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# Iridium and rhodium "PNP" aminodiphosphine complexes used as catalysts in the oxidation of styrene

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Six PNP or aminodiphosphine ligands were synthesized and complexed to the transition metals iridium and rhodium to give  $[(\eta^5-C_5Me_5)MCl\{\eta^2-P,P'-(PPh_2)_2NR\}]PF_6$ , where M= Ir (1) and Rh (2) and R= cyclohexyl (a), *iso*-propyl (b), pentyl (c), phenyl (d), chlorophenyl (e) and methoxyphenyl (f). These complexes were fully characterized by NMR, elemental analyses and IR spectroscopy. Crystals of 1f and 2f were obtained, which showed a distorted octahedral geometry around the metal centers. These complexes showed good activity in the oxidation of styrene using *tert*-butyl hydroperoxide (TBHP) as the oxidant. The iridium complexes were more active than the rhodium complexes. Higher yields to benzaldehyde were achieved in comparison to styrene oxide for all catalysts.

Keywords: Aminodiphosphine; iridium; rhodium; styrene; oxidation

# 1. Introduction

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Significant quantities of feedstock, towards cheap starting materials, can be obtained from oils, which at present are burnt as fuel in the transport industry.<sup>1</sup> The oxidation of hydrocarbons provides a costeffective method of converting these starting materials into bulk chemicals and is an important transformation in the production of fine chemicals.<sup>1</sup> The oxidation of alkenes to their corresponding epoxides and carbonyl compounds is important in the synthesis of fine and pharmaceutical grade chemicals.<sup>2-14</sup> Epoxides are important building blocks and are used as intermediates and precursors for chemical production and in the preparation of resins and drugs.<sup>9</sup> Benzaldehyde is the second most important aromatic molecule and has a widespread application in the agro chemical industries and synthesis of dyes and perfumes.<sup>7</sup> The over-oxidation of benzaldehyde results in the formation of benzoic acid which is important in the food industry as a preservative inhibiting the growth of mould, yeast and bacteria.<sup>15</sup> Transition metal-based systems are able to catalyze epoxidation reactions,<sup>16</sup> and the choice of catalyst and oxidant can modify the course of the reaction.<sup>17</sup> For selective epoxidation, a suitable ligand system is required which is able to control the catalytic behaviour.<sup>17</sup> One such system could include the bi-dentate or multidentate aminodiphosphine or "PNP" ligands, which have been used extensively in ethylene oligomerization studies.<sup>18-24</sup> The use of cobalt complexes with these ligands in the oxidation of *n*-octane was recently reported.<sup>25</sup> These ligands are part of a system that displays high activity, stability and variability, which makes them ideally suited for catalytic applications.<sup>26-28</sup> The activity of the metal can be tailored through the modification of the ligand backbone, by using different donor substituents or central anionic atoms. The ligand then places a high demand on the stereochemistry of the complex allowing the reactions of the metal ions to be selective.29,30

In this study, a new approach has been undertaken in using iridium and rhodium aminodiphosphine complexes in the oxidation of styrene. One of the early studies was carried out by Collman and coworkers in 1967 using IrI(CO)(PPh<sub>3</sub>)<sub>2</sub> in the oxidation of cyclohexene.<sup>31</sup> In the early 1970's iridium and rhodium compound catalysed olefin epoxidation was carried out using simple organic salts, which performed poorly when compared to the Wacker palladium oxidation.<sup>32,33</sup> Since then, less attention has been paid to these transition metals.<sup>32-35</sup> More recently, Turlington and coworkers used half sandwich Ir complexes in the oxidation of styrene obtaining an 11% yield to benzaldehyde and phenyacetaldehyde.<sup>36</sup>



Figure 1. General structure of the complexes used as catalysts in the oxidation of styrene. (M=Ir (1) and Rh (2); R= cyclohexyl (a), *iso*-propyl (b), pentyl (c), phenyl (d), chlorophenyl (e) and methoxyphenyl (f);  $Cp^* = \eta^5$ - pentamethylcyclopentadienyl).

We herein report the synthesis and characterization of some new iridium (1) and rhodium (2) aminodiphosphine complexes and their application in the catalytic oxidation of styrene. Optimization of solvent (acetonitrile (MeCN) and dichloroethane (DCE), oxidants

(*tert*-butyl hydroperoxide (TBHP), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), *N*-methyl morpholine *N*-oxide (NMO)) and temperature (room temperature (RT), 50 °C and 80 °C) were carried out. The substituents on the nitrogen atom were varied by making use of six different types of functional groups (Fig. 1), with the intention of observing if these groups have an effect on the catalytic activity and selectivity to the products of oxidation.

# 2. Experimental

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#### 2.1 Synthesis and characterization of the compounds

All experiments were performed using standard Schlenk techniques under inert conditions in moisture free reaction glassware with anhydrous solvents. All solvents were analytical grade. To render the reaction glassware moisture free, it was heated with a heat gun, followed by cycles of vacuum and nitrogen pressure. The solvents utilized were dry unless otherwise stated. Diethyl ether and hexane were distilled from sodium benzophenoneketyl under nitrogen. Dichloromethane (DCM) was distilled from P2O5 and methanol from magnesium turnings. Deuterated solvents were used as received and stored in a desiccator. The NMR spectra were recorded at 400 MHz (<sup>1</sup>H), 100 MHz (<sup>13</sup>C) and 162 MHz (<sup>31</sup>P) using a Bruker Ultrashield 400 MHz spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C $\{^{1}H\}$  NMR chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. <sup>1</sup>H NMR and <sup>13</sup>C $\{^{1}H\}$  NMR signals were referenced to the residual hydrogen and carbon signal of DMSO. (2.50 ppm) and (39.52 ppm), respectively. <sup>31</sup>P NMR chemical shifts are reported in parts per million (ppm) from triphenylphosphine (-17.6 ppm). The 2D <sup>103</sup>Rh and <sup>31</sup>P NMR spectrum of compound 2c was recorded using a Bruker Ultrashield 500 MHz spectrometer. The FT-IR spectra were recorded using a Perkin Elmer Universal Attenuated Total Reflection (ATR) sampling accessory attached to an FT-IR series 100 spectrometer. The HRMS was recorded on a Waters Micromass LCT Premier TOF-MS. All PNP ligands were synthesized with modification of literature procedure.<sup>20</sup> The precursors [{MCl<sub>2</sub>Cp\*}<sub>2</sub>] (where M = Ir or Rh and Cp\* =  $\eta^5$ pentamethylcyclopentadienyl) were prepared according to reported procedures.37-39

Synthesis of  $[Ph_2PN(C_6H_{11})PPh_2]IrCp^*(Cl)]^+PF_6^-$  (1a). The synthesis was adapted from a known procedure.<sup>40</sup> To a 100 ml twoneck round bottom flask, acetone (6 ml) was added and purged with argon for 10 minutes. Thereafter, [Ph<sub>2</sub>PN(C<sub>6</sub>H<sub>11</sub>)PPh<sub>2</sub>] (0.250 mmol, 0.12 g) was added. Once completely dissolved,  $[{IrCl_2Cp^*}_2]$ (0.125 mol, 0.10 g) and NH<sub>4</sub>PF<sub>6</sub> (0.250 mmol, 0.04 g) were added to the flask, followed by the addition of methanol (12 ml). The yellow solution was allowed to stir for 6 h, after which DCM was added. The solution was then filtered through celite and the solvent was reduced to 2 ml. Upon addition of diethyl ether a yellow precipitate formed, which was filtered using a Hirsch funnel. The yellow powder was dried overnight in vacuo. Crystals were grown from diethyl ether and dichloromethane. Yield: 78%, 0.19 g. Melting point: 295-296 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 762 (w) (CH<sub>2n</sub> rocking); 827 (s)  $(PF_6)$ ; 938 (m) (P-N); 1071 (m) (cyclohexyl ring vibrations); 1436 (m) (PPh<sub>2</sub>). Anal. % Calcd for C<sub>40</sub>H<sub>46</sub>ClF<sub>6</sub>IrNP<sub>3</sub>: C: 49.3%; H: 4.8%; N: 1.4%. Found: C: 49.6%; H: 4.8%; N: 1.6%. HRMS (ESI)

Calcd for C<sub>40</sub>H<sub>46</sub>ClIrNP<sub>2</sub> 830.2423 . Found: 830.2417 NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR δ 0.87-1.43 (m, 10H, cyclohexyl ring); δ 1.52 (s, 15H, Cp\*); δ 3.59-3.69 (m, 1H, (cyclohexyl ring)); δ 7.44-7.77 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.28 (Cp\*); δ 33.82 (cyclohexyl ring); δ 24.30-24.94 (cyclohexyl ring); δ 127.51-133.39 (aromatic); δ 64.57 (cyclohexyl ring). <sup>31</sup>P NMR δ -152.99 – -131.04 (PF<sub>6</sub>); δ 34.50.

**Synthesis** of [[Ph<sub>2</sub>PN(C<sub>3</sub>H<sub>7</sub>)PPh<sub>2</sub>]IrCp\*(Cl)]<sup>+</sup>PF<sub>6</sub> (1b). Compound 1b was synthesized according to the procedure described for **1a** except that  $[Ph_2PN(C_3H_7)PPh_2]$  (0.250 mmol, 0.11 g) was used. Yield: 88 %, 0.21 g. Melting point: 270-272 °C. IRvmax  $(ATR)/cm^{-1}$ : 833 (s)  $(PF_6)$ ; 945 (m) (P-N); 1436 (m)  $(PPh_2)$ ; 1482 (w) (CH<sub>3</sub>). Anal. % Calcd for C<sub>37</sub>H<sub>42</sub>ClF<sub>6</sub>IrNP<sub>3</sub>: C: 47.5%; H: 4.5%; N: 1.5%. Found: C: 47.0%; H: 4.3%; N: 2.0%. HRMS (ESI) Calcd for C<sub>37</sub>H<sub>42</sub>ClIrNP<sub>2</sub> 790.2110. Found: 790.2092. NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR  $\delta$  0.94 (d, 6H, (CH<sub>3</sub>)<sub>2</sub>; <sup>2</sup>J = 6.60 Hz);  $\delta$  1.54 (s, 15H, Cp\*); δ 3.91-4.12 (m, 1H, CH); δ 7.41-7.78 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.27 (Cp\*); δ 23.6 (CH<sub>3</sub>)<sub>2</sub>); δ 56.1 (CH); δ 128.31-133.07 (aromatic). <sup>31</sup>P NMR  $\delta$  -154.38 - -131.04 (PF<sub>6</sub>);  $\delta$ 34.89.

Synthesis of  $[[Ph_2PN(C_5H_{11})PPh_2]IrCp^*(Cl)]^+PF_6^-$ (1c). Compound 1c was synthesized according to the procedure described for **1a** except that  $[Ph_2PN(C_5H_{11})PPh_2]$  (0.25 mmol, 0.11 g) was used. Yield: 54 %, 0.13 g. Melting point: 262-263 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 751 (m) (CH<sub>2</sub>); 833 (s) (PF<sub>6</sub>); 999 (m) (P-N); 1437 (m) (PPh<sub>2</sub>); 2930 (w) (CH<sub>3</sub>). Anal. % Calcd for C<sub>39</sub>H<sub>46</sub>ClF<sub>6</sub>IrNP<sub>3</sub>: C: 48.6%; H: 4.8%; N: 1.5%. Found: C: 49.0%; H 4.3%; N 1.6%. HRMS (ESI) Calcd for C<sub>39</sub>H<sub>46</sub>ClIrNP<sub>2</sub> 818.4185. Found: 818.2413. NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR  $\delta$  0.60 (t, 3H, CH<sub>3</sub>; <sup>3</sup>J= 6.78 Hz); δ 0.92-0.97 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>); δ 1.07-1.24 (m, 2H, CH<sub>2</sub>); δ 1.58 (s, 15H, Cp\*); δ 3.36-3.39 (m, 2H, CH<sub>2</sub>); δ 7.35-7.79 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.39 (Cp\*); δ 13.38 (CH<sub>3</sub>); δ 21.26 (CH<sub>2</sub>); δ 28.02 (CH2); & 29.15 (CH2); & 51.59 (CH2); & 128.25-133.34 (aromatic). <sup>31</sup>P NMR  $\delta$  -152.99 – -135.43 (PF<sub>6</sub>); δ 34.19.

**Synthesis of [[Ph<sub>2</sub>PN(Ph)PPh<sub>2</sub>]IrCp\*(Cl)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (1d).** Compound **1d** was synthesized according to the procedure described for **1a** except that [Ph<sub>2</sub>PN(Ph)PPh<sub>2</sub>] (0.25 mmol, 0.12 g) was used. Yield: 77 %, 0.19 g. Melting point: 249-251 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 827 (*s*) (PF<sub>6</sub>); 946 (*m*) (P-N); 1439 (*m*) (PPh<sub>2</sub>); 1494 (*w*) (Ph). Anal. % Calcd for C<sub>40</sub>H<sub>40</sub>ClF<sub>6</sub>IrNP<sub>3</sub>: C: 49.6%; H: 4.2%; N: 1.4%. Found: C: 49.1%; H: 4.0%; N: 2.9%. HRMS (ESI) Calcd for C<sub>40</sub>H<sub>40</sub>ClIrNP<sub>2</sub> 824.1954. Found: 824.1945. NMR: (400 MHz.; DMSO): <sup>1</sup> H NMR δ 1.56 (s, 15H, Cp\*); δ 6.64 (d, 2H, CH; <sup>2</sup>*J*= 7.53 Hz); δ 7.14-7.21 (m, 3H, CH); δ 7.41-7.77 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.25 (Cp\*); δ 124.08-133.54 (aromatic). <sup>31</sup>P NMR δ -152.99 – -135.43 (PF<sub>6</sub>); δ 35.84

Synthesis of  $[[Ph_2PN(C_6H_4Cl)PPh_2]IrCp^*(Cl)]^+PF_6^-$  (1e). Compound 1e was synthesized according to the procedure described for 1a except that  $[Ph_2PN(C_6H_4Cl)PPh_2]$  (0.25 mmol, 0.12 g) was used. Yield: 83%, 0.21 g. Melting point: 237-239 °C.  $IRv_{max}$ (ATR)/cm<sup>-1</sup>: 827 (s) (PF<sub>6</sub>); 900 (m) (P-N); 1439 (m) (PPh\_2); 1494 (w) (Ph\_2). Anal. % Calcd for  $C_{40}H_{39}ClF_6IrNP_3$ : C: 47.9%; H: 3.9%; Published on 15 March 2016. Downloaded by New York University on 23/03/2016 13:34:52

N: 1.4%. Found: C: 48.2%; H: 4.1%; N: 1.6%. HRMS (ESI) Calcd for C<sub>40</sub>H<sub>39</sub>Cl<sub>2</sub>IrNP<sub>2</sub> 858.1564. Found: 858.1555. NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR δ 1.55 (s, 15H, Cp\*); δ 6.63 (d, 2H, CH; <sup>2</sup>*J*= 8.84 Hz); δ 7.28 (m, 2H, CH; <sup>2</sup>*J*= 8.88 Hz); δ 7.42-7.79 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.83 (Cp\*); δ 125.46 -133.67 (aromatic). <sup>31</sup>P NMR δ -152.99 - -135.43 (PF<sub>6</sub>); δ 37.05

Synthesis [[Ph<sub>2</sub>PN(C<sub>7</sub>H<sub>7</sub>O)PPh<sub>2</sub>]IrCp\*(Cl)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> of (1f). Compound 1f was synthesized according to the procedure described for 1a in that [Ph<sub>2</sub>PN(C<sub>7</sub>H<sub>7</sub>O)PPh<sub>2</sub>] (0.25 mmol, 0.12 g) was used. Yield: 87%, 0.22 g. Melting point: 239-242 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 832 (s) (PF<sub>6</sub>); 951 (m) (P-N); 1234 (m) (aromatic ether); 1437 (m) (PPh<sub>2</sub>); 1506 (w) (Ph<sub>2</sub>). Anal. % Calcd for C<sub>41</sub>H<sub>42</sub>ClF<sub>6</sub>IrNOP<sub>3</sub>: C: 49.3%; H: 4.2%; N: 1.4%. Found: C: 49.0%; H 3.8%; N 1.7%. HRMS (ESI) Calcd for C<sub>40</sub>H<sub>42</sub>ClIrNOP<sub>2</sub> 854.2059. Found: 854.2033. NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR δ 1.59 (s, 15H, Cp\*);  $\delta$  3.66 (s, 3H, CH<sub>3</sub>);  $\delta$  6.60 (d, 2H, CH; <sup>2</sup>J= 8.84 Hz);  $\delta$  6.78 (d, 2H, CH;  ${}^{2}J=9.00$  Hz);  $\delta$  7.31-7.78 (m, 20H, aromatic).  ${}^{13}C$  NMR δ 8.34 (Cp\*); δ 55.34 (CH<sub>3</sub>); δ 128.21 -133.42 (aromatic). <sup>31</sup>P NMR δ-152.99 - -135.43 (PF<sub>6</sub>); δ 37.05.

Synthesis of  $[[Ph_2PN(Cy)PPh_2]RhCp^*(Cl)]^+PF_6^-$  (2a). The synthesis was adapted from a known procedure.<sup>40</sup> To a 100 ml twoneck round bottom flask, acetone (6 ml) was added and purged with argon for 10 minutes. Thereafter, [Ph<sub>2</sub>PN(Cy)PPh<sub>2</sub>] (0.250 mmol, 0.12 g) was added. Once completely dissolved,  $[{RhCl_2Cp^*}_2]$ (0.125 mol, 0.08 g) and NH<sub>4</sub>PF<sub>6</sub> (0.250 mmol, 0.04 g) were added to the flask, followed by the addition of methanol (12 ml). The yellow solution was allowed to stir for 6 h, after which DCM was added. The solution was then filtered through celite and the solvent was reduced to 2 ml. Upon addition of diethyl ether an orange precipitate formed, which was filtered using a Hirsch funnel. The orange powder was dried overnight in vacuo. Crystals were grown from diethyl ether and dichloromethane. Yield: 90%, 0.20 g. Melting point: 256-258 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 762 (w) (CH2<sub>n</sub> rocking); 829 (s)  $(PF_6)$ ; 905 (m) (P-N); 1063 (m) (cyclohexyl ring vibrations); 1435 (m) (PPh<sub>2</sub>). Anal. % Calcd for C<sub>40</sub>H<sub>46</sub>ClF<sub>6</sub>RhNP<sub>3</sub>: C: 54.2%; H: 5.2%; N: 1.6%. Found: C: 54.0%; H 5.2%; N 1.8%. HRMS (ESI) Calcd for C40H46ClRhNP2 740.1849 . Found: 740.1851 NMR: (400MHz; DMSO): <sup>1</sup>H NMR δ 1.04-1.42 (m, 10H, cyclohexyl ring); δ 1.48 (s, 15H, Cp\*); δ 3.63-3.72 (m, 1H, (cyclohexyl ring)); δ 7.43-7.80 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.78 (Cp\*); δ 24.27-33.87 (cyclohexyl ring); δ 128.13-133.44 (aromatic); δ 64.57 (cyclohexyl ring). <sup>31</sup>P NMR  $\delta$  -152.99 – -131.04 (PF<sub>6</sub>);  $\delta$  67.62 (d).

Synthesis of  $[[Ph_2PN(C_3H_7)PPh_2]RhCp^*(Cl)]^+PF_6^-$  (2b). Compound 2b was synthesized according to the procedure described for 2a in that  $[Ph_2PN(C_3H_7)PPh_2]$  (0.13 mmol, 0.05 g) was used. Yield: 94%, 0.09 g. Melting point: 242-244 °C.  $IRv_{max}$  (ATR)/cm<sup>-1</sup>: 834 (*s*) (PF<sub>6</sub>); 949 (*m*) (P-N); 1436 (*m*) (PPh<sub>2</sub>); 1482 (*w*) (CH<sub>3</sub>). Anal. % Calcd for  $C_{37}H_{42}ClF_6RhNP_3$ : C: 52.5%; H: 5.0%; N: 1.7%. Found: C: 53.0%; H: 5.0%; N: 2.2%. HRMS (ESI) Calcd for  $C_{37}H_{42}ClRhNP_2$  700.1536. Found: 700.1530. NMR: (400 Mhz.; DMSO): <sup>1</sup>H NMR δ 0.94 (d, 6H, (CH<sub>3</sub>)<sub>2</sub>; <sup>2</sup>J= 6.64 Hz); δ 1.48 (s, 15H, Cp\*); δ 4.05-4.19 (m, 1H, CH); δ 7.40-7.98 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.80 (Cp\*); δ 23.77 (CH<sub>3</sub>)<sub>2</sub>); δ 55.6 (CH); δ 128.14-133.37 (aromatic). <sup>31</sup>P NMR  $\delta$  -154.38 - -131.04 (PF<sub>6</sub>);  $\delta$  67.79 (d).

of  $[[Ph_2PN(C_5H_{11})PPh_2]RhCp*(Cl)]^+PF_6^-$ Synthesis (2c). Compound 2c was synthesized according to the procedure described for **2a** in that  $[Ph_2PN(C_5H_{11})PPh_2]$  (0.25 mmol, 0.13 g) was used. Yield: 95 %, 0.21 g. Melting point: 240-242 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 750 (m) (CH<sub>2</sub>); 834 (s) (PF<sub>6</sub>); 999 (m) (P-N); 1436 (m) (PPh<sub>2</sub>); 2960 (w) (CH<sub>3</sub>). Anal. % Calcd for C<sub>39</sub>H<sub>46</sub>ClF<sub>6</sub>RhNP<sub>3</sub>: C: 53.6%; H: 5.3%; N: 1.6%. Found: C: 53.8%; H: 4.9%; N: 2.0%. HRMS (ESI) Calcd for C<sub>39</sub>H<sub>46</sub>ClRhNP<sub>2</sub> 728.1849. Found: 728.1849. NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR δ 0.59 (t, 3H, CH<sub>3</sub>; <sup>3</sup>J= 6.74 Hz); δ 0.89-0.97 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>); δ 1.07-1.20 (m, 2H, CH<sub>2</sub>); δ 1.52 (s, 15H, Cp\*); δ 3.36-3.39 (m, 2H, CH<sub>2</sub>); δ 7.34-7.79 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.94 (Cp\*); δ 13.38 (CH<sub>3</sub>); δ 21.26 (CH<sub>2</sub>); δ 27.98 (CH<sub>2</sub>); δ 29.24 (CH<sub>2</sub>); δ 50.68 (CH<sub>2</sub>); δ 128.27-132.94 (aromatic). <sup>31</sup>P NMR δ -152.99 - -135.43 (PF<sub>6</sub>); δ 67.07 (d).

**Synthesis of [[Ph<sub>2</sub>PN(Ph)PPh<sub>2</sub>]RhCp\*(Cl)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (2d).** Compound **2d** was synthesized according to the procedure described for **2a** except that [Ph<sub>2</sub>PN(Ph)PPh<sub>2</sub>] (0.25 mmol, 0.12 g) was used. Yield: 77 %, 0.19 g. Melting point: 249-251 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 827 (*s*) (PF<sub>6</sub>); 941 (*m*) (P-N); 1439 (*m*) (PPh<sub>2</sub>); 1494 (*w*) (Ph<sub>2</sub>). Anal. % Calcd for C<sub>40</sub>H<sub>40</sub>ClF<sub>6</sub>RhNP<sub>3</sub>: C: 54.6%; H: 4.6%; N: 1.6%. Found: C: 54.9%; H: 4.5%; N 1.2%.HRMS (ESI) Calcd for C<sub>40</sub>H<sub>40</sub>ClRhNP<sub>2</sub> 734.1380. Found: 734.1368 . NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR δ 1.54 (s, 15H, Cp\*); δ 6.65-6.67 (d, 2H, CH); δ 7.18-7.19 (m, 3H, CH); δ 7.41-7.78 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.83 (Cp\*); δ 124.99-133.40 (aromatic). <sup>31</sup>P NMR δ -152.99 - -135.43 (PF<sub>6</sub>); δ 68.42 (d).

**Synthesis of [[Ph<sub>2</sub>PN(C<sub>6</sub>H<sub>4</sub>Cl)PPh<sub>2</sub>]RhCp\*(Cl)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (2e).** Compound **2e** was synthesized according to the procedure described for **2a** except that [Ph<sub>2</sub>PN(C<sub>6</sub>H<sub>4</sub>Cl)PPh<sub>2</sub>] (0.25 mmol, 0.12 g) was used. Yield: 87%, 0.20 g. Melting point: 223-225 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 827 (*s*) (PF<sub>6</sub>); 901 (*m*) (P-N); 1439 (*m*) (PPh<sub>2</sub>); 1494 (*w*) (Ph<sub>2</sub>). Anal. % Calcd for C<sub>40</sub>H<sub>39</sub>ClF<sub>6</sub>RhNP<sub>3</sub>: C: 52.5%; H: 4.3%; N: 1.5%. Found: C: 52.3%; H: 4.6%; N: 2.0%. HRMS (ESI) Calcd for C<sub>40</sub>H<sub>39</sub>Cl<sub>2</sub>RhNP<sub>2</sub> 768.0990. Found: 768.0995. NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR δ 1.51 (s, 15H, Cp\*); δ 6.65 (d, 2H, CH; <sup>2</sup>*J*= 8.92 Hz); δ 7.28 (d, 2H, CH; <sup>2</sup>*J*= 6.88 Hz); δ 7.42-7.76 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.83 (Cp\*); δ 128.38-133.54 (aromatic). <sup>31</sup>P NMR δ -152.99 - -135.43 (PF<sub>6</sub>); δ 69.69 (d).

**Synthesis of [[Ph<sub>2</sub>PN(C<sub>7</sub>H<sub>7</sub>O)PPh<sub>2</sub>]RhCp\*(Cl)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (2f). Compound <b>2f** was synthesized according to the procedure described for **2a** in that [Ph<sub>2</sub>PN(C<sub>7</sub>H<sub>7</sub>O)PPh<sub>2</sub>] (0.25 mmol, 0.12 g) was used. Yield: 84%, 0.19 g. Melting point: 224-225 °C. IRv<sub>max</sub> (ATR)/cm<sup>-1</sup>: 833 (*s*) (PF<sub>6</sub>); 949 (*m*) (P-N); 1231 (*m*) (aromatic ether); 1436 (*m*) (PPh<sub>2</sub>); 1507 (*w*) (Ph<sub>2</sub>). ). Anal. % Calcd for C<sub>41</sub>H<sub>42</sub>ClF<sub>6</sub>RhNOP<sub>3</sub>: C: 54.1%; H: 4.7%; N: 1.5%. Found: C: 54.5%; H 4.3%; N 1.4%. HRMS (ESI) Calcd for C<sub>40</sub>H<sub>39</sub>ClRhNOP<sub>2</sub> 764.1485. Found: 764.1478. NMR: (400 MHz.; DMSO): <sup>1</sup>H NMR δ 1.56 (s, 15H, Cp\*); δ 3.66 (s, 3H, CH<sub>3</sub>); δ 6.60 (d, 2H, CH; <sup>2</sup>*J*= 8.84 Hz); δ 6.77 (d, 2H, CH; <sup>2</sup>*J*= 9.00 Hz); δ 7.32-7.59 (m, 20H, aromatic). <sup>13</sup>C NMR δ 8.91 (Cp\*); δ 55.34 (CH<sub>3</sub>); δ 128.21 -133.42 (aromatic). <sup>31</sup>P NMR δ -152.99 - -135.43 (PF<sub>6</sub>); δ 69.86 (d).

<b>Table 1.</b> Single crystal structural information of complexes 16	and <b>2f</b>
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Compound	1f	2f
Mol. Formula	C <sub>41</sub> H <sub>42</sub> ClIrNOP <sub>2</sub> ,F <sub>6</sub> P	C41H42CINOP2Rh,F6P
Mol. Weight	999.34	910.03
Temperature (k)	173	173
Wavelength (Å)	Μο Κα (0.71073)	Μο Κα (0.71073)
Crystal symmetry	Monoclinic	Monoclinic
Space Group	P21/c	P21/c
a (Å)	14.0391(9)	14.0480(4)
b (Å)	13.7146(8)	13.7160(6)
c (Å)	21.6343(14)	21.6798(9)
α, β, γ (°)	90, 105.8, 90	90, 105.8, 90
Volume (Å <sup>3</sup> )	4007.4(4)	4017.5(3)
Ζ	4	4
Density (g/m <sup>3</sup> )	1.656	1.505
Absorption coefficient (mm <sup>-1</sup> )	3.580	0.673
F(000)	1984	1856
Crystal size (mm)	0.13 x 0.19 x 0.22	0.12 x 0.15 x 0.18
$\Theta$ range for data collection	1.5, 28.4	4.0, 27.5
Reflection (collected, independent, R <sub>int</sub> )	118247, 10018, 0.080	77581, 9164, 0.103
Observed Data [I > 2.0 sigma(I)]	8191	5603
Nref, Npar	10018, 493	9164, 493
R, wR2, S	0.0274, 0.0612, 1.01	0.0464, 0.1213, 1.03
Largest diff. peak, hole (e.Å <sup>-3</sup> )	0.87, -0.93	0.96, -0.86
No of C— $H \cdots X$ interactions	3	3
No of C-H $\pi$ (Cg-Ring) interactions	2	2
No of $\pi$ $\pi$ (Cg- Cg) interactions	24	24

# 2.2 Crystal structure analysis

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Single-crystal X-ray diffraction data of complex **1f** were collected on a Bruker KAPPA APEX II DUO diffractometer using graphitemonochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection was carried out at 173(2) K (Table 1). Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT.<sup>41</sup> The data were scaled and absorption correction performed using SADABS.<sup>41</sup> The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods based on F<sup>2</sup> using SHELXL-97.<sup>42</sup> X-ray single crystal intensity data of

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complex **2f** were collected on a Nonius Kappa-CCD diffractometer, also using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å at 173 (2) K). Temperature was controlled by an Oxford Cryostream cooling system. The data collection was evaluated using the Bruker Nonius "Collect" program. Data were scaled and reduced using DENZO-SMN software.<sup>43</sup> Absorption correction was performed using SADABS.<sup>41</sup> The program Olex2 was used to prepare molecular graphic images.<sup>44</sup> All non-hydrogen atoms were refined anisotropically. The ADP restraints and the rigid bond restraints were used on all six fluorine atoms. All hydrogen atoms were placed in idealized positions and refined in riding models with U<sub>iso</sub> assigned values 1.2 or 1.5 times those of their parent atoms and the distances of C-H were constrained to 0.95 Å for aromatic hydrogen atoms and 0.98 Å for CH<sub>3</sub>.

#### 2.3 Oxidation of styrene

All reagents were weighed and handled in air. All products were analyzed using a PerkinElmer Auto System gas chromatograph fitted with a Flame Ionisation Detector (FID) set at 290 °C. A Varian DB-5 capillary column (25 m x 0.15 mm x 2 $\mu$ m) was utilized with the injector temperature set at 250 °C. The catalyst to substrate ratio was kept constant at 1:100. A two-necked pear shaped flask was charged with 5 mg of the respective catalyst, benzophenone (as an internal standard), styrene, the respective oxidant and 10 ml of the solvent). The flask was equipped with a reflux condenser, stirred, and heated to the respective temperature. After intervals, an aliquot was removed using a Pasteur pipette and (0.5  $\mu$ l) was injected into the GC and quantified.

## 3. Results and discussion

#### 3.1 Synthesis ad characterization of the compounds

The new complexes (1 and 2) were synthesized by adaptation of a reported general method.<sup>40</sup> The respective PNP ligands were added to (2:1; v/v) methanol:acetone mixtures after which the metal complex precursor and NH<sub>4</sub>PF<sub>6</sub> salt were added. For the iridium complexes (1) a vellow precipitate formed after 1 h of stirring at room temperature, whilst an orange precipitate formed for the rhodium complexes (2). The complexes were characterized by NMR, IR, HRMS and in some cases single crystal x-ray diffraction. A downfield shift is noted in the <sup>31</sup>P NMR spectra of the rhodium complexes compared to the iridium complexes. Furthermore, the <sup>31</sup>P NMR spectra for the rhodium complexes show a doublet resonance at  $\sim 67$  ppm, while a singlet resonance is seen for the iridium complexes at ~34 ppm. This is consistent with literature for rhodium complexes of similar nature.45,46 The substituents on the nitrogen atom (a-f) have very little effect in the shift of the phosphorus peak, as the peak shift is mainly influenced by the phenyl groups on the nitrogen atom, and this is also noted in the v<sub>PPh2</sub> of the free ligand and the complex in the IR spectra. To show the correlation between the phosphorous and Rh metal, a 2D <sup>103</sup>Rh and <sup>31</sup>P NMR HMQC experiment of compound 2c was carried out (Fig. 2). Transition metal NMR has the advantage over normal proton NMR, in that the transition metal nuclei offer very large shielding ranges, therefore there is higher sensitivity to subtle structural perturbations.<sup>47</sup> In this case the phosphorous nuclei were used as a source of polarization

transfer as P is a 100%  $I = \frac{1}{2}$  nucleus with a high receptibility.<sup>48</sup> The  ${}^{2}J({}^{31}P, {}^{103}Rh)$  value was calculated from the routine  ${}^{31}P$  NMR spectrum and is consistent with that shown in literature of similar compounds.<sup>48,49</sup> The *J* coupling constant ( ${}^{2}J = 119.4$  Hz) is due to the fact that two equivalent  ${}^{31}P$  nuclei are present which is consistent with the spectrum shown in Fig. 2.<sup>50</sup> This constant is an indicator of the Rh-P bond strength.<sup>48,51</sup> Bulky ligands, such as the one present in this study, weaken the metal-phosphorous bond, which results in a slightly lower *J* values and is also noted in a series of Rh-P complexes that bear such ligands.<sup>51</sup>



**Figure 2.**  $2D^{103}$ Rh and  ${}^{31}$ P NMR spectrum of compound **2c**.

The HRMS and elemental analyses match those of the calculated values and the sharp melting points indicate that these complexes are pure.

#### 3.2 Description of crystal structures

Yellow and orange crystals of 1f and 2f, respectively, were obtained by vapor diffusion of diethyl ether into a dichloromethane solution. Structural views of complexes 1f and 2f are shown in Fig. 3. The selected interatomic distances and angles for 1f and 2f are listed in Table 2. For both the complexes the iridium/rhodium centers are distorted octahedrally and the chloro group is coordinated perpendicular to the strained four membered chelate ring, whilst the Cp\* ligand is trans to the PNP nitrogen donor. Ir-Cl(1) and Rh-Cl(1) bond lengths are 2.3855(9) Å and 2.3785(9) Å for 1f and 2f, respectively, and are comparable to the corresponding values observed for similar Ir and Rh complexes.45,46 The interatomic distances of Ir…N and Rh…N bonds are 2.942 Å and 2.938 and the P-N-P angles are  $101.02(14)^{\circ}$  and  $101.82(16)^{\circ}$  for 1f and 2f respectively. These findings indicate that the phosphinoamine nitrogen atoms do not bind to the metal ions. In addition, the average P(1)…P(2) distances are 2.633 Å (1f) and 2.646 Å (2f). The P-N bond lengths (~1.70 Å) obtained for compounds 1f and 2f lie in a typical P-N single bond range.45,46,52,53 The Rh-P bond lengths of 2f are 2.2998(9) Å for Rh-P(1), 2.3079(9) Å for Rh-P(2), whilst for 1f the bond length, Ir-P(1) is 2.2916(8) Å and 2.2958(8) Å for Ir-P(2). These are similar to related rhodium and iridium complexes.45,46

The Rh–C(ring) and Ir–C(ring) distances are 2.188(4)-2.231(3) and 2.197(3)-2.245(4) Å, respectively, and again are comparable with those found in other pentamethylcyclopentadienyl compounds of rhodium(III) and iridium(III).<sup>45,46</sup> Although the nitrogen atom of the

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diphosphinoamine ligand is part of a tertiary amine, the nitrogen atoms are located within the plane defined by two phosphorus and an ipso carbon atoms.

Table 2. Selected bond lengths  $(\text{\AA})$  and bond angles (°) of complexes 1f and 2f.

Bond distances (Å)	1f	2f
M-P(1)	2.2916(8)	2.2998(9)
M-P(2)	2.2958(8)	2.3079(9)
M-Cl(1)	2.3855(9)	2.3785(9)
M-Cp*(1-5)	2.245(4), 2.227(3), 2.197(3), 2.237(3), 2.233(3)	2.227(4), 2.214(4), 2.188(4), 2.231(3), 2.220(4)
P(1)-N(1)	1.702(2)	1.703(3)
P(2)-N(1)	1.709(2)	1.706(3)
P(1)-C(11)	1.821(3)	1.821(4)
P(1)-C(17)	1.808(3)	1.819(3)
P(2)-C(30)	1.815(3)	1.813(3)
P(2)-C(36)	1.817(3)	1.819(3)
N(1)-C(23)	1.436(4)	1.449(4)
Bond angles (°)	1f	2f
P(1)-M-P(2)	70.04(3)	70.10(3)
P(1)-N(1)- P(2)	101.02(14)	101.82(16)
P(1)-M-Cl(1)	87.21(3)	87.58(3)
P(2)-M-Cl(1)	84.85(3)	84.96(3)

The nitrogen atom is sp<sup>2</sup>-hybridized. Such hybridization is occasionally found in compounds with a P–N bond.<sup>54,55</sup> Additionally, the aromatic ring attached to the nitrogen atom is largely twisted against the P–N–P plane (ca. 60–90°) as shown also in other X-ray crystal structures.<sup>45,46</sup> The diphosphinoamine ligands show a twist which may be due to steric interactions with the nitrogen atom, and in cases where there is no coordinated metal it has been shown to be due to intramolecular charge-transfer as noted in compounds such as *p*-dimethylaminobenzonitrile.<sup>56-58</sup> The crystal structures reveal that in all compounds, C-bound H atoms are involved in intermolecular C—H…halogen and  $\pi$ - $\pi$  interactions. This links the fluorine of the counter ion to the compound via the phenyl ring attached to the phosphorous atom.



Figure 3. Structure of complexes 1f and 2f with labeling scheme. The phenyl groups of P(2) are removed/omitted for clarity.

#### 3.4 Oxidation of styrene

Both the iridium (1) and rhodium catalysts (2) were studied under optimum conditions (previously determined by varying catalyst, substrate and oxidant ratios) where a catalyst:substrate molar ratio of 1:100 and substrate:oxidant molar ratio of 1:2.5 were used. When 1,2-dichloroethane (DCE) was used as a solvent, after 3 h, using catalyst 1a, a 62% conversion was found, with a 15% yield to benzaldehyde and a 1% yield to styrene oxide. When the reaction was run for a further 6 h, the conversion increased to 96% and the yield to benzaldehyde increased to 18% and styrene oxide to 2%. When the solvent was changed to acetonitrile (MeCN), after 9 h, 83% conversion was observed, with a 30% yield to benzaldehyde and 24% yield to styrene oxide with the balance always being benzoic acid. Higher catalytic activity in acetonitrile is attributed to its polarity, where the different phases are uniform promoting mass transfer.<sup>10</sup>

The Ir (1) catalysts are slightly more active than the Rh (2) catalysts as shown by the reaction rates (Fig.4). This is due to the active oxo Rh(III) complex having a lower affinity for the olefin.<sup>34</sup> Such cases also have been observed with Rh( $C_2H_4$ )<sub>2</sub>( $C_2H_5$ ) complexes.<sup>34</sup> The highest activities were exhibited by catalysts **1e** (88%) and **2e** (83%), with the chlorophenyl group on the nitrogen atom. Catalysts **1c** and **2d** were least active. Comparable activity between catalysts **1** and **2** with cyclohexyl (**a**) substituted and functionalized phenyl groups are noted (**e** and **f**). The difference in the activity of the catalysts bearing the different substituents could be attributed to their basicity.<sup>20</sup> The basic nature of the ligand is attributed to the substituent on the nitrogen atom, which lowers the activity with an increase in basicity. Published on 15 March 2016. Downloaded by New York University on 23/03/2016 13:34:52.

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Figure 4. Conversion of styrene over catalysts 1 and 2 in MeCN. *Conditions*: Catalyst:styrene (1:100); Styrene: TBHP (1:2.5); Temperature: 80 °C.

This basic substituent is likely to increase the electron density at the metal center, which makes it easier for the oxidation process to occur, where the oxidation state of the metal goes from a M(I) to M(III) species (Scheme 1). However, the formation of the active tert-butoxy radical becomes more difficult, since the high basic nature of the complex stabilizes the M<sup>III</sup> oxidation state. Thus less basic and electron withdrawing substituents such as 1e and 2e are more active in comparison to 1c and 2c, where the alkyl substituent increases the basic nature of the complex. The yields to benzaldehvde for both catalysts are comparable, however, catalysts 1 are more selective to styrene oxide than catalysts 2 (Fig. 5). The TONs towards benzaldehvde for catalysts 2 are slightly greater than those of catalysts 1, however, the TONs towards styrene oxide are higher for catalysts 1 (Table 3). This is an indication that deeper oxidation is more prevalent when using catalysts 1, which also reflects their high activity.

The catalyst with the chlorophenyl group (1e) is most selective to styrene oxide, also giving the highest yield (28%) and TON (23). The catalysts with the methoxy substituent (f) and the unsubstituted phenyl group (d) exhibit similar activity and selectivity.



Figure 5. Yield to benzaldehyde and styrene oxide over catalysts 1 and 2 in MeCN.

*Conditions*: Catalyst:styrene (1:100); Styrene: TBHP (1:2.5); Temperature: 80 °C.

Catalysts with the cyclohexyl (a) and isopropyl (b) substituted nitrogen atoms are comparable in terms of activity and yield to benzaldehyde and styrene oxide and this comparable activity is also noted in chromium catalysts bearing the same functional groups in ethylene oligomerisation.<sup>20</sup> This is due to these ligands having similar basic properties. Increasing the chain length by at least four carbons improves the selectivity, giving good selectivity to benzaldehyde and poor selectivity to styrene oxide by catalyst 1c.<sup>20</sup> This again is likely due to the basic nature of catalyst 1c, since the increase in carbon chain length increases the basic nature of the catalyst. This controls the reaction whereby the metal goes from a M(I) to M(III) species, thus controlling the selectivity to one product (benzaldehyde).

 Table 3. Turnover numbers for catalysts 1 and 2 towards benzaldehyde and styrene oxide.

	Turnover number (TON)				
Catalysts	1		2		
	Benzaldehyde	Styrene Oxide	Benzaldehyde	Styrene oxide	
a	23	19	25	15	
b	24	15	27	10	
c	25	5	27	12	
d	26	12	23	7	
e	18	23	22	17	
f	24	12	27	9	

Unlike other studies reported, such as styrene oxidation carried out by iridium cyclopentadienyl half sandwich complexes using PhIO as an oxidant, where low yields to benzaldehyde (6-11%) and no selectivity to styrene oxide was found,<sup>36</sup> these systems achieve a relatively good yield to both benzaldehyde and styrene oxide. In a further comparison, bis(pyridylimino)isoindolato-iridium complexes gave a 55% conversion over a 48 h period with 50% vield to the epoxide.<sup>59</sup> Furthermore, triphenylphosphine complexes of Ir and Rh used in the oxidation of styrene gave low yields to styrene oxide.<sup>32,33</sup>. Using a PNNP system, Stoop et al. also reported low conversions in the epoxidation of styrene.60 Early research by Aneetha et al. using Ru(III) triphenylphosphine complexes reported yields only to styrene oxide.<sup>61</sup> Most studies involving ruthenium complexes report higher yields to styrene oxide, but very little or no vield to benzaldehvde under ambient conditions.<sup>62-66</sup> Few studies have been reported on homogenous systems using cobalt, since much of the work has been done on heterogenizing these complexes using supports such as zeolites.<sup>10,12,67,68</sup> Li et al. reported a 63% conversion using cobalt-encapsulated zeolite Y with higher selectivity to benzaldehyde than styrene oxide.<sup>67</sup> With Schiff based polymer-cobalt complexes, 20% selectivity to benzaldehyde was found.69

The key feature of this system was the recovery of the catalyst. It has been reported that when using phosphine based ligands the catalysts are destroyed due to progressive oxidation of the ligands.<sup>70</sup> The used catalysts were recovered and characterized and the melting points (catalyst **1c** recovered melting point: 263-264 °C) NMR (Fig. 6) and single crystal XRD (Fig. 7) are comparable to those of the fresh catalysts.

Furthermore, the catalysts **1c** and **2c** were recovered and re-used over 3 cycles (Fig. 8) (see supporting information). However, the amount of catalyst recovered decreased over time, due to mechanical loss and the small quantities involved.



Figure 6. <sup>31</sup>P NMR of the recovered and fresh catalysts 1c and 2c.



Figure 7. Structure of recovered complex 1c with labelling scheme. The phenyl groups of P(2) are removed/omitted for clarity.

The conversion over catalyst **1c** after cycle 1 decreased slightly from the original run (53% to 41%) and thereafter increased to be essentially constant at 49% in cycle 2 and 48% in cycle 3, results of which are probably within experimental error. Also, the repeat reactions were slightly more dilute. The yield to benzaldehyde is comparable to the first run, however, the yield to styrene oxide increases from cycle 1 (2%) to cycle 3 (6%). The recycled catalyst **2c** showed a decrease in conversion compared to the first run, but significantly increased in cycle 3 (from 45% to 65%). This could be due to concentration effects. The yield to benzaldehyde is comparable to the first run, however, the yield to styrene oxide decreased (from 15% to 5%).



Figure 8. Conversion of styrene by recovered catalysts over 1c and 2c over three cycles in MeCN. *Conditions*: Catalyst:styrene (1:100); Styrene: TBHP (1:2.5); Temperature: 80 °C.







**Scheme 1.** Proposed mechanism for the oxidation of styrene by complexes 1 and 2.

To elucidate the mechanism by which these two products form, styrene oxide was used as a substrate with catalyst 1 under optimum conditions. The reaction was monitored over 9 h, during which time no conversion took place. When benzaldehyde was used as a substrate, under the same conditions, the deeper oxidized product, benzoic acid and the cleaved product benzene formed. On the basis of this experimental work and the mechanism proposed by Li et al. on a cobalt system, a probable mechanism is proposed in Scheme 1.<sup>8</sup> The metal complex (M(I)) can activate and bind to oxygen from the oxidant (*t*-BuOOH) forming a peroxo M(III) species (**A**) (eqn 1) which then reacts with styrene to form the intermediate (**B**) eqn (2).<sup>1,67,71,72</sup> Rearrangement of intermediate **B** to form **C** and generation of the catalyst occurs (eqn 4). The formation of benzaldehyde and styrene oxide via two different pathways occurs through **D** (eqn 4).<sup>1,20,67,71-73</sup>

# Conclusions

New iridium and rhodium complexes have been synthesized and fully characterized and were used as catalysts in the oxidation of styrene. The iridium catalysts are more active than the rhodium catalysts. This could be due to the active oxo Rh(III) complex having a lower affinity for the olefin. The yield to benzaldehyde by both catalysts is comparable and is much higher than that of styrene oxide. However, the iridium catalysts give a higher yield to styrene oxide. The catalysts bearing the chloro phenyl group on the nitrogen atom is most active and gives the highest vield to styrene oxide. The difference in the activity of the catalysts bearing the different substituents on the nitrogen atom, of the ligand backbone, could be attributed to the basicity of the ligand backbone. The catalysts were recovered, characterized and recycled over 3 cycles. The activity and yield to styrene oxide drops, however, the yield to benzaldehyde remains constant. The work shows that, though somewhat neglected, PNP complexes of Ir and Rh may indeed have considerable potential in the selective oxidation of styrene.

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### Notes and references

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New Ir and Rh "PNP" aminidiphoshphine complexes have been synthesised, characterised and used as catalysts in styrene oxidation with *tert*-butyl hydroperoxide as the oxidant. The Ir catalysts were more active than the Rh catalysts with high yields to benzaldehyde in comparison to styrene oxide.