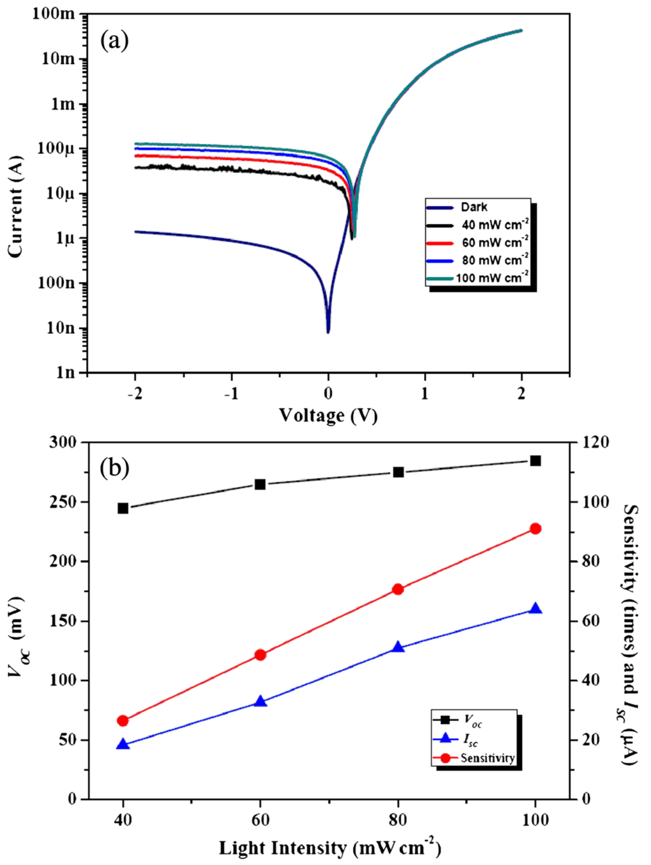


**Figure 5.** (a) The light intensity dependent *I-V* plot of Au/1/n-Si heterojunction. (b) The light intensity dependence of photoelectrical parameters of Au/1/n-Si heterojunction.

also reported by different authors.[105,107] For instance, the Tecimer group[105] formed an Au/(Zn-doped)PVA/n-GaAs Schotky barrier diode and determined its electrical properties in the temperature range of 80–350 K in steps of 30 K. They showed that the ideality factor decreased from 12.850 to 2.805, while the zero-bias barrier height increased from 0.145 eV to 0.606 eV with increasing temperature.

*I*–*V* measurements of the Au/1/n-Si structure were also carried out in the dark and under 40–100 mW cm$^{-2}$ illumination conditions and drawn in Fig. 5(a). The measurements showed that *I*–*V* characteristics of the device have a strong dependence on light and the reverse current is enhanced by photo-illumination. This signifies that light generates a carrier-contributing photocurrent due to the production of electron–hole pairs at the interface as a result of the light absorption. Figure 5(b) shows the effects of light intensity on light sensitivity, open circuit current ($I_{sc}$) and closed circuit voltage ($V_{oc}$). As seen in Fig. 5(b), while the reverse current of the diode −2 V increases 27 times under 40 mW cm$^{-2}$, it increases 91 times under 100 mW cm$^{-2}$. Similarly, the $I_{sc}$ value of the structure increases from 18 to 64 μA and the $V_{oc}$ value increases from 245 to 285 mV under the same illumination conditions.

## Conclusions

In summary, our study on the synthesis and characterization of rhodium(I) complexes bearing P—NH type ligands and their use in the transfer hydrogenation of various ketones and fabrication of organic–inorganic heterojunctions has led to the following conclusions and insights:

1. Novel, Rh(I) —cod complexes based on a P—NH backbone were easily synthesized from $[Rh(cod)(\mu\text{-}Cl)]_2$ and aminophosphines at room temperature. The complexes have been characterized by multinuclear one- and two-dimensional NMR, elemental analysis and IR spectroscopy, and all spectra are in agreement with the structures proposed.
2. The rhodium complexes catalyzed the reduction of acetophenone derivatives via hydrogen transfer from iso-PrOH. These compounds have also exhibited promising catalytic activity in the transfer hydrogenation reaction of various ketones in basic iso-PrOH. Specifically, the $[Rh(cod)(PPh_2NH—C_6H_4—4\text{-}CH(CH_3)_2)Cl]$ catalytic system demonstrates good catalytic activity and, in certain cases, alcohols with up to 99% conversion (TOF ≤ 588 h$^{-1}$) could be obtained.
3. The procedure is quite simple and efficient towards various ketones and does not require an induction period. Thus further work in this direction and in the possible utilization of these kinds of complexes for catalytic purposes are in progress.
4. Rhodium(I) complex/n-Si heterojunctions have shown excellent rectifying properties at room temperature. Their electrical parameters have been extracted using current–voltage measurements. Furthermore, current–voltage measurements under various illumination conditions and a temperature range of 300–380 K have presented the temperature- and light-sensing characteristics of the devices.

### Acknowledgment

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## References

[1] E. Derent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, *455*, 247–253.
[2] H. Yang, M. Alvarez, N. Lugan, R. Mathieu, *J. Chem. Soc. Chem. Commun.* **1995**, 1721–1722.
[3] G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067–2089.
[4] H. Brunner, A. F. M. Mokhlesur Rahman, *Chem. Ber.* **1984**, 710–724.
[5] M. R. I. Zuburi, J. D. Woollins, *Comments Inorg. Chem.* **2003**, *24*, 189–252.
[6] H.-J. Chen, J. M. Barendt, R. C. Haltiwanger, T. G. Hill, A. D. Norman, *Phosphorus, Sulfur* **1986**, *26*, 155–162.
[7] M. Aydemir, A. Baysal, F. Durap, B. Gümgüm, S. Özkar, L. T. Yıldırım, *Appl. Organomet. Chem.* **2009**, 23, 467–475.
[8] P. Bhattacharyya, J. D. Woollins, *Polyhedron* **1995**, *14*, 3367–3388.
[9] A. Baysal, M. Aydemir, F. Durap, B. Gümgüm, S. Özkar, L. T. Yıldırım, *Polyhedron* **2007**, *26*, 3373–3378.
[10] K. R. Reddy, K. Surekha, G. H. Lee, S. M. Peng, S. T. Lui, *Organometallics* **2000**, *19*, 2637–2639.
[11] D. P. Catsoulocas, B. R. Steele, G. A. Herapoulos, M. Micha-Screttas, C. G. Screttas, *Tetrahedron Lett.* **2003**, *44*, 4575–4578.
[12] M. L. Clarke, D. J. Cole-Hamilton, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **2001**, 2721–2723.
[13] S. Urgaonkar, M. Nagarajan, J. G. Verkade, *Tetrahedron Lett.* **2002**, *43*, 8921–8924.
[14] Y. Wang, X. Li, K. Ding, *Tetrahedron Lett.* **2002**, *43*, 159–161.
[15] S. Urgaonkar, J. G. Verkade, *Adv. Synth. Catal.* **2004**, *346*, 611–616.
[16] J. Cheng, Y. H. Sun, F. Wang, M. J. Guo, J. H. Xu, Y. Pan, Z. G. Zhang, *J. Org. Chem.* **2004**, *69*, 5428–5432.
[17] C. Saluzzo, J. Breuzard, S. Pellet-Rostaing, M. Vallet, F. L. Guyader, M. Lemaire, *J. Organomet. Chem.* **2002**, *643–644*, 98–104.
[18] N. W. Boaz, J. A. Ponasik, J. Large, E. S. Large, *Tetrahedron: Asymmetry* **2005**, *16*, 2063–2066.
[19] B. Pugin, H. U. Blaser, *Adv. Synth. Catal.* **2006**, *348*, 1743–1751.
[20] R. A. W. Johnstone, A. H. Wilby, I. D. Entwistle, *Chem. Rev.* **1985**, *85*, 129–170.
[21] M. Yiğit, B. Yiğit, İ. Özdemir, E. Çetinkaya, B. Çetinkaya, *Appl. Organometal. Chem.* **2006**, *20*, 322–327.
[22] R. Noyori, M. Yamakawa, S. Hashiguchi, *Acc. Chem. Res.* **1990**, *23*, 345–350.
[23] S. Ram, R. E. Ehrenkaufer, *Synthesis* **1988**, 91–95.
[24] G. Brieger, T. J. Nestrick, *Chem. Rev.* **1974**, *74*, 567–580.
[25] a) H. Takaya, T. Ohta, R. Noyori, in Catalytic Asymmetric Synthesis (Ed.: L. Ojima), VCH, New York, **1993**; ch. 3; b) R. Noyori, in Asymmetric Catalysis in Organic Synthesis, Wiley, New York, **1994**; ch. 2.
[26] S. Gladiali, G. Mestroni, in Transition Metal for Organic Synthesis, Vol. *2* (Ed.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**, pp. 97–119.
[27] H. Siegel, V. Himmele, *Angew. Chem.* **1980**, *92*, 182–187.
[28] C. Botteghi, S. Paganelli, A. Schionato, M. Marchetti, *Chirality* **1991**, *3*, 355–369.
[29] K. Nishide, M. Node, *Chirality* **2002**, *14*, 759–767.
[30] T. Ooi, T. Ichikawa, K. Maruoka, *Angew. Chem.* **2001**, *113*, 3722–3724.
[31] Y.-Y. Kuo, M. F. Haddow, A. Perez-Rodondo, G. R. Owen, *J. Chem. Soc. Dalton Trans.* **2010**, 39, 6239–6248.
[32] H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *345*, 103–151.
[33] T. Ikariya, K. Murata, R. Noyori, *Org. Biomol. Chem.* **2006**, *4*, 393–406.
[34] S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226–236.
[35] R. Noyori, T. Ohkuma, *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73.
[36] R. Schimid, *Chimia* **1996**, *50*, 110–113.
[37] S. C. Stinson, *Chem. Eng. News* **1999**, 77, 101–120.
[38] H.-U. Blaser, F. Spindler, M. Studer, *Appl. Catal. A* **2001**, 221, 119–143.
[39] C. Ruiz, E. M. García-Frutos, G. Hennrich, B. Gómez-Lor, *J. Phys. Chem. Lett.* **2012**, *3*, 1428–1436.
[40] H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. Shakya Tuladhar, K. Song, S. E. Watkins, Y. Geerts, *J. Am. Chem. Soc.* **2011**, *133*, 3272–3275.
[41] N. R. Armstrong, W. Wang, D. M. Alloway, D. Placencia, E. Ratcliff, M. Brumbach, *Macromol. Rapid Commun.* **2009**, *30*, 717–731.
[42] Y. S. Ocak, M. Kulakci, T. Kilicoglu, R. Turan, K. Akkilic, *Synthetic. Met.* **2009**, *159*, 1603–1607.
[43] X. Ren, P. K. Chan, J. Lu, B. Huang, D. C. Leung, *Adv. Mater.* **2013**, *25*, 1291–1295.

[44] F. Yakuphanoglu, M. Kandaz, B. F. Senkal, *Sensor Actuator. Phys.* **2009**, *153*, 191–196.
[45] J. Burschka, A. Dualeh, F. Kessler, E. Baranoff, N.-L. Cevey-Ha, C. Yi, M. K. Nazeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2011**, *133*, 18042–18045.
[46] T. Kilicoglu, Y. S. Ocak, *Microelectron. Eng.* **2011**, *88*, 150–154.
[47] N. Sekar, V. Y. Gehlot, *Resonance* **2010**, *15*, 819–831.
[48] H. Temel, S. Pasa, Y. S. Ocak, I. Yılmaz, S. Demir, I. Ozdemir, *Synth. Meth.* **2012**, *161*, 2765–2775.
[49] M. Aydemir, A. Baysal, N. Meric, B. Gümgüm, *J. Organomet. Chem.* **2009**, *694*, 2488–2492.
[50] M. Aydemir, A. Baysal, *Polyhedron* **2010**, *29*, 1219–1224.
[51] M. Aydemir, N. Meriç, A. Baysal, B. Gümgüm, M. Toğrul, Y. Turgut, *Tetrahedron: Asymmetry.* **2010**, 21, 703–710.
[52] M. Aydemir, N. Meric, F. Durap, A. Baysal, M. Toğrul, *J. Organomet. Chem.* **2010**, *695*, 1392–1398.
[53] H. Wei, Y. J. Zhang, Y. Dai, J. Zhang, W. Zhang, *Tetrahedron Lett.* **2008**, *49*, 4106–4109.
[54] P. C. J. Kamer, P. W. N. M. Leeuwen, J. N. H. Reek, *Acc. Chem. Res.* **2001**, *34*, 895–904.
[55] I. Ojima, Catalytic Asymmetric Synthesis, 2nd edn, Wiley-VCH, New York, **2000**.
[56] M. Aydemir, A. Baysal, N. Meric, C. Kayan, B. Gümgüm, S. Özkar, E. Sahin, *J. Organomet. Chem.* **2011**, *696*, 2584–2588.
[57] M. Aydemir, A. Baysal, B. Gümgüm, *Appl. Organomet. Chem.* **2012**, *26*, 1–8.
[58] M. Aydemir, N. Meriç, A. Baysal, *J. Organomet. Chem.* **2012**, *720*, 38–45.
[59] E. Cesarotti, A. Chiesa, G. D. Alfonso, *Tetrahedron Lett.* **1982**, *23*, 2995–2996.
[60] M. Aydemir, N. Meriç, C. Kayan, F. Ok, A. Baysal, *Inorg. Chim. Acta* **2013**, *398*, 1–10.
[61] G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1990**, *28*, 88–90.
[62] M. Aydemir, A. Baysal, N. Gürbüz, İ. Özdemir, B. Gümgüm, S. Özkar, N. Çaylak, L. T. Yıldırım, *Appl. Organomet. Chem.* **2010**, *24*, 17–24.
[63] A. Baysal, M. Aydemir, F. Durap, B. Gümgüm, S. Özkar, L. T. Yıldırım, *Polyhedron* **2007**, *26*, 3373–3378.
[64] M. Aydemir, A. Baysal, F. Durap, B. Gümgüm, S. Özkar, L. T. Yıldırım, *Appl. Organomet. Chem.* **2009**, *23*, 467–475.
[65] K. G. Gaw, M. B. Smith, J. W. Steed, *J. Organomet. Chem.* **2002**, *664*, 294–297.
[66] M. R. I. Zubiri, H. I. Milton, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chim. Acta* **2004**, *357*, 1243–1246.
[67] A. D. Burrows, M. F. Mahon, M. T. Palmer, *J. Chem. Soc. Dalton Trans.* **2000**, *2*, 1669–1677.
[68] D. Morales-Morales, R. Redon, C. Yung, C. M. Jensen, *Chem. Commun.* **2000**, 1619–1620.
[69] H. L. Milton, M. V. Wheatley, A. M. Z. Slawin, *Polyhedron* **2004**, *23*, 3211–3220.
[70] Q. Zhang, G. Hua, P. Bhattacharyya, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **2003**, 3250–3257.
[71] F. Majoumo, P. Lönnecke, O. Kühl, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **2004**, *630*, 305–308.
[72] M. Aydemir, A. Baysal, N. Meric, B. Gümgüm, *J. Organomet. Chem.* **2009**, *694*, 2488–2492.
[73] M. Aydemir, A. Baysal, *Polyhedron* **2010**, *29*, 1219–1224.
[74] M. Aydemir, N. Meriç, A. Baysal, *J. Organomet. Chem.* **2012**, *720*, 38–45.
[75] C. Kayan, N. Meriç, M. Aydemir, A. Baysal, D. Elma, B. Ak, E. Şahin, N. Gürbüz, İ. Özdemir, *Polyhedron* **2012**, *42*, 142–148.
[76] M. Aydemir, F. Durap, A. Baysal, N. Meric, A. Buldağ, B. Gümgüm, S. Özkar, L. T. Yıldırım, *J. Mol. Catal. Chem.* **2010**, *326*, 75–81.
[77] M. Aydemir, A. Baysal, S. Özkar, L. T. Yıldırım, *Inorg. Chim. Acta* **2011**, *367*, 166–172.
[78] A. M. Maj, K. M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, *J. Organomet. Chem.* **2001**, *626*, 157–160.
[79] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102.
[80] Y. Chen, S. Yekta, A. K. Yudin, *Chem. Rev.* **2003**, *103*, 3155–3211.
[81] T. Jerphagnon, J.-L. Renaud, C. Bruneau, *Tetrahedron: Asymmetry* **2004**, *15*, 2101–2111.
[82] T. Ikariya, A. J. Blocker, *Acc. Chem. Res.* **2007**, *40*, 1300–1308.
[83] A. M. Maj, K. M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, *J. Organomet. Chem.* **2001**, *626*, 157–160.
[84] R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931–7944.
[85] G. Zassinowich, G. Mestroni, S. Gladiali, *Chem. Rev.* **1992**, *92*, 1051–1069.
[86] C. F. De Graauw, J. A. Peters, H. Van Bekkum, J. Huskens, *Synthesis* **1994**, 1007–1017.
[87] D. Schröder, H. Schwarz, *Angew. Chem. Int. Ed.* **1990**, *29*, 910–912.
[88] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F. A. England, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed.* **1998**, *37*, 1703–1707.
[89] E. P. Kelson, P. P. Phengsy, *J. Chem. Soc. Dalton Trans.* **2000**, 4023–4024.
[90] J. S. Chen, Y. Li, Z. Dong, B. Li, J. Gao, *Tetrahedron Lett.* **2004**, *45*, 8415–8418.
[91] J. Hannedouche, G. J. Clarkson, M. Wills, *J. Am. Chem. Soc.* **2004**, *126*, 986–987.
[92] R. Guo, X. Chen, C. Elphelt, D. Song, R. H. Morris, *Organic Lett.* **2005**, *7*, 1757–1759.
[93] P. Pelagatti, M. Carcelli, F. Calbiani, C. Cassi, L. Elviri, C. Pelizzi, U. Rizzotti, D. Rogolino, *Organometallics* **2005**, *24*, 5836–5844.
[94] J. W. Faller, A. R. Lavoie, *Organometallics* **2001**, *20*, 5245–5247.
[95] J.-X. Gao, X.-D. Yi, P.-P. Xu, C.-L. Tang, H.-L. Wan, T. Ikariya, *J. Organomet. Chem.* **1999**, *592*, 290–295.
[96] J.-X. Gao, H. Zhang, X.-D. Yi, P.-P. Xu, C.-L. Tang, H.-L. Wan, K.-R. Tsai, T. Ikariya, *Chirality* **2000**, *12*, 383–388.
[97] Z.-R. Dong, Y.-Y. Li, J.-S. Chen, B.-Z. Li, Y. Xing, J.-X. Gao, *Org. Lett.* **2005**, *7*, 1043–1045.
[98] T. Kilicoglu, *Thin Solid Films* **2008**, *516*, 967–970.
[99] E. H. Rhoderick, Metal–semiconductor Contacts, Oxford University Press, Oford, **1978**.
[100] K. Akkilic, Y. S. Ocak, S. Ilhan, T. Kilicoglu, *Synth. Meth.* **2008**, *158*, 969–972.
[101] M. Aziz, *Solid State Electron.* **2008**, *52*, 1145–1148.
[102] M. El-Nahass, K. Abd-El-Rahman, A. Darwish, *Microelectron J.* **2007**, *38*, 91–95.
[103] H. Norde, *J. Appl. Phys.* **1979**, *50*, 5052–5053.
[104] R. Tung, *Appl. Phys. Lett.* **1991**, *58*, 2821–2823.
[105] J. H. Werner, H. H. Güttler, *J. Appl. Phys.* **1991**, *69*, 1522–1530.
[106] H. Tecimer, A. Türüt, H. Uslu, Ş. Altındal, İ. Uslu, *Sensor Actuator. Phys.* **2013**, 194–201.
[107] Y. S. Ocak, M. A. Ebeoglu, G. Topal, T. Kilicoglu, *Phys. Condens. Matter.* **2010**, *405*, 2329–2333.