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Silicaethylphosphatrioxaadamantane—A new support for palladium catalysts and evaluation in Suzuki coupling reactions

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ABSTRACT

New highly active heterogeneous silicaethylphosphatrioxaadamantane palladium catalysts with very low millimole per gram palladium load are reported. Applied to a broad range of Suzuki substrate pairs in 0.1–0.2 mol%, these catalysts are very effective, reusable and resistant to leaching for reactions in hot xylene or with microwave irradiation of EtOH:H_2O:DME solutions.

1. Introduction

Tertiary phosphines were first immobilised in the early seventies [1]. Since then, a wide variety of phosphines have been developed and immobilised both onto polystyrene and silica. They have been widely used as a mode of attachment for transition-metal catalysts [2]. Palladium-catalysed coupling reactions remain one of the most useful transformations in organic synthesis [3]. The presence of bulky phosphine ligands has been demonstrated to give efficient results. Thus, a range of homogeneous palladium phosphatrioxaadamantane catalysts have been developed and applied as very effective ligands for Suzuki coupling reactions [4], Sonogashira and α-arylation reactions, [5] and Buchwald–Hartwig aminations [6]. Phenylphosphatrioxaadamantane has also been used as a ligand for the formation of highly efficient rhodium(I) hydroformylation catalysts [7]. The advantages with respect to the palladium retention, phosphine retention, catalyst separation and reuse in the case of immobilised catalysts have resulted in several studies utilising silica supported phosphinopalladium catalysts. For example, Framery et al. have demonstrated the efficiency of palladium aryldicyclohexylphosphine functionalised SBA-15 silica for Suzuki–Miyaura cross-coupling of various substituted aryl chlorides with arylboronic acids [8]. An MCM-41-supported bidentate phosphine palladium(0) was reported by Cai et al. to be a highly active catalyst for the heterogeneous Suzuki reaction of aryl halides with arylboronic acids and can be reused many times without loss of activity [9]. Likewise Singh reported on Heck coupling using Pd(0) complexes of (P, N) ligands anchored on silica gel via a propyl linker group [10].

Despite the many reported uses and impressive performance of homogeneous palladium phosphatrioxaadamantane catalysts, immobilised analogues have not been reported.

We recently published on novel silica immobilised palladium thioglycolate and silica immobilised palladiumdimercaptoethane catalysts along with the initial studies of these catalysts in Heck and Suzuki carbon–carbon coupling chemistries [11]. In an extension of this programme we report now on the immobilisation of the phosphaadamantane function onto silica via an ethyl linker group and the development of heterogeneous catalysts for use in Pd-catalysed Suzuki couplings.

The phosphine was immobilised as described in Scheme 1 from compound **1** which is formed by radical addition of phosphatrioxaadamantane to vinyltrimethoxysilane and subsequently grafted onto silica to give material **2**. A variety of different pore size silicas (particle size 60–200 μm) were used as supports including 60 Å, 90 Å, 110 Å and 150 Å so that any effects of pore size on activity of the Pd-catalysts synthesised from the supported phosphine would be identified.

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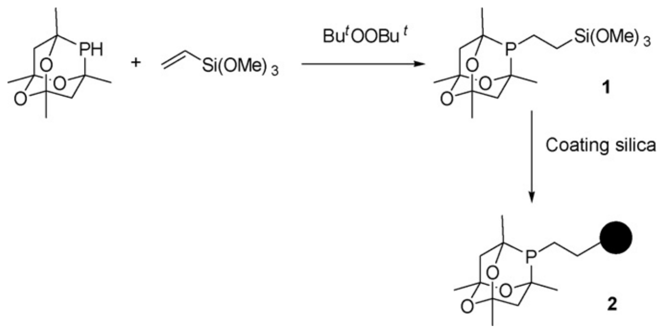


Scheme 1.

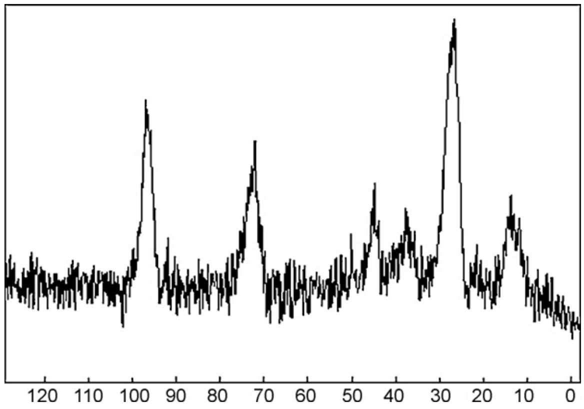


Fig. 1. ^{13}C CPMAS NMR **2c**.

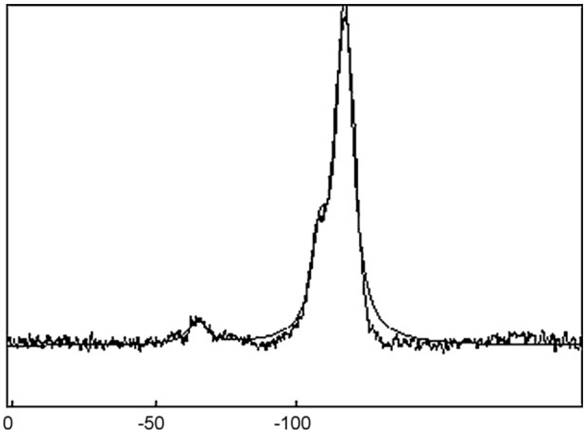


Fig. 2. ^{29}Si MAS NMR **2c**.

Table 1
Key parameters of the materials

Silica pore size (Å)[a]	P_{cage} (mmol/g), specific surface areas ($m^2\,g^{-1}$) for materials **2**	Pd (mmol/g) for materials **3** and **4**
a 60	0.3, 296	0.016, 0.019
b 90	0.7, 228	0.009, 0.008
c 110	0.5, 261	0.016, 0.009
d 150	0.6, 155	0.018, 0.008
e 150	0.5, 215	0.014, 0.006

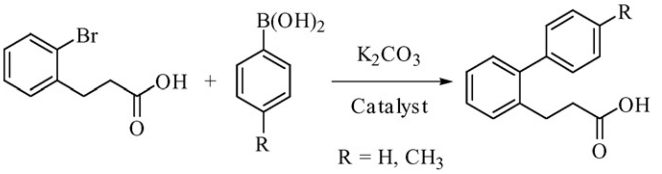
[a] **a–d**: particle size 60–200 μm, **e**: particle size 315–500 μm.

The functionalised silica materials were characterised by a combination of methods including nitrogen sorption porosimetry and solid state ^{13}C and ^{29}Si NMR. The phosphine loading (as measured by phosphorus analysis and provided in Table 1) showed a sharp increase between the 60 Å and 90 Å silicas but thereafter varied only slightly and irregularly with changing silica pore size. Reasonably high measured surface areas were found for the phosphine supported material **2** and as a consequence of the variations in phosphine loading, these surface areas display a narrower range of values than might have been expected for the different materials.

Examples of the solid state spectra for **2c** are shown in Figs. 1–3. The T:Q ratio (that is ratio of functional group silicon to the framework silicon) was readily obtained from the fitted ^{29}Si MAS NMR spectra [12] and is in general agreement with the loadings quoted in Table 1 based on phosphorus elemental analysis.

Two different palladium compounds dichlorobisditriphenylphosphino palladium, *trans*-$[PdCl_2(PPh_3)_2]$ and bis(dibenzylideneacetone)palladium(0) $[Pd(dba)_2]$ were readily immobilised (Scheme 2) when the materials **2** were stirred in refluxing chloroform solutions of these palladium compounds (20 mL of 10 mM Pd g^{-1} **2)** for 5 h. Loadings of ∼0.095 mmol g^{-1} were readily achieved by this method. In order to maximise palladium retention and inhibit palladium clustering we were particularly interested in assessing the catalytic activity for very low palladium loaded materials, so for the catalytic work described here, the material was exposed to dilute dichloromethane, DCM, solutions of the palladium compounds (40 mL of 1.25 mM Pd g^{-1} **2**) at room temperature for 5 h. Thus materials **3** and **4** were obtained (Scheme 2) with palladium uptake as determined by ICP-OES on the digested materials as given in Table 1.

Table 2
Results of Suzuki reactions in hot xylene



Catalyst	Conversion* (cycle 1, cycle 2) catalyst 3	Conversion* (cycle 1, cycle 2) catalyst 4
a	94%, 95%[a]	98%, 91%[a]
b	93%, 94%[a]	91%, 98%[a]
c	92%, 99%, >99%, >99%, >99%[b]	95%, >99%, >99%, 99%, 95%[b]
d	97%, >99%[b]	93%, 92%[b]
e	92%, 94%[a]	96%, >99%[a]

[*] An aryl halide (1 mmol), a boronic acid (1.5 mmol), K_2CO_3 (2 mmol) and the corresponding Pd catalyst (0.1 mol%) were heated at 120 °C in xylene (4 mL) for 2 h. Conversions calculated by LCMS.

[a] R=H.

[b] $R=CH_3$.