

Exploring the Concept of Polymer Immobilised Ionic Liquid Phase (PIILP) Catalysis

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Introduction

The project focussed on exploring the concept of using Polymer Immobilised Ionic Liquids as supports for catalysis. A series of heteroatom donor modified polymer immobilised ionic liquids were prepared and used to stabilise palladium nanoparticles. The Suzuki-Miyaura cross-coupling reaction was used to test the efficiency of the catalyst and the results showed that reduction of the palladium in situ was either just as efficient if not more efficient than when the palladium was reduced before being used in the reaction. Furthermore, the catalyst compares favourably with those currently available on the market and is highly efficient across a wide range of substrates.

Synthesis of Monomers and Cross-linker

Figure one below shows the experiments that were carried out to produce each monomer. Figure 1 shows the synthesis of the cross-linker but this was carried out by a different colleague. As can be seen, monomer one and the cross-linker are similar in structure. Monomer 2 is the monomer that was particularly exclusive to the project. There are other colleagues carrying out the same experiments except monomer two is slightly different; instead of a PPh₂ group, other heteroatom groups such as CN and NH₂ were used. ¹H NMR (nuclear magnetic resonance) was obtained for monomer 1 and 2 and ³¹P NMR was obtained for monomer 2. These showed that both monomers were produced in high purity.

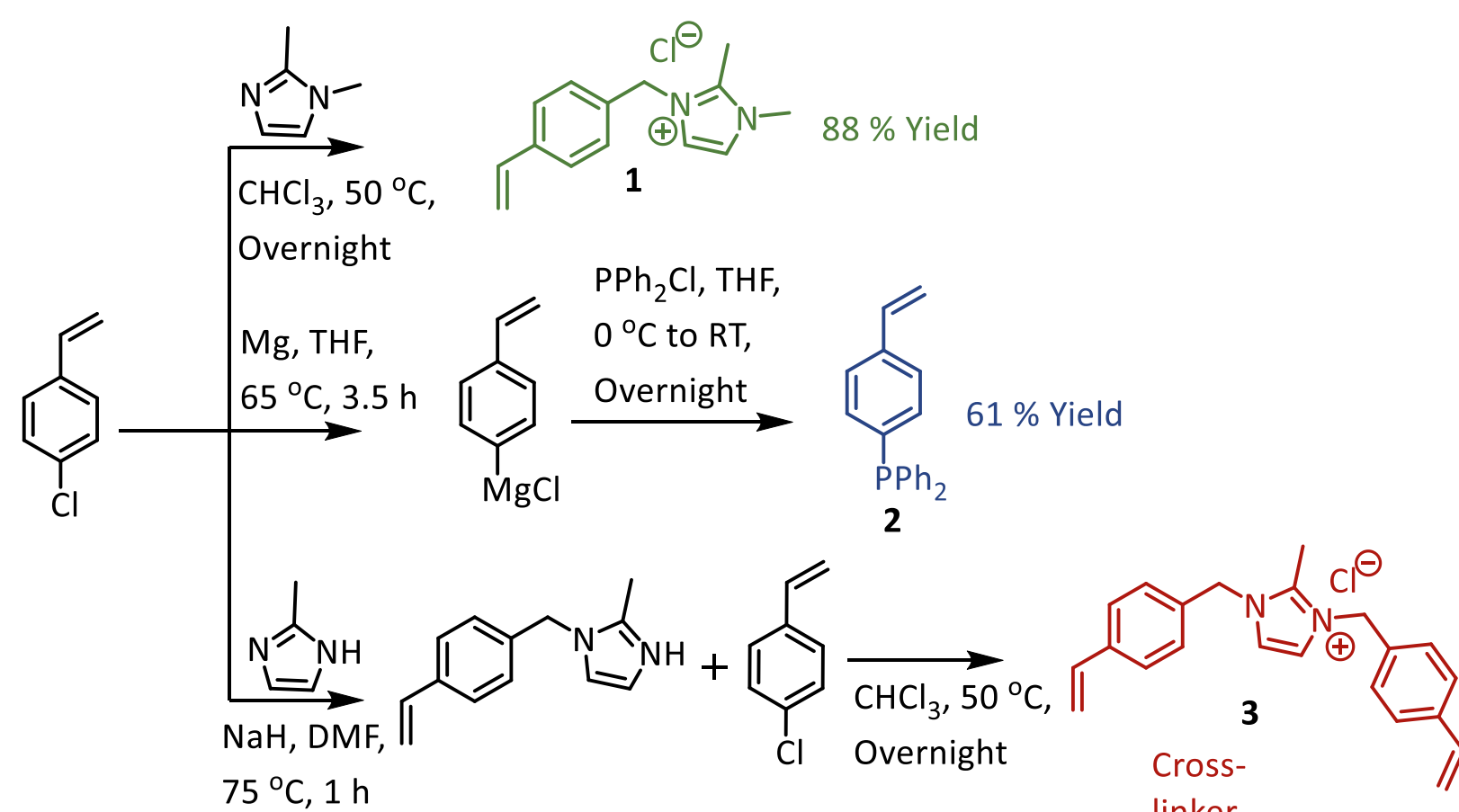


Figure 1: The experiments undertaken to produce each monomer and the cross-linker.

Synthesis and Analysis of the Palladium Nanoparticles.

Figure 2a below, shows the synthesis of the palladium nanoparticles (PdNPs). ³¹P NMR was obtained on polymer 4 before palladium was loaded onto the polymer to prove that monomer 2 was included. ³¹P Solid-state NMR, Figure 2b, and TEM (transmission electron microscopy), Figure 3, were also obtained. The top solid state ³¹P NMR spectrum in Figure 2b shows that all of the phosphorus contained in the polymer is in one chemical environment at -6.616 ppm (parts per million). The other smaller peaks are just spinning sidebands that are not part of the polymer but appear due to the spectrometer. The bottom solid state ³¹P NMR spectrum in Figure 2b shows that there are different phosphorus environments in the PdNPs which is to be expected as there is a distribution of palladium nanoparticles. The TEM in Figure 3 shows that the palladium nanoparticles are between 4 and 10 nanometres.

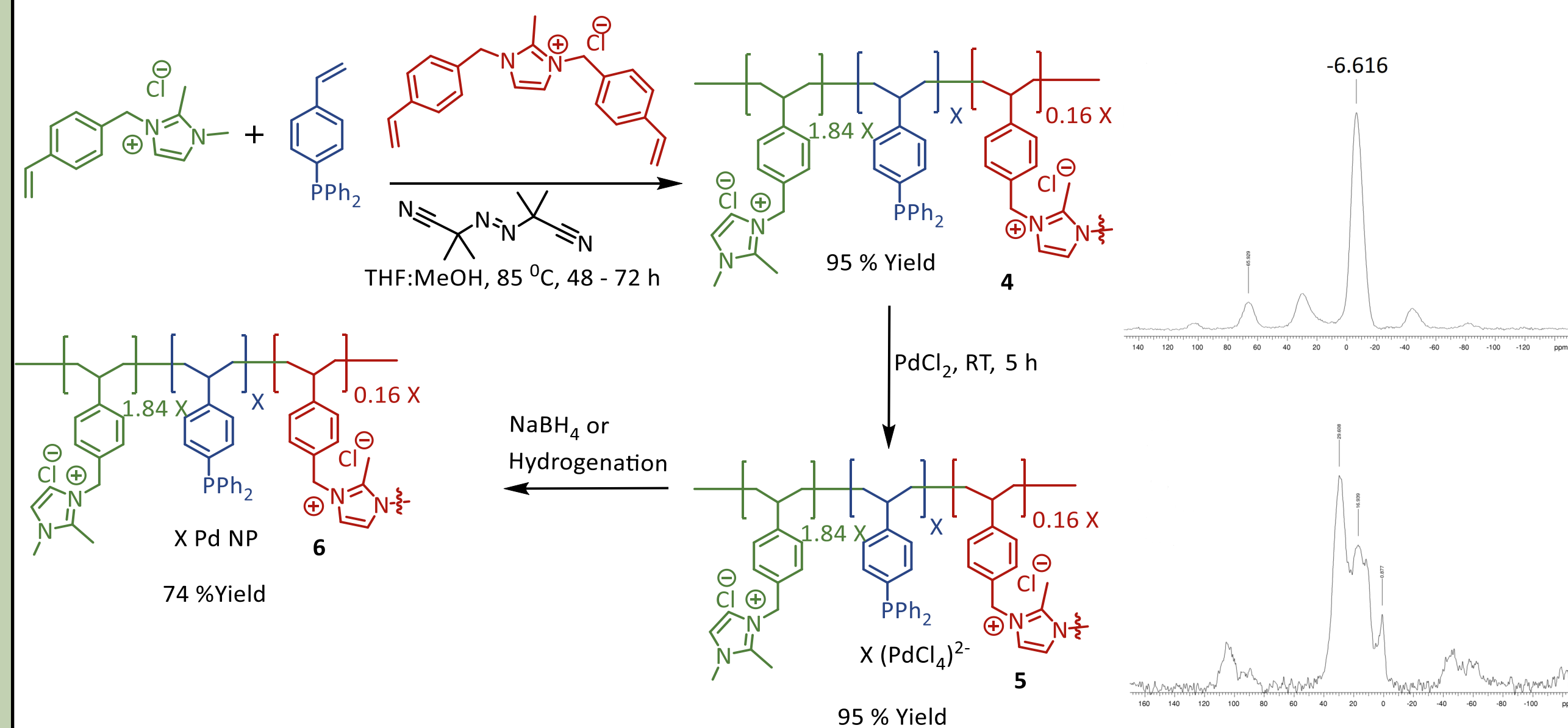


Figure 2a: Synthesis of polymer 4, impregnation by exchange of chloride with [PdCl₄]²⁻ to afford 5 and reduction to afford PdNP@PIILP 6. Figure 2b: Top, ³¹P NMR of compound 4 showing only one phosphorus environment present in the polymer. Figure 2b: bottom, ³¹P NMR of compound 6 showing several different phosphorus environments which is to be expected.

Figure 3: TEM of compound 6. The little black dots present are the nanoparticles which clearly show a variation in size.

Results and Discussion

The Suzuki-Miyaura Cross Coupling reaction was used to test the efficiency of the catalyst. Table 1 shows the results obtained when the PdNPs were generated by reduction with sodium borohydride and also when the PdNPs are produced in situ from (PdCl₄)²⁻. As can be seen from table 1, the catalyst generated from the (PdCl₄)²⁻@PIILP either competed with or outperformed the pre-prepared PdNP@PIILP. This is thought to be due to a more dilute solution of nanoparticles resulting in a smaller chance of aggregation of the nanoparticles produced. This means that there is a larger surface area for catalysis to occur. Catalysis is thought to occur either on the surface of the nanoparticles that are bound to the polymer or the nanoparticles dissociate from the polymer then catalysis occurs before the nanoparticles re-associate to the polymer again. Lastly, complete reduction of the (PdCl₄)²⁻ by hydrogenation was not obtained and therefore, was not used.

Table 1: Suzuki Miyaura Cross Coupling Reactions.^a

Entry	Electrophile	Time (h)	% conv. PdNP@PIILP	% conv. (PdCl ₄) ²⁻ @PIILP	Entry	Electrophile	Time (h)	% conv. PdNP@PIILP	% conv. (PdCl ₄) ²⁻ @PIILP
1		19	58	72	18		5	74	-
					19		19	92	95
2		6	87	80	20		19	86	96
3		5	66	71	21		0.5	99	-
4		19	89	-	22		0.25	91 ^b	98
5		19	41	39	23		5	100	-
					24		2	75	96
6		19	14 ^b	47	25		5	100	-
7		19	75 ^d	-	26		2	99	-
					27		1	98	96
8		5	9	-	28		0.5	10	99
9		19	11	18	29		1	59	100
10		19	18 ^c	-	30		2	99	-
11		5	8	-	31		4	96	100
12		19	37 ^b	94 ^b	32		4	98	98
13		0.5	9 ^c	-	33		19	21	22
14		2	90	-	34		19	20 ^d	-
15		1	62	99	35		19	26	37
16		19	52	81					
17		5	87	80					

a) Reaction conditions: 0.1 mol% catalyst based on repeat unit and assumed complete Pd loading, 1 mmol electrophile, 1.13 mmol phenylboronic acid, 1.2 mmol K₂CO₃, 1.2 mL EtOH, 1.2 mL H₂O, 30 °C.

b) Determined by GC with 1 mmol decane std, average of 2 runs

c) Determined by GC with 1 mmol decane std, average of 4 runs

d) Determined by GC with 1 mmol decane std, 1 run at 50 °C

e) Determined by GC with 1 mmol decane std, average of 2 runs at 50 °C

Further Study and Conclusion

There is clearly scope for further study in this area including focussing on recyclability of the catalyst, studies on varying the nucleophile and how sensitive the catalyst is to potential poisoning. Also, further characterisation of the PdNPs for example by carrying out XPS (X-ray photoelectron spectroscopy) to determine what oxidation state the PdNPs are in.

A study into the concept of PIILP was carried out. Successful synthesis of (PdCl₄)²⁻ impregnated polymer and its reduction to PdNP@PIILP was carried out. Catalytic studies to investigate the efficiency of the polymer for the Suzuki-Miyaura cross-coupling showed that the catalyst was effective across a wide range of substrates and is comparable to other catalysts readily available from chemical suppliers.