Supporting Information

Self-assembly of P-chiral supramolecular phosphine on rhodium and a direct evidence for Rh-catalyst-substrate

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1. Experiment section

All manipulations were carried out under an inert atmosphere using standard Schlenk line techniques or m-Braun glove box. Solvents were dried by standard procedure.\(^1\) THF distilled from sodium/benzophenone under argon atmosphere. Acetonitrile and methylene chloride were distilled on calcium-hydride. \([\text{(COD)}_2\text{RhBF}_4]\) and \(N\)-acetyldehydrophenylalanine were purchased from Sigma-Aldrich All other reagents/chemicals, solvents were purchased from local suppliers (Spectrochem Pvt. Ltd.; Avra Synthesis Pvt. Ltd.; Thomas Baker Pvt. Ltd. etc). The asymmetric hydrogenation was run in an Amar Equipment high pressure autoclave equipped with inlet/outlet and pressure regulators.

Solution NMR spectra were recorded on a Bruker Avance 400 and 500 MHz instruments at 298 K unless mentioned otherwise. Chemical shifts are referenced to external reference TMS (\(^1\)H and \(^13\)C). Coupling constants are given as absolute values. Multiplicities are given as follows s: singlet, d: doublet, t: triplet, m: multiplet, br: broad. FT-IR spectra were recorded on a Bruker \(\alpha\)-T spectrophotometer in the range of 4000-400 cm\(^{-1}\) by using CaF\(_2\) pallets. Mass spectra were recorded on Thermo scientific Q-Exactive mass spectrometer. Synthesis of self-assembled Rh-complex according to our previous report.\(^2\)

2. Demonstrating the self-assembly

2.1 Effect of concentration on H-bonding in L1:

In a NMR tube 0.0017 g (0.005 mmol) of \(L1\) was dissolved in 0.5 ml of CDCl\(_3\) to make 10 mM solution of \(L1\). The \(^1\)H NMR of 10 mM solution was recorded at 25 °C and chemical shift of NH and NH\(_2\) protons was identified. Next, in the same NMR tube another 0.0017 g (0.005 mmol) of \(L1\) (to make 20 mM solution of \(L1\)) was added and proton NMR was recorded. In similar manner, 30 mM, 40 mM, and 50 mM solution of \(L1\) was prepared and \(^1\)H NMR was measured. Table S1 summarizes the change in chemical shift of NH and NH\(_2\) protons of \(L1\) with increasing concentrations.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>(L1) (g)</th>
<th>(L1) conc. (mM)</th>
<th>NH (ppm)</th>
<th>NH(_2) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0017</td>
<td>10</td>
<td>6.43</td>
<td>4.59</td>
</tr>
<tr>
<td>2</td>
<td>0.0017 + 0.0017</td>
<td>20</td>
<td>6.55</td>
<td>4.62</td>
</tr>
<tr>
<td>3</td>
<td>0.0034 + 0.0017</td>
<td>30</td>
<td>6.66</td>
<td>4.65</td>
</tr>
<tr>
<td>4</td>
<td>0.0050 + 0.0017</td>
<td>40</td>
<td>6.76</td>
<td>4.68</td>
</tr>
<tr>
<td>5</td>
<td>0.0067 + 0.0017</td>
<td>50</td>
<td>6.85</td>
<td>4.70</td>
</tr>
</tbody>
</table>
2.2 Effect of concentration on H-bonding in C1:
Along the same lines, in a NMR tube 0.0048 g (0.005 mmol) of C1 was dissolved in 0.5 ml of CDCl3 to make 10 mM solution of C1. The \textsuperscript{1}H NMR of 10 mM solution was recorded at 25 °C and chemical shift of NH\textsubscript{2} protons was recorded. Next, in the same NMR tube another 0.0048 g (0.005 mmol) of C1 (to make 20 mM solution of C1) was added and proton NMR was recorded. In similar manner, 30 mM, 40 mM, and 50 mM solution of C1 was prepared and \textsuperscript{1}H NMR was measured. Table S2 summarizes the change in chemical shift of NH and NH\textsubscript{2} protons of C1 with increasing concentrations.

Table S2: Monitoring the change in chemical shift of NH\textsubscript{2} proton as a function of concentration of the C1.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>self-assembled Rh-complex (g)</th>
<th>C1 conc. (mM)</th>
<th>NH\textsubscript{2} (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0048</td>
<td>10</td>
<td>5.15</td>
</tr>
<tr>
<td>2</td>
<td>0.0048 + 0.0048</td>
<td>20</td>
<td>5.16</td>
</tr>
<tr>
<td>3</td>
<td>0.0096 + 0.0048</td>
<td>30</td>
<td>5.17</td>
</tr>
<tr>
<td>4</td>
<td>0.0144 + 0.0048</td>
<td>40</td>
<td>5.18 [(5.26+5.11)/2]</td>
</tr>
<tr>
<td>5</td>
<td>0.0192 + 0.0048</td>
<td>50</td>
<td>5.19 [(5.28+5.09)/2]</td>
</tr>
</tbody>
</table>

![NMR spectra](Scale: 0.4724 ppm/cm, 236.2 Hz/cm)
Fig. S1. $^1$H NMR spectra of P-stereogenic supramolecular phosphine (L1) at different concentration.

![H NMR spectra of P-stereogenic supramolecular phosphine (L1) at different concentration.](image1)

Fig. S2. IR spectra of P-stereogenic supramolecular phosphine (L1) at different concentration.

![IR spectra of P-stereogenic supramolecular phosphine (L1) at different concentration.](image2)

Fig. S3. $^1$H NMR spectra of self-assembled Rh-complex (C1) at different concentration.

![H NMR spectra of self-assembled Rh-complex (C1) at different concentration.](image3)
2.3 Effect of temperature on H-bonding in L1:
In the NMR tube 0.0017 g (0.005 mmol) of L1 was dissolved in 0.5 ml of CDCl₃ to make 10 mM solution. The ¹H NMR was measured at different temperature starting from 298 K to 293K, 283 K, 273 K and 263 K. The change in chemical shift of the NH and NH₂ protons as a function of decreasing temperature is summarized in Table S3.

Table S3 : Monitoring the change in chemical shift of NH and NH₂ proton as a function of temperature of the L1.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Temperature (K)</th>
<th>L1 conc. (mM)</th>
<th>NH (ppm)</th>
<th>NH₂ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298</td>
<td>10</td>
<td>6.37</td>
<td>4.55</td>
</tr>
<tr>
<td>2</td>
<td>293</td>
<td>10</td>
<td>6.43</td>
<td>4.58</td>
</tr>
<tr>
<td>3</td>
<td>283</td>
<td>10</td>
<td>6.50</td>
<td>4.62</td>
</tr>
<tr>
<td>4a</td>
<td>273</td>
<td>10</td>
<td>6.59</td>
<td>4.66</td>
</tr>
<tr>
<td>5a</td>
<td>263</td>
<td>10</td>
<td>6.69</td>
<td>4.70</td>
</tr>
</tbody>
</table>

2.4 Effect of temperature on H-bonding in C1:
Similarly, 0.0048 g (0.005 mmol) of C1 was charged to the NMR tube which was dissolved in 0.5 ml of CDCl₃ to make a 10 mM solution of C1. The ¹H NMR of this 10 mM solution was recorded at different temperatures starting from 298 K to 293K, 283 K, 273 K and 263 K. There was hardly any change in the chemical shift of NH₂ proton as a function of decreasing temperature and Table S4 presents the change in chemical shift as a function of temperature.

Table S4 : Monitoring the change in chemical shift of NH and NH₂ proton as a function of temperature of the C1.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>C1 conc. (mM)</th>
<th>Temperature (K)</th>
<th>NH₂ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>298</td>
<td>5.12</td>
</tr>
</tbody>
</table>
Fig S5. $^1$H NMR spectra of L1 at different temperature.
3. Synthesis of deuterated supramolecular phosphine ligand (L1.D)

In the 50 ml Schlenk flask 0.136 g (0.4 mmol) of ligand L1 was dissolved in 2 ml CD$_3$OD. The above reaction solution was stirred for 2.5 hours at room temperature. The progress of their action was monitored by $^1$H NMR spectroscopy. After the reaction was complete, volatiles were evaporated under vacuum. The residue was dried under high vacuum and $^1$H NMR was recorded in CDCl$_3$ (Fig. S7-S10). $^2$H NMR was recorded in 0.5 ml THF (THF-d$_8$:THF, 0.1:0.4 ml). (ESI Fig. S7-S11).

$^2$H NMR (500 MHz, THF-d$_8$, 298 K) $\delta = 7.87$ (s, ND), 5.45 (s, ND2). $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta = 7.45$ (d, $J = 7.25$ Hz, 1H, Ar), 7.33 (br. s., 3H, Ar), 7.16 - 7.30 (m, 5H, Ar), 7.04 - 7.14 (m, 2H, Ar), 6.97 (t, $J = 6.87$ Hz, 1H, Ar), 6.74 - 6.84 (m, 1H, Ar), 4.85 (d, $J = 5.34$ Hz, 0.80H, NH), 2.39 (s, 3H, CH$_3$). $^{13}$C NMR (126 MHz, CDCl$_3$, 298 K) $\delta = 156.6$ (s, CO), 142.3 (s, Ar), 142.1 (s, Ar), 138.7 (t, $J = 7.7$Hz, Ar), 137.7 (d, $J = 10.5$ Hz, Ar), 135.9 (d, $J = 10.4$ Hz, Ar), 135.5 (d, $J = 11.5$ Hz, Ar).
Hz, Ar), 133.5 (d, J = 20.1 Hz, Ar), 132.7 (s, Ar), 130.4 (s, Ar), 130.1 (d, J = 4.8 Hz, Ar), 129.4 (d, J = 7.6 Hz, Ar), 129.2 (d, J = 18.2 Hz, Ar), 128.8 (d, J = 8.5 Hz, Ar), 128.6 (d, J = 6.6 Hz, Ar), 126.0 (d, J = 18.2 Hz, Ar), 129.2 (d, J = 20.9 Hz, Ar), 120.5 (d, J = 20.4 Hz, Ar), 21.10 (d, J = 21.1 Hz, CH3). **ESI-MS (+ve)** (For M = C_{20}H_{19}N_{2}OP) m/z = 335.13 [M+H]^+.

Fig. S7. $^2$H NMR spectrum of L1.D in THF-D$_8$:THF (0.1:0.4 ml) solvent.

Fig. S8. $^1$H NMR spectrum of L1.D in CDCl$_3$. 
Fig. S9. $\text{^{13}C}$ NMR spectrum of \textbf{L1.D} in CDCl$_3$.

Fig. S10. $\text{^{13}C}$ NMR (DEPT) spectrum of \textbf{L1.D} in CDCl$_3$. 
4. Synthesis of deuterated self-assembled Rh-complex (C1.D)

In a vacuum dried Schlenk flask [Rh(COD)_2BF_4] (1 eqv., 0.0985 mmol) and phosphine ligand L1.D (2 eq., 0.1974 mmol) was taken inside the glove box. The above mixture was dissolved in 8 ml DCM and reaction content was stirred for 2 hours at room temperature. After completion of reaction, the reaction content was evaporated and concentrated to 2 ml. 20 ml diethyl ether was added to above content to obtain yellow coloured precipitate. The resultant solid was separated by cannula filtration, washed with diethyl ether (10 ml x 3 ml) and dried under vacuum. The resultant residue was identified as C1.D after complete characterization (see fig. ESI S12-S16).

$^2$H NMR (500 MHz, THF-d$_8$, 298 K) $\delta$ = 8.29 (s, ND), 5.55 (s, ND2). $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 8.23-6.00 (m 26H, Ar), 5.75-4.95 (m, 5H, CH), 2.90-2.14 (m, 8H, CH$_2$), 2.14 (m, 6H, CH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$, 298 K) $\delta$ = 157.3 (s, CO), 156.8 (s, CO), 142.8 (s, Ar), 141.7 (s, Ar), 140.1 (s, Ar), 139.6 (s, Ar), 132.6 (s,
Ar), 132.2 (s, Ar), 131.7 (s, Ar), 131.6 (s, Ar), 130.5 (s, Ar), 130.0 (s, Ar), 128.6 (s, Ar), 126.0 (s, Ar), 125.6 (s, Ar), 125.4 (s, Ar), 123.0 (s, Ar), 121.6 (s, Ar), 118.7 (s, CH), 104.4 (s, CH), 65.7 (s, CH$_2$), 47.2 (s, CH$_2$), 32.6 (s, CH$_2$), 27.9 (s, CH$_2$), 23.5 (s, CH$_2$), 21.5 (s, CH$_3$). **ESI-MS** (+ve) (For M = C$_{48}$H$_{50}$N$_4$O$_2$P$_2$Rh) m/z = 879.24 [M]$^+$. 

**Fig. S12.** $^2$H NMR spectrum of **C1.D** in THF-D$_8$:THF (0.1:0.4 ml) solvent.

**Fig. S13.** $^1$H NMR spectrum of **C1.D** in CDCl$_3$. 
Fig. S14. $^{13}$C NMR spectrum of C1.D in CDCl$_3$.

Fig. S15. $^{13}$C NMR (DEPT) spectrum of C1.D in CDCl$_3$. 
5. Stoichiometric study of self-assembled Rh-complex and S2

In the NMR tube C1 0.0048 g, 0.005 mmol was dissolved in CD$_3$CN to make 10 mM solution. The NH$_2$ proton chemical shift was confirm by $^1$H NMR ESI S17). In the same NMR tube S2 0.010 g, 0.005 mmol was added and $^1$H NMR was measured (see in ESI S18). Similar experiment was done with deuterium labeled self-assembled Rh-complex (C1.D) and S2, and $^2$H NMR was recorded in THF-d$_8$:THF (0.1:0.4 ml) solvent. For this experiment deuterium labelled self-assembled Rh-complex C1.D (0.0048 g, 0.005 mmol) was dissolved in THF-d$_8$:THF (0.1:0.4 ml) to prepare 10 mM solution and $^2$H NMR was measured to confirm the chemical shift of ND and ND$_2$. After that S2 (0.010 g, 0.005 mmol) was added in the same NMR tube and $^2$H NMR was recorded (see in ESI S17-S21).
$^2$H NMR (500 MHz, THF-d$_8$, 298 K) $\delta = 8.45$ (s, $ND$), 5.61 (s, $ND_2$). $^1$H NMR (400 MHz, CD$_3$CN, 298 K) $\delta = 7.81$-7.10 (m, 33H, Ar and $NH$), 5.10-4.10 (m, 9H, $CH$ and $NH_2$), 2.41 (m, 4H, $CH_2$), 2.12 (m, 9H, $CH_3$), 1.53 (m, 2H, $CH_2$), 1.27 (m, 2H, $CH_2$). ESI-MS (+ve) (For C$_{59}$H$_{55}$D$_4$LiN$_5$NaO$_5$P$_2$Rh) m/z = 1116.24 [M]$^+$. 

Fig. S17. $^1$H NMR spectrum of C1 in CD$_3$CN.

Fig. S18. $^1$H NMR spectrum of self-assembled Rh-complex C1+ S2 in CD$_3$CN.
Fig. S19. $^2$H NMR spectrum of **C1.D+S2** in THF-D$_8$:THF (0.1:0.4 ml) solvent.
Fig. S20. ESI-MS (+ve mode) spectrum of C1.D+S2.

Chemical Formula: C_{24}H_{23}D_{2}LiN_{2}NaO_{4}P_{2}Rh
m/z: 1116.34 (100.0%), 1117.34 (63.2%),
1118.34 (21.6%)

Fig. S21. Stacked IR spectra of ligand L1 (black), self-assembled complex C1 (blue) and complex C1 + substrate S2 (red).
Fig. S22. IR spectrum of neat C1, neat S1 and stoichiometric experiment of C1+S1.

Fig. S23. IR spectrum of neat C1, neat S2 and stoichiometric experiment of C1+S2.

6. References: