



Charge-tagged polar phosphine ligands in Pd-catalysed reactions in aqueous and ionic media

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ABSTRACT

A new range of polar imidazolium and phosphate-containing ligands was synthesised from readily available starting materials in high yielding multi-step transformations. These ligands were used to generate Pd catalysts for Suzuki and Heck C–C coupling reactions in organic and organic/aqueous media. The catalysts performed well in aqueous media in the Suzuki reaction and less well in the Heck reaction, related to substrate solubility in the aqueous media. When moving to ionic liquids, the Heck reaction dramatically improved, especially in media compatible with the polar catalysts and the non-polar reagents. In all cases, the catalysts were stable to the formation of Pd black, a form of degradation that frequently befalls Pd catalysts. The catalysts could be successfully recycled without loss of activity.

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Introduction

The primary role of ligands in the context of homogeneous catalysis is to modify the metal in question towards stability, activity, product selectivity, isolation, and recycling. The role that ligands play in determining many of the features of metal-based catalysts has led to a prolific number and wide variety of ligands being prepared,¹ including those that are phase-switchable,² which are highly useful in the mechanistic study of catalysed reactions.^{1a} While heterogeneous catalysts are readily recovered and reused,³ homogeneous catalysts suffer a persistent disadvantage because of the difficulties associated with recovering and recycling them. Polar phosphine ligands assist the recovery and reuse of catalysts in several possible ways. Firstly, if the ligands are sufficiently polar, they may be extracted into an aqueous phase post-reaction, having been held in the organic phase during the reaction.² Secondly, they may be held in an altogether separate phase, which may be aqueous or another non-miscible phase such as, for example, an ionic liquid.⁴ Such biphasic systems facilitate the recovery and reuse of catalysts,⁵ a pertinent example being the Rhône-Poulenc process. Here, a Rh catalyst is used in a biphasic medium to convert lower alkenes into higher value aldehydes and alcohols.⁶ Triphenylphosphine trisulphonate is the ligand,⁶ and it imparts to the catalyst a level of water solubility which reduces leaching of Rh into the

organic reaction product to very low levels. Polar ligands also assist the move towards more benign solvent systems, even if recovery of the catalyst is not under consideration, because aqueous or ionic liquid-based solvents can be employed.⁷ Thus, it was an objective of the present study to investigate the synthesis, and application in catalysis, of different P-type ligands with the polarity being derived from phosphate-containing and imidazolium-containing moieties. These ligands would be assessed in Pd-catalysed C–C bond-forming Heck⁸ and Suzuki⁹ reactions in polar organic, organic aqueous and ionic liquid systems, including recycling experiments.

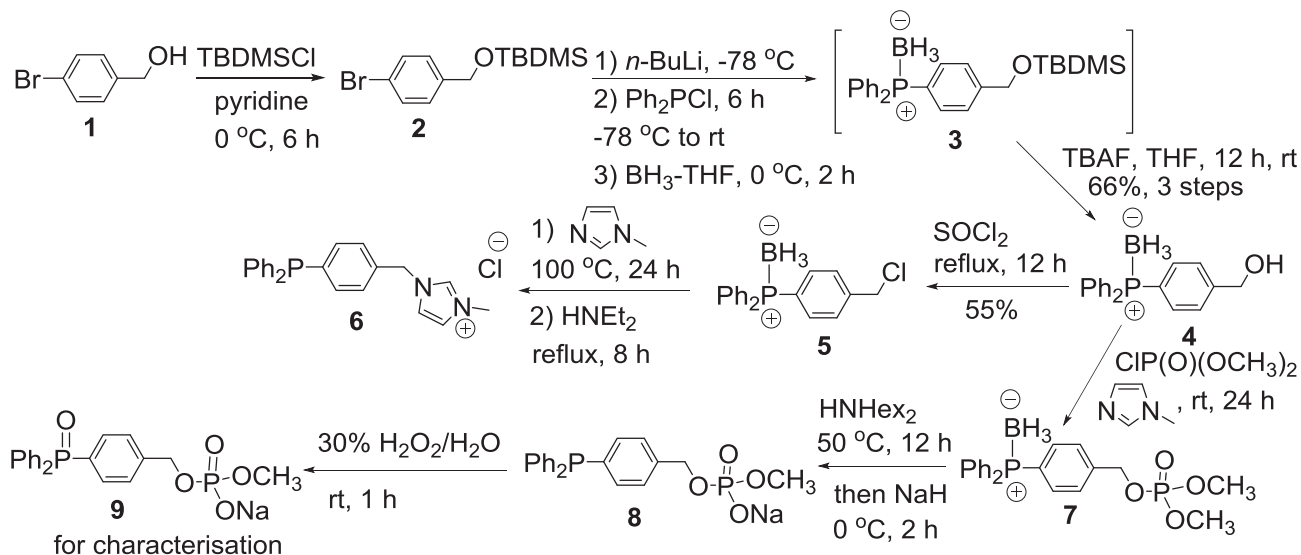
Results and discussion

The synthesis of these ligands was achieved by multi-step sequences which converted suitable starting materials into more complex derivative structures, making use of Ph₂PCl and Ph₂PH as sources of the P atom. These two reagents are useful as electrophiles and nucleophiles, respectively. In the case of Ph₂PCl as the substrate, a nucleophile may attack the P atom, ejecting chloride to form a new P–C bond. In the latter, the P–H is deprotonated thereby converting it into a nucleophile suitable for reactions with, for example, α,β -unsaturated esters. In all cases, the products of these reactions were transformed into polar entities.

4-Bromobenzyl alcohol (**1**) was protected as its silyl ether **2** (Scheme 1), and the resulting product subjected to lithium-halogen exchange with *n*-butyllithium.¹⁰ Reaction of the lithiated

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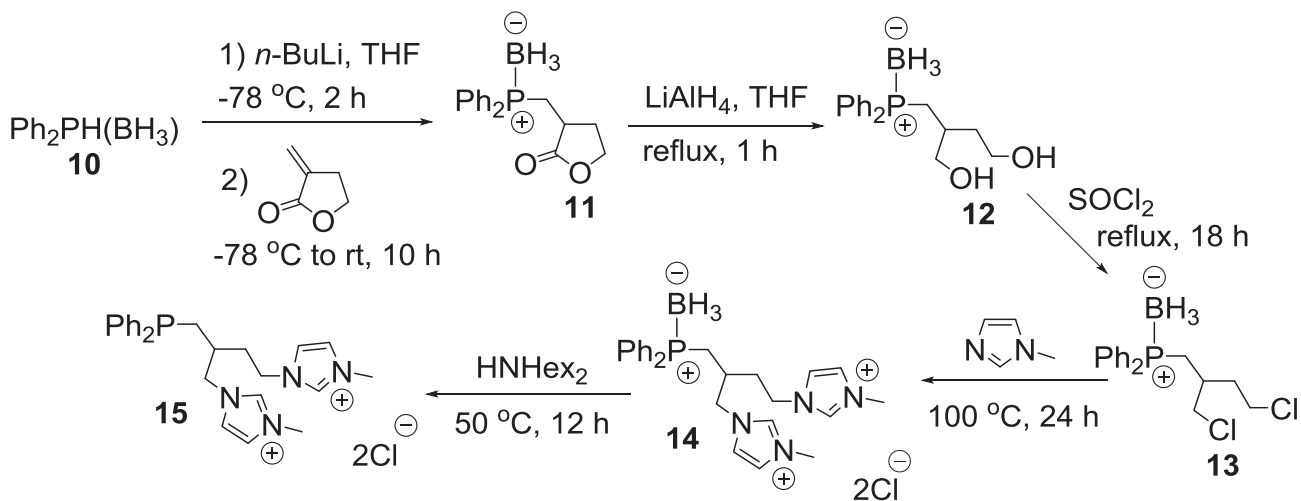


Scheme 1. Synthesis of mono phosphate-based polar ligands.

intermediate with Ph_2P , and P-protection of the reaction product with BH_3 -THF, afforded the triphenylphosphine derivative **3**. If the P-atom was left unprotected during conversion of the benzyl alcohol into its corresponding chloride under the action of thionyl chloride (see below), the P atom was oxidised into its unwanted $\text{P}(\text{O})$ derivative. Unmasking of the OH group under the action of tetra-*n*-butylammonium fluoride on **3** furnished benzyl alcohol **4** in 66% overall yield from **1**, after column chromatography on silica gel. A two proton singlet at 4.72 ppm in the ^1H NMR spectrum of the product was consistent with the anticipated benzyl alcohol CH_2 group. This product afforded the anticipated broad doublet signal at 20.8 ppm ($J = 61.3$ Hz) in the ^{31}P NMR spectrum thereof, accompanied by a range of doublet signals in the aromatic region of the ^{13}C NMR spectrum, caused by $\text{P}-\text{C}$ coupling over a number of bonds. Uneventful conversion of the benzyl alcohol into its chloride analogue **5** under the action of thionyl chloride and the reaction of **5** with excess *N*-methylimidazole at 100°C , followed by P-deprotection with neat diethylamine,¹¹ afforded the desired imidazolium-containing phosphine **6** in 60% yield from **4**. The free phosphine and the diethylamine-borane complex were readily separated by extraction with CH_2Cl_2 and water: the phosphine was soluble in the organic phase while the amine-borane complex was soluble in the aqueous phase. Compound **6** produced diagnos-

tic signals for the imidazolium moiety in the ^1H NMR and ^{13}C NMR spectra thereof, accompanied by a sharp singlet at -5.1 ppm in its ^{31}P NMR spectrum, which provided evidence for deprotection of the P atom. Alternatively, benzyl alcohol **4** could be reacted with dimethyl chlorophosphate (CAUTION! This substance is highly toxic and requires special handling techniques) to convert it into phosphate **7**. Deprotection of the P atom and partial hydrolysis of the phosphate ester of **7** with neat dihexylamine, followed by cation exchange with NaH, afforded the corresponding sodium phosphate **8**, which was characterised as its phosphine oxide **9**. In this instance, dihexylamine was chosen for the P deprotection step because the ligand would be soluble in the aqueous layer and it was desirable for the amine-borane complex to be soluble in the organic phase. The ^1H NMR spectrum of the $\text{P}=\text{O}$ product **9** showed a characteristic two proton doublet at 4.88 ppm ($J_{\text{H,P}} = 8.2$ Hz) and a three proton doublet at 3.56 ppm ($J_{\text{H,P}} = 9.5$ Hz), while the ^{31}P NMR spectrum thereof showed two sharp singlet signals at 31.7 ppm ($\text{P}(\text{O})$) and 1.1 ppm (OPO).

In a second approach towards polar phosphines, diphenylphosphine-borane **10** was lithiated using *n*-butyllithium and the lithium phosphide was subsequently reacted with α -methylene- γ -butyrolactone in a Michael-type reaction to produce adduct **11** (Scheme 2). The lactone was readily reduced to the corresponding



Scheme 2. Synthesis of bis imidazolium-based polar ligands.

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