

Project title: Heteroatom Donor Mesoporous Ionic Liquid Functionalised Silica: Supports for Nanoparticle Catalysis  
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## 1. Introduction

### Background

Catalysts are substances that influence the progress of a reaction without being consumed by it. Current catalysts in this class are difficult to separate from product material, suffer from loss of metal catalyst through leaching and have problems with catalyst nanoparticles joining together (aggregating) which reduces efficiency. Here, supporting groups on an insoluble silica support are used to reduce these problems leading to a more environmentally friendly and efficient catalyst.

### Aims:

- Synthesise an ionic liquid, a phosphine and pure silica
- Produce 4 silica compounds with varying groups attached loaded with palladium catalyst
- Test catalytic activity with benchmark compounds

### Advantages of Silica Supported Catalysts:

- Easier to separate from product
- Prevent metal leaching
- Prevent aggregation of catalyst nanoparticles
- Increase efficiency of catalysis

## 2. Ionic Liquid Impregnated Silica

### Synthesis

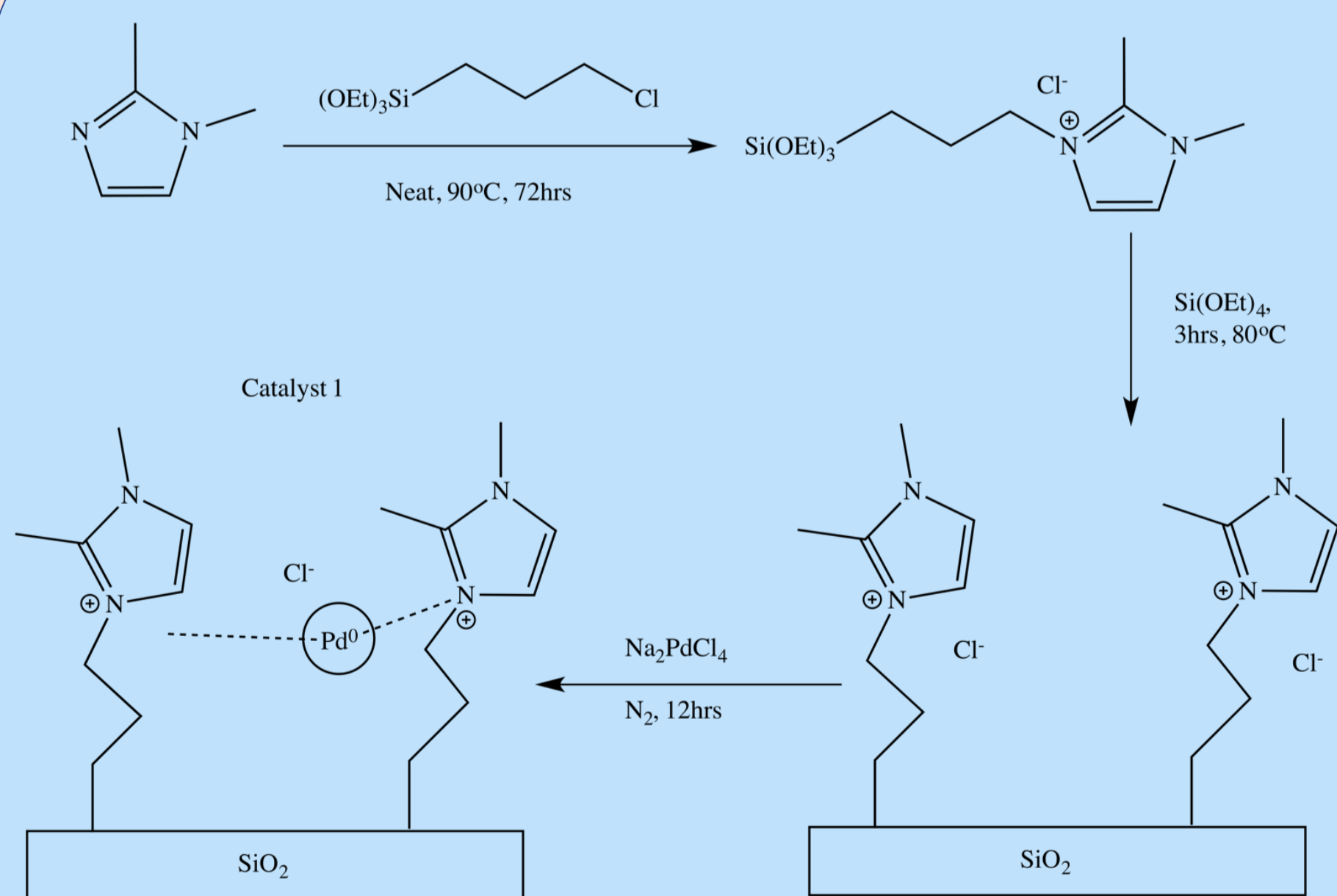


Fig. 1; Synthesis of imidazolium salt impregnated silica with the palladium catalyst constrained by the charged groups

### Results and Discussion

Catalyst 1 (fig.1) was tested with a benchmark catalytic reaction – fig 2. This reaction must be completed by all catalysts in this area as the very minimum.

The reaction appeared to have occurred as expected by <sup>1</sup>H NMR analysis (technique measuring the position of each hydrogen atom in the molecule), but a gas chromatography analysis (removes each compound in the sample individually by the boiling point) was less conclusive - potentially due to machine contamination. Due to time constraints, only one run was attempted and hence the measurements could not be repeated.

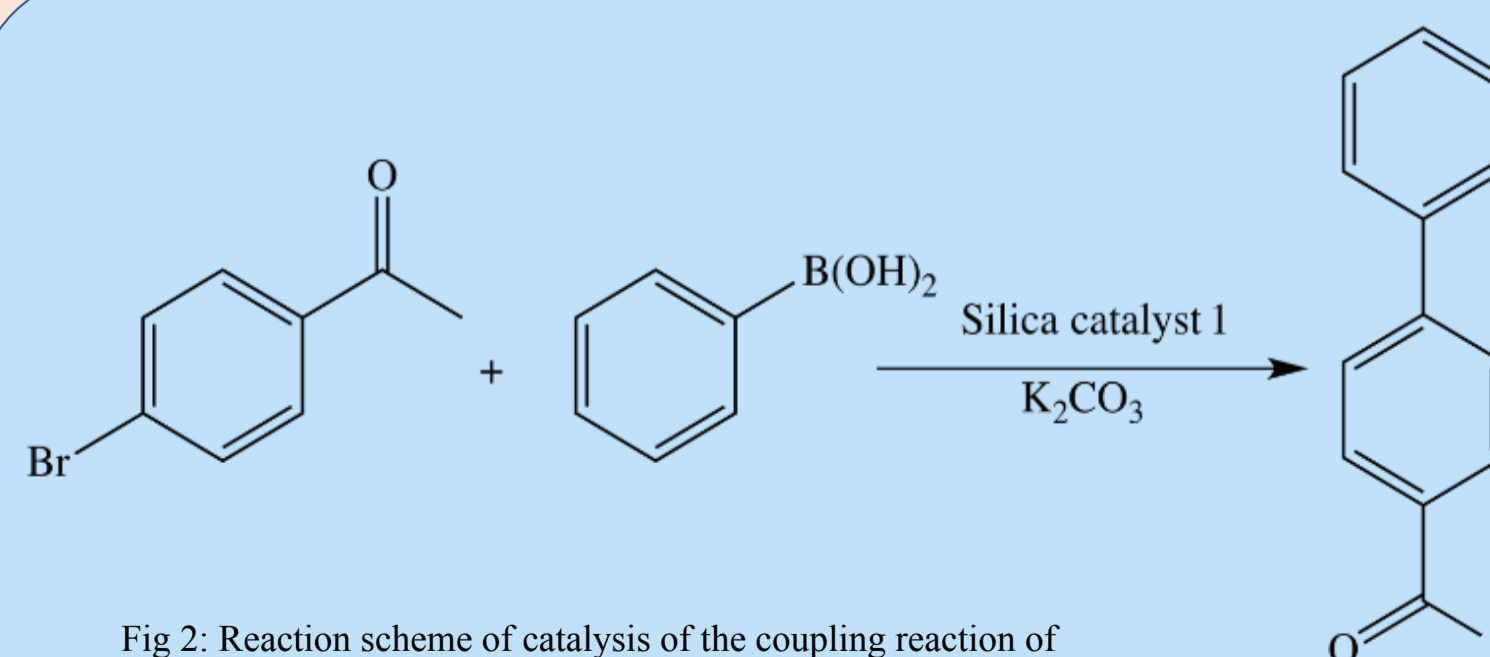


Fig 2: Reaction scheme of catalysis of the coupling reaction of bromoacetophenone and phenylboronic acid with silica catalyst 1

## 3. Phosphine Development

### Initial Work

The phosphine fig.3a was the initial phosphine intended for silylation before being incorporated onto the surface of the silica along with the imidazolium salt. However, despite attempting the silylation with 3 different catalysts, the phosphine did not react. Test reactions using styrene and chlorostyrene (fig.3b&c) showed reaction.

### Phosphine Oxide

As the initial phosphine (fig.3a) failed to react as expected, it was oxidised and the same reactions were reattempted. In all 3 catalysts cases, the reaction succeeded leading to the conclusion that the lone pair on the initial phosphine must be coordinating to the metal of the catalyst and thus preventing silylation occurring at the double bond.

Unfortunately, no method could be found to remove the oxide alone rendering this molecule useless.

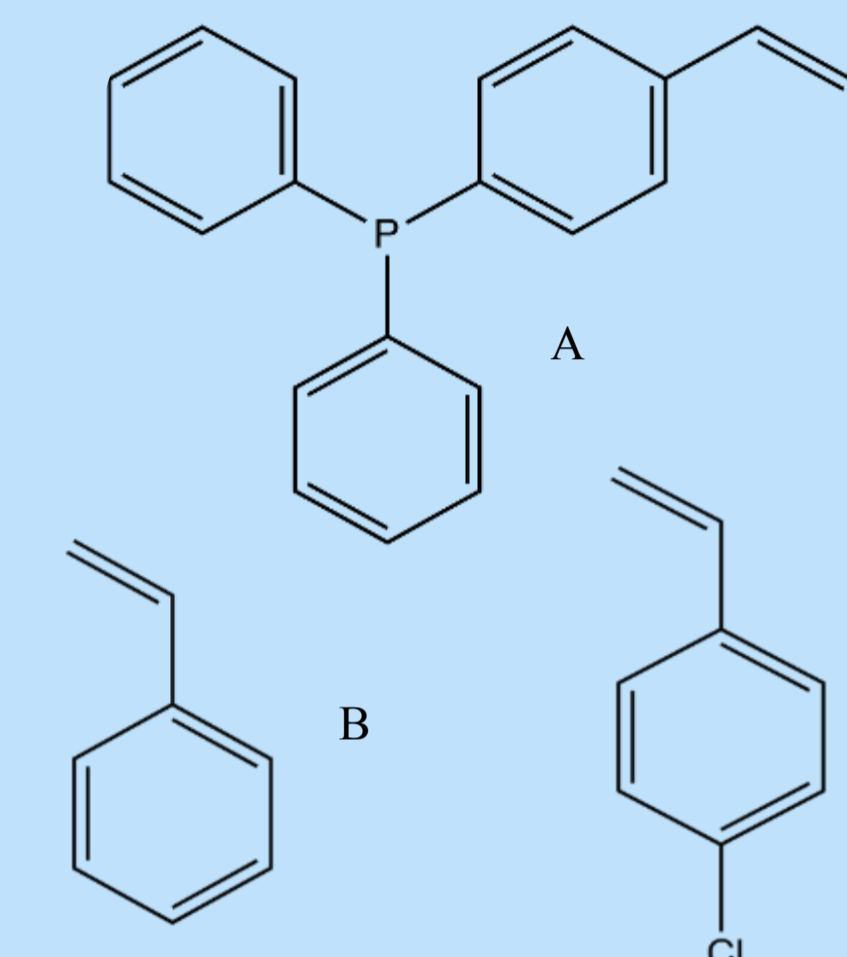


Fig. 3a; diphenyl(4-vinylphenyl)phosphine  
Fig. 3b; styrene  
Fig. 3c; chlorostyrene

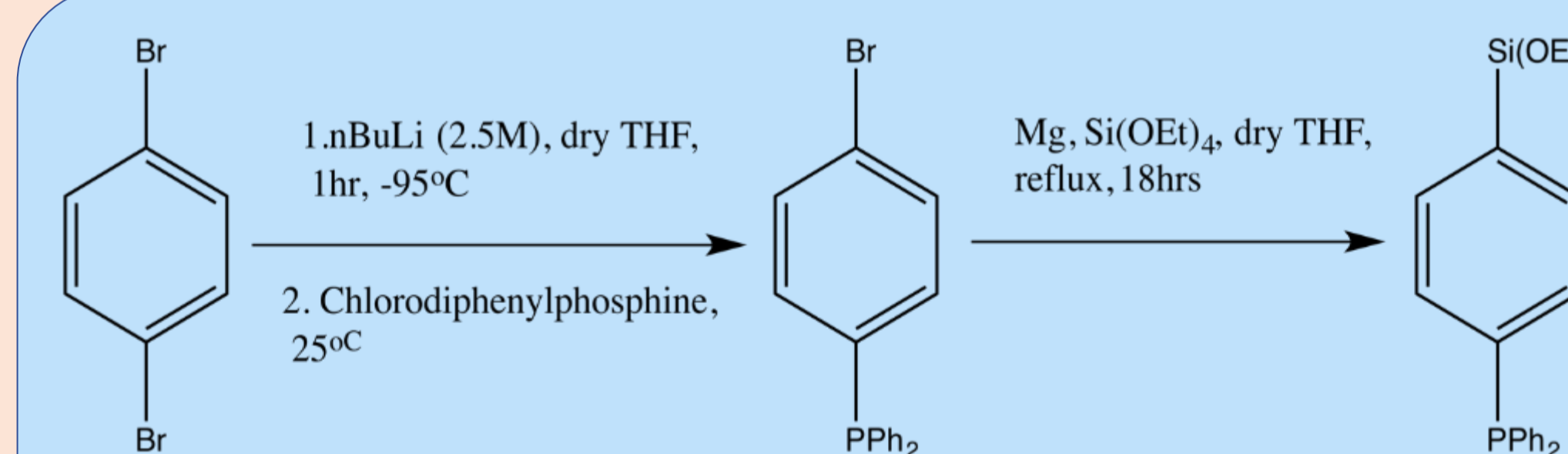


Fig.4; Synthesis of 4-siloxyphenyldiphenylphosphine

### Final Phosphine

The final phosphine (synthesis fig.4) was developed late in the project and as such catalyst testing was not done, however the work will be continued by the Doherty group to produce a phosphine silica.

## 4. The Future

### Further Work

- Synthesise a phosphine silica and a combined ionic liquid/phosphine silica for testing
- Test catalytic properties of phosphine and ionic liquid silicas
- Produce other catalysts supported by silica