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Recyclable polymer-supported Pd catalysts for aryl amination reactions

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Abstract—Polymer-supported palladium catalysts were prepared from three commercially available phosphine-functionalised polymers (PS-PR$_2$), Pd$_2$(dba)$_3$ and P(t-Bu)$_3$. Catalyst stability was investigated using VT ^{31}P NMR spectroscopy. One of the catalysts can be reused in the amination of bromobenzene and chlorotoluene, up to three times, without loss in yield. Recyclability of the catalysts is dependent on the method of preparation and the nature of the polymer-bound phosphine.
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1. Introduction

Phosphine-functionalised polymer resins are commonly used as a means of support, as well as a source of ligand in many catalytic reactions.[1] For example, diphenyl-phosphine functionalised polymer resins **1** and **3** (Fig. 1) have been used in the immobilisation of several palladium complexes for use as heterogeneous catalysts in Heck and Suzuki-Miyaura cross-coupling reactions.[2] In some cases, the recovered catalysts were reported to retain activity over several repeated experiments. Nevertheless, the scope of these supported catalysts is limited to fairly activated ArX substrates, where X = I, Br or OTf. Unless the aryl group contains electron-deficient substituents, reactions with aryl chlorides are generally difficult.[2e]

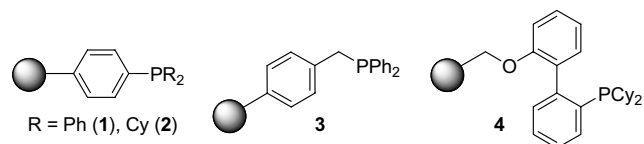Concurrent with the discovery of catalysts that can promote reactions with unactivated and/or sterically

demanding aryl bromides and chlorides,[3] attempts were made to immobilise these catalysts onto solid supports. A number of these have been successful in catalytic reactions, but very often catalyst recovery and reuse were either not discussed[4] or unsuccessful.[5] The most successful catalyst in this regard is that reported by Parrish and Buchwald—polystyrene-supported dicyclohexylbiphenyl-phosphine **4** (Fig. 1) afforded catalysts that can promote aryl amination and Suzuki reactions, using aryl iodide, bromide or chloride as starting materials. The catalyst can be successfully recycled up to three times with no significant deterioration in performance.[6] Although this is undoubtedly impressive, the preparation of phosphine-functionalised polymer resin **4** is by no means trivial.

In a previous letter, we described the ability of the phosphine-functionalised polymers **1–3** to capture the monoligated catalyst [Pd{P(t-Bu)$_3$}].[7] We speculate that this could also be exploited as a means of immobilising these catalytic species. The resultant supported complex could be catalytically active via two possible mechanisms: (i) The dissociation of the coordinatively unsaturated palladium species from the polymer support, thus effecting catalytic reactions in the homogeneous phase (Scheme 1, Eq. 1); or (ii) the dissociation of the tri-*tert*-butylphosphine ligand to generate the catalytically active palladium species, which could catalyse the reaction heterogeneously (Scheme 1, Eq. 2).[8] If these processes could be effected reversibly, it may be possible to develop a new type of highly active and recoverable catalyst.

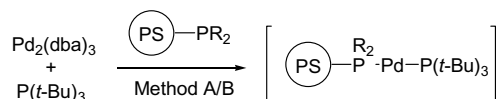**Figure 1.** Phosphine-functionalised polymer supports.
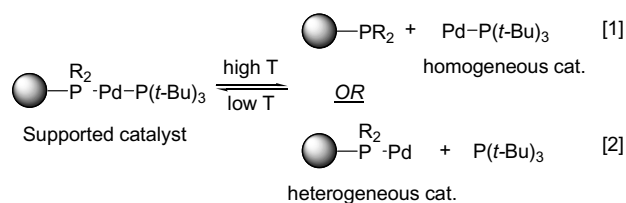
Scheme 1. Dissociative pathways for polymer-bound palladium catalysts.

In both of the scenarios presented above, the coordination of the palladium complex to the tethered phosphine moiety on the polymer support will be an important factor in determining the catalyst's stability, reactivity and recyclability. Herein, we report the synthesis, characterisation and catalytic behaviour of palladium catalysts derived from $P(t\text{-Bu})_3$ and three commercially available phosphine-functionalised polymer resins PS-TPP, PS-PCy_2 and PS-CH_2PPh_2.

2. Preparation of PS-Pd catalysts

Monoligated palladium catalysts are usually generated in situ by mixing a slightly sub-stoichiometric equivalent of $Pd_2(dba)_3$ precursor and $P(t\text{-Bu})_3$. Under these conditions, the resultant mixture is likely to consist of a series of slowly equilibrating 12- and 14-electron complexes, $Pd(PR_3)$ and $Pd(PR_3)_2$, respectively (Scheme 2).[9]

With this in mind, two methods of preparing the polymer-bound palladium catalysts were employed (Scheme 2):[9] In the first method (A), the polystyrene-resin was added to a THF solution containing a mixture of $Pd_2(dba)_3$ and $P(t\text{-Bu})_3$ (Pd:P ratio of 1:0.8), which was stirred gently at room temperature overnight. In the alternate procedure (B), the mixture was heated at

Scheme 2. Preparation of polymer-supported Pd catalysts. Method A: THF, rt, overnight; Method B: THF, reflux, 5–14 h.

80 °C, in an attempt to promote swelling and diffusion of reagents through the cross-linked polymer, as well as to facilitate the generation of the coordinatively unsaturated species. Additionally, to elucidate the role of the tri-*tert*-butylphosphine in these catalysts, $Pd_2(dba)_3$ was also supported onto **2** and **3** using method B, in the absence of the trialkylphosphine.[10]

The loading, as well as the metal-to-ligand ratio of the supported catalysts were determined using %Pd and %P analyses (Table 1). Using **1** as a support, there is a noticeable decrease in the Pd:P ratio upon heating the reaction mixture from 1:4 to 1:6.5 (entries 1 and 2). In comparison, the ratio was retained at 1:3 when polymer **3** was used (entries 3 and 4). This indicates that PS-TPP **1** does not coordinate strongly to palladium(0). Using polymer **2**, an initially high Pd:P ratio was obtained (entry 5), which decreased to 1:3, obtained by heating the catalyst mixture for 14 h (entries 6 and 7). As this complex $[Pd(PR_3)\{P(t\text{-Bu})_3\}]$ is the bulkiest, we attributed this to the slower diffusion, dissociation and/or accommodation of the palladium complex within the macroporous structure.[11]

3. Variable temperature[31]P NMR

To examine the release of palladium species into the homogeneous phase, VT ^{31}P-$\{^1H\}$ spectra of the immobilised catalysts were recorded in toluene[d_8] using a normal (solution-phase) NMR probe, with resin beads swollen but suspended above the magnetic coil. The NMR spectra were recorded at 10 °C intervals between ambient temperature and 100 °C, and then in reverse back to room temperature. The liberation of any phosphorus-containing moieties into the solution phase would thus be indicated by the observation of corresponding resonance signals. Visual inspection of the NMR samples after these experiments could also reveal signs of catalyst decomposition, such as the development of colour (green or pink/red) and/or the formation of palladium black.

Substantial catalyst leaching and/or decomposition were observed for all the catalysts prepared at room temperature (method A). These were indicated visually, and/or

Table 1. Pd and P loadings of polymers prepared by different methods[a]

Entry	PS	Method	T/h	Pd loading[b]	P loading[c]	Pd:P
1	TPP	A	14	0.43	1.77	1:4
2	TPP	B	5	0.22	1.43	1:6.5
3	CH_2PPh_2	A	14	0.50	1.50	1:3
4	CH_2PPh_2	B	5	0.37	1.06	1:3
5	PCy_2	A	14	0.52	0.17	3:1
6	PCy_2	B	5	0.15	1.14	1:7.5
7	PCy_2	B	14	0.36	1.04	1:3
8	CH_2PPh_2[d]	B	14	0.53	2.61	1:5
9	PCy_2[d]	B	14	0.56	2.42	1:4

[a] Loading of commercial PS-TPP, PS-CH_2PPh_2 and PS-PCy_2 resins were 1.39, 1.37 and 1.24 mmol/g, respectively, as specified by the manufacturer.
[b] mmol Pd/g, calculated from %Pd determined by ICP-AES analysis.
[c] mmol P/g, calculated from %P determined by elemental analysis.
[d] No $P(t\text{-Bu})_3$ added.