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# Rhodium complex of bis(diphenylphosphinomethyl) dopamine-coated magnetic nanoparticles as efficient and reusable catalyst for hydroformylation of olefins

Mohammed Nasiruzzaman Shaikh<sup>\*,a</sup>, M. Bououdina<sup>b</sup>, Abiola Azeez Jimoh<sup>a</sup>, Md. Abdul Aziz<sup>a</sup>, Aasif Helal<sup>a</sup>, Abbas Saeed Hakeem<sup>a</sup>, Zain H. Yamani<sup>a</sup>, Tae-Jeong Kim<sup>c</sup>

Magnetic nanoparticles(MNP) functionalized by a new bis(diphenylphosphinomethyl)dopamine (**bpd**) of type **MNP@bpd** were prepared, characterized and their reusability as catalysts were assessed by hydroformylation reaction.



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Rhodium complex of bis(diphenylphosphinomethyl) dopaminecoated magnetic nanoparticles as efficient and reusable catalyst for hydroformylation of olefins

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A new bis(diphenylphosphinomethyl) dopamine (**bpd**) ligand has been prepared and anchored on the surface of magnetic nanoparticles (MNPs). The obtained ligand and the surface functionalized nanoparticles of type **MNP@bpd** have been characterized by various analytical techniques, such as NMR, IR, TEM, XRD, and VSM. TEM shows homogeneous distribution of the particles with the size ranging 5-7 nm. XRD Rietveld analysis confirm the formation of pure and single  $Fe_3O_4$  phase with high crystallinity. The ligands anchoring on the magnetic nanoparticles surface have been confirmed by the shift of the characteristic Fe-O vibration band in the FT-IR spectrum, and has been supported by the stepwise weight loss in TGA as a function of temperature. The phosphorus content determined by ICP-MS is approximately 0.39 mmol of phosphine per gram of the nanoparticles. Magnetization-field curves recorded at room temperature reveal superparamagnetic behavior. The materials **MNP@bpd** have proven to be an excellent catalyst after *in-situ* addition of rhodium (Rh) metal precursor for the hydroformylation reaction of styrene and its derivatives. The extent of reusability of the catalyst has been tested and was found to be active even after seven consecutive cycles.

### Introduction

In recent years, catalyzed hydroformylation has drawn much attention as a commercially important reaction in the production of aldehydes from aliphatic and substituted aromatic olefins with *syngas* [1-8]. The aldehyde products can be converted into numerous useful chemicals via condensation, hydrogenation, amination and other processes. Consequently, a large number of reports on homogeneous catalysis to produce oxo- chemicals are available in the literature [9-13]. Homogeneous catalysts are dominant because they react in the same phase as the reactant. By nature, homogeneous catalysts are soluble in organic solvents, so that all catalytic sites are accessible and easy to tune by organic functional group inter-conversion. However, the solubility poses the main challenge in homogeneous catalysis; that is, to separate the catalyst from the desired product after the reaction. This limits the scope of homogeneous catalysis for some applications, and is occasionally considered as crucial drawback for product commercialization.

During the last two decades, great efforts have been devoted to develop alternatives to homogeneous catalysis in order to minimize separation costs and maximize product purity. Heterogeneous catalysis is the most obvious alternative, as it uses catalysts that are easy to separate and reuse. In addition, it can minimize the use of large quantities of environmentally toxic organic solvents that are needed for separation of the homogeneous catalysts and

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purification of the reaction products. Most heterogeneous catalysts are based on solid supports such as silica [14-16]. Silica is highly stable, robust and easy to functionalize; thereby organic functional groups can be easily anchored by either covalent binding or surface adsorption in order to provide catalytic centers. However, majority fraction of the catalytic sites can dip inside the solid support, becoming inaccessible and decreasing the overall catalytic activity. In addition, the bonds holding the catalyst to the solid support can break, causing the catalyst to leach out of the solid support and hence results in increasing the possibility of separation complications.

As an alternative support to silica, nanoparticles have attracted much attention owing to their robustness and high surface area. Because of the high surface area of nanoparticles supports, catalyst centers anchored to nanoparticles are more exposed to the reactant and therefore have increased catalytic activity. If homogeneous units are anchored onto nanoparticle supports, they can often still behave as if they were dissolved in solution, which improves the overall catalytic activity. The choice of nanoparticles can also be strategically made so that additional functionality is introduced into the catalytic system. For example, superparamagnetic iron oxide nanoparticles (SPIONs) opened up a promising research strategy for developing surface-coated recyclable catalysts because they can easily be separated from solution using a magnetic field [17-23].

Because iron oxide nanoparticles can be prepared from low costmaterials via simple synthetic approaches, and since suitable ligands can easily be anchored on their surface [24-27], they offer excellent potential as a catalyst support. Furthermore, their insolubility in organic solvents and magnetic nature render them easily separable from the heterogeneous reaction system; this greatly reduces the efforts required to isolate the catalyst and products. In addition, it is easy to tune the physical and chemical properties, including the shape, size, and morphology, of these magnetic particles [28-30]. In line with this effort, Alper et al. recently reported magnetic particle-supported heterogeneous catalytic systems using polyaminoamido (PAMAM) dendrons, and the catalytic results obtained were encouraging [31]. They reported up to 100% conversion with excellent regio-selectivity towards branched to linear aldehyde ratio. In addition, Chouansong et al. reported the triphenylphosphine ligand coated magnetic nanoparticles with moderately high conversion of olefins [32].

Encouraged by this research, we synthesized new homogeneous species, bis(diphenylphosphinomethylated)dopamine ligands, and anchored them on magnetic nanoparticle surfaces followed by detail characterization. These particles were exploited for the conversion of a series of olefins into aldehydes, using Rh(I) as the metal centre.

### Experimental

### Materials and analysis

unless otherwise stated. All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried using standard procedures. Deionized (DI) water was used wherever needed. The <sup>1</sup>H signatures were collected on a JEOL JNM-LA 500 Spectrometer, and the respective chemical shifts ( $\delta$ ) were defined using tetramethylsilane (TMS) as an internal standard. <sup>31</sup>P NMR spectra were recorded on the same machine using 85% H<sub>3</sub>PO<sub>4</sub> as an internal reference. The FT-IR spectra of the functionalized MNPs were obtained from a Nicolet 720 in the range of 400 to 4000  $\text{cm}^{-1}$ , using KBr. Thermal analysis was performed on the Mettler-Toledo with model TGA1 STAR<sup>e</sup> System on around 10 mg of dry samples under argon atmosphere with a heating rate of 10 °C/min with the temperature ranges 0-800 °C. X-ray diffraction patterns were recorded using high resolution Rigaku Ultima IV diffractometer equipped with Cu-Ka radiation. The data were acquired over the 20 range between 15 and 85°. Rietveld refinements were performed using PDXL program.The phosphorous content in the sample was determined by inductively coupled mass spectrometry (ICP-MS) method (Thermo Scientific, model XSERIES 2), by dissolving it in concentrated HNO<sub>3</sub>. The surface morphology of the NPs was discerned by field emission scanning electron microscopy (FESEM, LYRA 3 Dual Beam, Tescan) operated at 30 kV. FESEM samples were prepared either from suspension or dry powder and coated with gold in an automatic gold coater for 90 s. The Energy Dispersive X-ray spectra (EDX) for the chemical and elemental analysis of NPs were collected from X-Max detector by Oxford Inc. TEM micrograph were obtained from an highresolution transmission electron microscopy (HRTEM) (JEOL JEM-2100F) equipped with an energy dispersive X-ray spectrometer (EDX) operated at 200 kV. 300 mesh copper grids coated with carbon films were used for the imaging. The transmission electron microscopy (TEM) samples were prepared by dropping on a copper grid from an ethanolic suspension and drying at room temperature. Magnetic measurements were carried out at room temperature using PMC Micromag 3900 model Vibrating Sample Magnetometer (VSM) equipped with 1 tesla magnet and a sensitivity of 0.5 µemu. The conversion of the catalytic product were calculated by Gas chromatography (GC) (Shimadzu) and products were identified by the Gas chromatography integrated with massspectrometry (GC-MS) with model GCMS-QP2010 Ultra from Shimadzu.

Chemicals procured from Sigma-Aldrich were used as-received

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### **General procedure**

Synthesis of magnetic nanoparticles (MNPs). Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles in the range of 5-7 nm were synthesized (Scheme 1) according to the procedure reported in the literature [33-35]. Hydrated FeCl<sub>2</sub> (2 g, 10 mmol) and FeCl<sub>3</sub> (8.08 g, 20 mmol) were dissolved in 200 mL of DI water under argon at 90°C with vigorous stirring. Concentrated NH<sub>4</sub>OH was slowly added until the solution attained a pH of 9, attended by precipitation. The mixture was

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allowed to stand for 4 h. The precipitate (black color) was washed several times with DI water and dried.

Synthesis of bis(diphenylphosphinomethyl) dopamine (bpd). Dopamine was functionalized by a double phosphinomethylation step on the primary amine via the reaction of dopamine hydrochloride and diphenylphosphinomethanol, as per Scheme 1. Diphenylphosphine (1.75 mL, 10 mmol) was added to a suspension of 2.9 g paraformaldehyde (9.5 mmol) in 10 mL of anhydrous toluene under argon. The mixture was stirred for 4 h at 120°C to obtain a clear solution to which 0.76 g of dopamine hydrochloride (4 mmol) was added and refluxed for 24 h at 120°C. The resulted creamy suspension was filtered and subsequently washed first with toluene and then with chloroform and DI water to give bpd as solid with 90% yield. <sup>31</sup>P NMR (200 MHz, in DMSO-*d*<sub>6</sub>):  $\delta$  -28.71 (s, PPh<sub>2</sub>) ppm. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.79 (t, 2H, NCH<sub>2</sub>*CH*<sub>2</sub>), 3.12 (t,



### Scheme 1. Preparation of ligand (bpd) and MNP@bpd

2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.14 (br d, 4H, CH<sub>2</sub>P), 6.47 (d, 1H, C<sub>6</sub>H<sub>3</sub>), 6.55(s, 1H, C<sub>6</sub>H<sub>3</sub>), 6.72 (d, 1H, C<sub>6</sub>H<sub>3</sub>), 7.43 (br s, 12H, CH), 7.56 (br s, 8H, CH), 9.03, 9.11 (2H, OH). FT-IR in KBr (in cm<sup>-1</sup>): 3124, 2926, 2571, 1628, 1436. Anal. Calcd for  $C_{34}H_{33}NO_2P_2\bullet$ CHCl<sub>3</sub>: C, 62.84; H, 5.12; N, 2.09. Found: C, 62.68; H, 4.85; N, 2.32.

**Synthesis of MNP@bpd.** The magnetite nanoparticles (MNPs) were functionalized (Scheme 1) by modifying a reported procedure [34] as follows: 200 mg of MNPs were suspended in 10 mL anhydrous CHCl<sub>3</sub> to which a solution containing 200 mg of bis(diphenylphosphinomethyl) dopamine in anhydrous methanol was added under argon. The mixture was sonicated for 6 h. The **MNPs@bpd** were collected with the help of a strong magnet after washing repeatedly with methanol.

**Catalytic hydroformylation reaction. MNP@bpd.** 30 mg of **MNP@bpd** with 1 mmol of the appropriate substrate were placed in anhydrous tetrahydrofuran (THF) in a 45 mL Teflonlined autoclave. [Rh(NBD)Cl]<sub>2</sub> (0.003 mmol, 1.3 mg) was added to this solution under argon. The sealed autoclave was purged 3 times with *syngas* (1:1 CO and H<sub>2</sub>), pressurized at 200 psi and kept at 90°C for 16 h. After cooling to room temperature, the catalyst was magnetically separated, washed five times with dichloromethane (5 X 4 mL) and preserved for use in subsequent cycles. The products were passed through short silica gel column and injected into GC and GC-MS for identification.

### **Results and discussion**

Synthesis: The magnetic nanoparticles were prepared by coprecipitation using Fe(II) and Fe(III) precursors in a 1:2 molar ratio. The medium of the reaction was made alkaline using concentrated ammonium hydroxide, and the pH was kept constant at 9 for 4 hours [33]. The black solid material was collected using a strong magnet after repeated washing with water to remove unreacted iron precursors. The surface of the MNPs was decorated with functionalized dopamine bound via its hydroxyl groups. The dopamine was phosphinomethylated using a straightforward reaction with a quantitative yield [35, 36]. The first step of this reaction was to prepare the phosphinoalcohol from the reaction of diphenylphosphine and paraformaldehyde in dry toluene under heating at 120°C for 4 h, until the turbid solution became clear (Scheme 1). In this reaction, equimolar amounts of dopamine hydrochloride were added in situ into the reaction system, which was boiled at 120°C for another 24 h. A sticky solid was precipitated and after drying under vacuum, a cream-colored solid was obtained with 90% yield. The obtained bpd ligand in anhydrous methanol was sonicated with the suspended solution of MNPs in chloroform for 6 h and produced a light black powder after repeated washing with methanol.



Fig. 1 TEM images of a)  $Fe_3O_4$  and b)  $Fe_3O_4$ @bpd in same magnification c) particle size distribution curve

**Characterization.** The bis(diphenylphosphinomethylated) ligand was characterized by nuclear magnetic resonance (NMR) spectroscopy in deuterated dimethyl sulfoxide (DMSO-



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### d<sub>6</sub>).

Fig. 2 HRTEM images of a)  $Fe_3O_4@bpd$  b) selected area diffraction (SAED) in set c) interplaner distances are 0.306 and 0.214 nm corresponding to (220) and (400) planes.

In the <sup>1</sup>H NMR spectrum, the shift ( $\delta$ ) of the CH<sub>2</sub>-P proton occurred at 4.14 ppm, and the presence of the ethylene side chain was confirmed by the alkyl proton shifts at 2.79 and 3.12 ppm. The <sup>31</sup>P NMR spectrum exhibited a shift at -28.71 ppm, which was consistent with the data in the literature [10, 37-38] (Supporting information). TEM images reveal spherical-shaped and uniformly distributed particles (Figs 1a and 1b) with average diameters between 5-7 nm. High-resolution TEM (HRTEM) images are shown in figure 2.



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Fig. 3 XRD pattern of the a)  $Fe_3O_4$  and b)  $Fe_3O_4$  (**bpd**)

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M<sub>s</sub> (emu/g)

60.17

55.58

The higher order of crystallinity in the synthesized nanoparticles containing the ligand was evidenced from the Selected Area Diffraction Pattern (SADP) (Fig 2b) and the high resolution fringes (Fig 2c). The crystalline nature of the

energy levels (keV). The presence of bpd on the surface of the MNPs was further characterized by Fourier transform infrared

*M*<sub>r</sub> (emu/g)

0.658

 $H_c$  (Oe)

a		Fe₃O₄ Fe₃O₄@bpd	3.97 2.98	
			sı tı M a c d	
	•	Spectrum 2	fegO46i Citeration Cit	
0 0.5 1 1.5 2 2.5 3 3.5	4 4.5 5 5.5 6 6.5 7 7.5	8 8.5	Car	

pectroscopy (FT-IR). The ransmittance spectra of MNPs, bpd, and MNPs@bpd re shown in Fig 5. All of the haracteristic peaks of the lopamine compound were bserved; including the strong ppearance of the Fe-O ibration shift at 593 cm<sup>-1</sup> from he parent's MNPsat 587 cm<sup>-1</sup>. he presence of 2933 cm<sup>-1</sup> aromatic C-H stretching), as vell as the 1630  $\text{cm}^{-1}$  and 1431  $m^{-1}$ bands (Fig.5c) clearly lemonstrated the anchoring of the phosphinylated dopamine the surface of MNPs. on Thermal gravimetric analysis (TGA) study was conducted to investigate the thermal stability

Fig. 4 Elemental mapping of a) iron b) phosphorous of and c)rhodium and d) EDX spectra of  $Fe_{3}O_{4}$ @bpd after the catalytic reaction and e) solid  $Fe_{3}O_{4}$  f) solid  $Fe_{3}O_{4}$ @bpd in presence of magnet

MNP@bpd was further ascertained from their XRD signature (Fig. 3) The XRD peaks at 20=30.20°, 35.70°, 43.10°, 53.40°, 57.10° and 63.20° and the corresponding indices are marked against the peaks. All observed peaks can be indexed within cubic spinel structure, in agreement with JCPDS card No. 19-629. No additional peaks were detected thus confirming the high purity of the formed MNPs, without the presence of any other oxide or hydroxide phase(s). The broad diffraction peaks confirmed the nanocrystalline nature of the material [39-40]. Rietveld refinements of XRD patterns confirm the purity of the formed spinel cubic structure. The refined parameters are in table 1 and it can be noticed that the value of crystallite size is around 7-8 nm, in excellent agreement with the value (5-7 nm) determined from TEM observations (Supporting information) and this data is further supported by the particle size distribution data (Fig. 1c). However, the value of microstrain increases from 0.160% for Fe<sub>3</sub>O<sub>4</sub> to 0.421% for MNP@bpd, which is due to the ligand surrounding Fe<sub>3</sub>O<sub>4</sub>. The uniform anchoring of the bpd ligand on the surface of nanoparticles were demonstrated by the Energy Dispersive x-ray Spectroscopy (EDX) elemental mapping shown in Fig. 4. It was revealed that the phosphorous containing ligand and their subsequent rhodium complexes obtained after the catalytic reaction were distributed homogeneously on the surface of the MNPs. However, figure 4d exhibited the EDX spectrum from the same area and marked the Rh at its designated

and the strong attachment of the organic ligand on the MNPs surface (Supporting information). The data showed that the weight loss at temperatures  $\leq$  100°C can be associated with the loss of water molecules [34]. The largest weight loss (~9%) occurred between 200 and ~450°C and could be attributed to the elimination of ligands from the surface, in few steps. The amount of bpd ligand on the surface was measured by correlation with the phosphorus content.



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Fig. 5 FT-IR spectrum of a) **bpd** b)  $Fe_3O_4$  c) **Fe\_3O\_4@bpd** with KBr pallet

The ICP data yielded approximately 0.39 mmol phosphine/g of the functionalized nanoagents. This amount of phosphine loading on the surface of magnetite was very high compared to the literature data [31, 32]. This can be attributed to the smaller size and less sterically hindered ligand and thereby occupying less area on the surface; thus, a larger number of ligands were able to bind through the phenolic oxygen to the Fe<sub>3</sub>O<sub>4</sub>. The possibility of leaching out of P and Rh was examined via ICP-MS measurements, the amount of **bpd** ligand remained unchanged and no Rh in the solution was traceable in early stages. This was corroborated by their ability to convert styrene completely into the corresponding formylated product in the 1<sup>st</sup> cycle. However, there was a significant (~35%) loss of from the MNP@bpd at the end of 7<sup>th</sup> cycle, due likely to successive leaching.

Magnetization-field (M-H) curves recorded at room temperature are illustrated in Fig 6. It can be clearly observed a superparamagnetic behavior for both samples. However, the presence of very small paramagnetic component (saturation cannot be reached) which was deduced using MicroMag software was observed. The magnetic parameters determined from M-H after removal of paramagnetic phase are reported in Table 1. It can noticed that the value of corecivity ( $H_c$ ) is very small within the range 3.97-2.98 Oe, while the remanence ( $M_r$ ) decreases slightly from 0.802 emu/g for Fe<sub>3</sub>O<sub>4</sub> to 0.658 emu/g for **MNP@bpd**. Similarly to the remanence, the saturation magnetization (Ms) reduces slightly by 5 emu/g for Fe<sub>3</sub>O<sub>4</sub> and **MNP@bpd**. The above changes are attributed to the attached bpd ligand on the surface of MNPs.

Table 1. Magnetic properties obtained from magnetisation-field (M-H) curves

Catalysis: The catalytic hydroformylation reaction was carried out on a series of olefins (table 2) in the presence of the syngas at different temperatures in a sealed autoclave pressured to 200 psi. From Table 2, it is clear that the catalyst was very active and selective toward linear aldehydes in the low temperature regime. A reversal of the selectivity was observed at high temperatures for styrene, reaching ~1.5. For example, when the catalytic reaction was run at room temperature (RT) and 50 °C for 24 hours using RhCl<sub>3</sub> as the metal precursor with styrene as the substrate in dry toluene, 35% and 100% conversion were observed with selectivities of 0.20 and 0.47 for linear and branched aldehyde, respectively. When the reaction was carried out at 120°C, the linear aldehyde (a desired product was the major product. In this reaction, a moderate amount (about 20%) of hydrogenated product was also observed, which could be attributed to the lower solubility of RhCl<sub>3</sub> in toluene This effect can mitigate the entrance of olefins into the

hydroformylation catalytic cycles. Significant changes were observed when dimeric Rh(NBD) in freshly distilled THF was used; the latter is considered as a good solvent for hydroformylation over hydrogenation because it has been reported to have led to formulation of desired products at  $90^{\circ}C$  [32].



Fig. 6 Magnetic hysteresis loops of the  $Fe_3O_4$  and  $Fe_3O_4$  **@bpd** at room temperature with 1 tesla magnet

The catalyst amount was optimized for the 1 mmol of substrate. In lower amount of catalyst (*ca* 15 mg) the 10-20 % hydrogenated product was resulted from the hydroformylation product. As the catalyst amount was increased to 30 mg, exclusively hydroformylated product was observed; these conditions (30 mg of catalyst loading and 200 psi applied pressure) are lower and hence, more benign than those reported in the literature for a similar system [31]. A series of substituted styrene were studied for the activity of the catalyst toward electron-withdrawing and electrondonating groups in different positions of the aromatic ring. However, no significant differences were observed and [26] and the

# Table 2. Hydroformylation<sup>a</sup> of olefins using **MNP@bpd** with the pressure of 200 psi using [Rh(NBD)Cl]<sub>2</sub> as metal precursor

result was in conformity with entries 5 and 7 in Table 2. In addition, the reactivity of 3-nitro styrene, entry 8, was found be comparatively higher in selectivity among the series at the same temperature.



Substrate	Time	Solv.	Temp	Conv <sup>b</sup>	L	В	Ratio <sup>℃</sup>
	(h)		(°C)	(%)			(L:B)

1 <sup>d</sup>	Styrene	24	Tol	RT	35	6	29	0.2
2 <sup>d</sup>	Styrene	24	Tol	50	100	32	68	0.47
3 <sup>d</sup>	Styrene	20	THF	120	100	60	40	1.50
4	Styrene	22	THF	90	100	48	52	0.92
5	4-	19	THF	90	100	50	42	1.19
	Methylstyrene							
6	4-Vinylanisole	18	THF	90	100	46	54	0.85
7	4-	18	THF	90	100	56	44	1.27
	Chlorosyrene							
8	3-Nitrostyrene	16	THF	90	100	57	43	1.32
9	2-	24	THF	90	8			
	Bromostyrene							
10	1-Octene	24	THF	90	100	49	15	3.26
11 <sup>e</sup>	Styrene	24	THF	90	27	14	13	1.07

<sup>a</sup>1 mmol of styrene in 10 mL anhydrous solvent under 200 psi pressure in

presence of syn gas (CO:H $_2$  1:1) using 30 mg of catalyst

<sup>b</sup>determined by GC

<sup>c</sup>determined by GC-MS

<sup>d</sup> with RhCl<sub>3</sub>

<sup>e</sup>in presence of MNP@bpd but without Rh metal

Surprisingly, the conversion of 2-bromostyrene was very low in same condition. This was may be due to the bigger size of the bromide adjacent to the alkene reaction site hinder olefin to coordinate with the metal to form saturated 18e species in the reaction cycle. The nanocatalysts were recycled after washing several times to remove all of the materials present after the first round of catalysis, by keeping a magnet at the bottom. The nanocatalyst was very active, even after the seven round at the same temperature, pressure and duration and it was demonstrated that with the use of 30 mg of catalyst, MNP@bpd, and the corresponding amount of [Rh(NBD)Cl]<sub>2</sub>, the selectivity ratio was 0.92, and this trend existed until the second round of the reaction. However, after the 3<sup>rd</sup> rounds, the selectivity was reversed for unknown reasons. The catalyst activity was investigated towards linear olefin as well; for example, the conversion of 1-Octene, was complete (Table 2, entry #10), the linear to branched ratio, reaching a value of about 3.26. Moreover, ca. 36% of the product contained isoalkene and its hydrogenated analogue (n-alkane), comparable with the data reported by Sharma and Jasra [41]. For comparison, the conversion of syngas and/or styrene by Rh-free MNP@bpd was found to be about 27% without any selectivity towards transformation into linear-to-branch aldehyde or otherwise.

### Conclusion

In conclusion, we demonstrated the synthesis of a new bis(diphenylphosphinomethyl) dopamine ligand and the anchoring of these ligand to magnetic nanoparticles through its phenolic hydroxide groups. The loading of the organic ligand on the surface of nanoparticles was found to be high. These nanomaterials exhibited high catalytic activity toward the conversion of alkenes to aldehydes; the reactions reached the maximum (100%) with a low *syngas* pressure. The recyclability was tested with the catalyst on styrene as the substrate, and it was found that even after seven cycles, without the addition of further Rh(I), the catalyst was

persistently active. The material was thermally stable even at high temperatures. We believe that this new material is therefore applicable for industrial catalytic hydroformylation process, and that it may find many more applications in catalysis, a few of which are currently under study in our lab.

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