



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

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## ABSTRACT

New highly active heterogeneous silicaethylphosphatrioxaadmantane 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<sub>2</sub>O:DME solutions.

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## 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 phosphatrioxaadmantane catalysts have been developed and applied as very effective ligands for Suzuki coupling reactions [4], Sonogashira and  $\alpha$ -arylation reactions, [5] and Buchwald–Hartwig aminations [6]. Phenylphosphatrioxaadmantane 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 chlo-

rides 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].

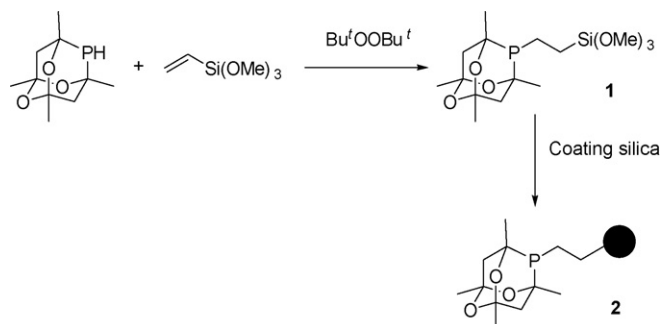
Despite the many reported uses and impressive performance of homogeneous palladium phosphatrioxaadmantane catalysts, immobilised analogues have not been reported.

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 phosphaadmantane 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 phosphatrioxaadmantane to vinyltrimethoxysilane and subsequently grafted onto silica to give material **2**. A variety of different pore size silicas (particle size 60–200  $\mu\text{m}$ ) 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.

**Table 1**  
Key parameters of the materials

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

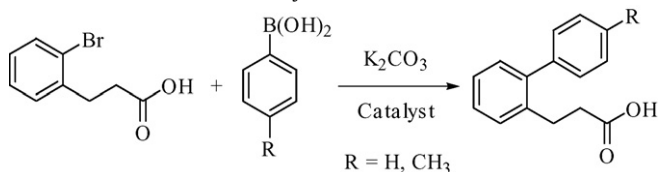
<sup>a</sup> **a–d**: particle size 60–200  $\mu\text{m}$ , **e**: particle size 315–500  $\mu\text{m}$ .

The functionalised silica materials were characterised by a combination of methods including nitrogen sorption porosimetry and solid state  $^{13}\text{C}$  and  $^{29}\text{Si}$  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  $^{29}\text{Si}$  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 dichlorobis(diphenylphosphino) palladium, *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and bis(dibenzylideneacetone)palladium(0) [Pd(dba)<sub>2</sub>] were readily immobilised (Scheme 2) when the materials 2 were stirred in refluxing

**Table 2**  
Results of Suzuki reactions in hot xylene

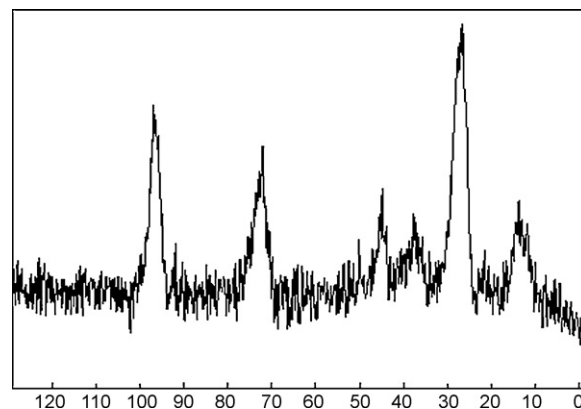
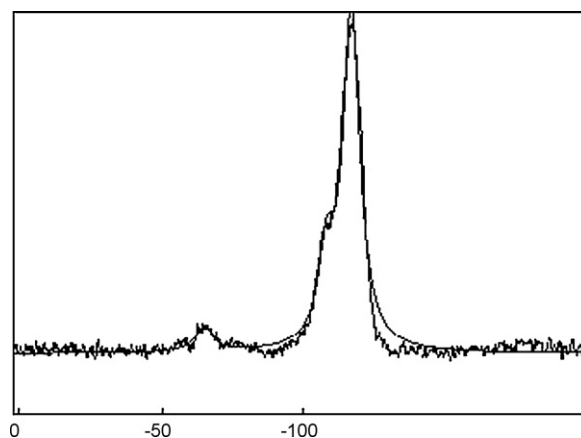


Catalyst	Conversion <sup>*</sup> (cycle 1, cycle 2) catalyst 3	Conversion <sup>*</sup> (cycle 1, cycle 2) catalyst 4
<b>a</b>	94%, 95% <sup>a</sup>	98%, 91% <sup>a</sup>
<b>b</b>	93%, 94% <sup>a</sup>	91%, 98% <sup>a</sup>
<b>c</b>	92%, 99%, >99%, >99%, >99% <sup>b</sup>	95%, >99%, >99%, 99%, 95% <sup>b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

<sup>\*</sup> An aryl halide (1 mmol), a boronic acid (1.5 mmol),  $\text{K}_2\text{CO}_3$  (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.

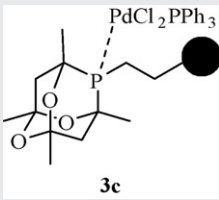
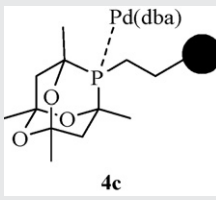
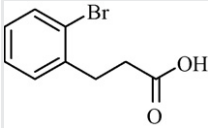
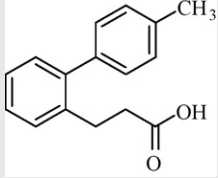
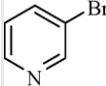
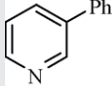
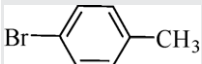
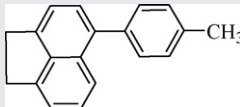
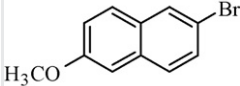
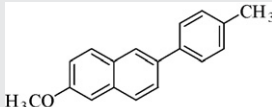
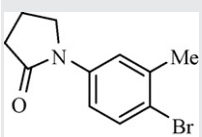
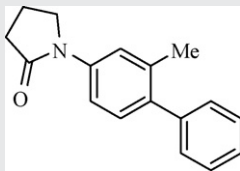
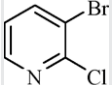
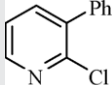
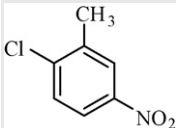
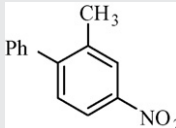
<sup>a</sup> R=H.

<sup>b</sup> R=CH<sub>3</sub>.

Fig. 1.  $^{13}\text{C}$  CPMAS NMR 2c.Fig. 2.  $^{29}\text{Si}$  MAS NMR 2c.

chloroform solutions of these palladium compounds (20 mL of 10 mM Pd  $\text{g}^{-1}$  2) for 5 h. Loadings of  $\sim 0.095 \text{ mmol g}^{-1}$  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  $\text{g}^{-1}$  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 3**Suzuki reactions with extended range of substrates  $\text{Ar-X} + \text{R-B(OH)}_2 \xrightarrow[\text{PAPdr}]{\text{K}_2\text{CO}_3} \text{Ar-R}$ 

Aryl halides	Products		
		92% <sup>a</sup>	95% <sup>b</sup>
		>99%	>99%
		69%	70%
		87%	84%
		68%	66%
		81%	85%
		49%	50%

<sup>a</sup> An aryl halide (1 mmol), a boronic acid (1.5 mmol),  $\text{K}_2\text{CO}_3$  (2 mmol) and the corresponding catalyst (0.1 mol%) were heated at 120 °C in xylene (4 mL) for 2 h. Conversions calculated by HPLC or LCMS.

<sup>a</sup> Recycles: 99%.

<sup>b</sup> Recycles: 95–99%.

Assuming 1:1 complexation of Pd with the phosphine, more than 90% of the immobilised phosphine remains free and actual Pd loadings from digested materials were found to be in the range 0.01–0.02 mmol  $\text{g}^{-1}$ .

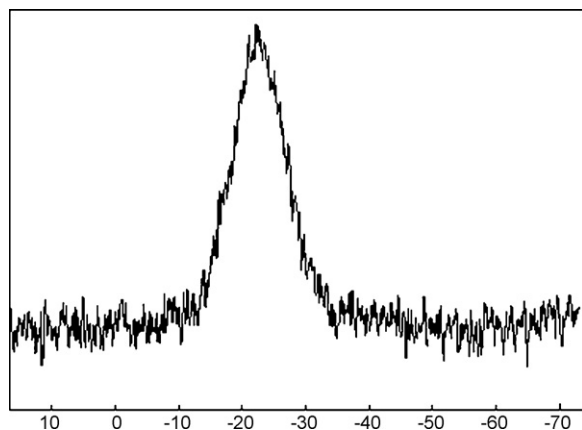
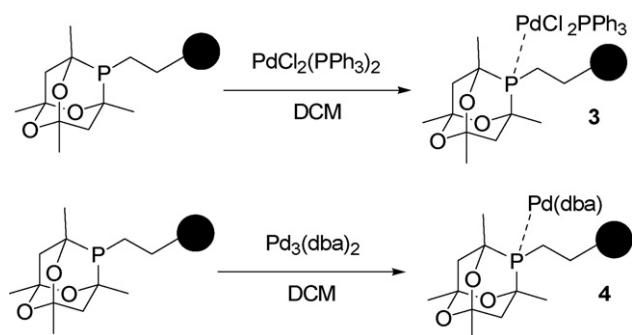
## 2. Screening of the materials **3** and **4** in Suzuki reactions

As shown below in Tables 2–4, the palladium catalysts give good conversion for a range of substrates and can easily be removed from the reaction mixture and recycled several times without loss of activity. Recycling was typically accomplished by filtration and washing of the catalyst followed by addition of fresh substrates, sol-

vent and base. Leaching tests were carried out using standard hot filtration (see Section 4) and these indicated a negligible degree of leaching. The large excess of Pd free phosphine sites in the materials should facilitate palladium retention.

The recycled conversions for **3c** and **4c** are impressive given the very low 0.1 mol% Pd employed. The particle size and pore diameter do not appear to have much effect on the conversion as measured after 2 h. Of further note is the similarity in catalytic behaviour of series **3** and **4** catalysts, despite the difference in oxidation states of the palladium catalyst precursor compounds employed.

A series of partial conversion experiments were conducted using successively recycled catalysts in order to assess reproducibility at

Fig. 3.  $^{31}\text{P}$  CPMAS NMR 2c.

Scheme 2.

Table 4

Microwave assisted Suzuki chemistry  $\text{R-X} + \text{R}'\text{B}(\text{OH})_2 \xrightarrow[\text{Catalyst}]{\text{MW, } 130^\circ\text{C, } 30\text{ min}}$   $\text{R-R}'$

Substrate	Products	Conversion <sup>a</sup> catalyst 3e
		90%, 96%, 97%, 95% <sup>b</sup>
		98%
		67%
		73%

<sup>a</sup> Reaction conditions: 1 mmol aryl halide, 1.5 mmol phenylboronic acid, 2 mmol  $\text{K}_2\text{CO}_3$ , 2.5 mL solvent, 0.1 mol% catalyst. MW,  $130^\circ\text{C}$ , 30 min. Conversions calculated by HPLC or LC-MS.

<sup>b</sup> Use of 4e: 91%, 93%, 92%, 93%.

partial conversion and thus possible conversion from leached catalyst. 3-Bromopyridine was reacted with phenylboronic acid under identical reaction conditions as described above with catalyst 3c. Conversions were found to be consistently in excess of 80% after 10 min. For three successive recycles conversions after 3 min to 3-phenylpyridine were in the range of 18–19% and this relatively narrow range is not indicative of contribution due to leached catalyst. Following an identical approach, catalyst 4c was used for the same transformation and it was also reused 3 times to give conversions in the range of 72–78% after 5 min. Thus the extent of partial conversion does not fluctuate greatly on recycling suggesting conversion due to leached catalyst is likely to be negligible over this series of runs. The catalysts were filtered and washed between runs.

Hot filtration leaching tests failed to confirm presence of leached Palladium either in digested residues of the hot filtrates from fresh catalysts 3c and 4c at the detection limit of ICP-OES or by assessment of further conversion in hot filtrates. Changes in the Pd content of the catalysts themselves measured after two recycles were negligible suggesting no detectable progressive change in the Pd loading.

Data on an expanded range of substrates using catalysts 3c and 4c, which proved active and long lived in the initial study, are given in Table 3.

The catalysts performed well with these more challenging substrates bearing in mind that no optimisation was undertaken. The conversion of the chloride substrate was relatively low.

Different reaction conditions were employed in order to demonstrate the versatility of these catalysts and also to see the effect on conversions. Microwave irradiation was found to reduce reaction times and improve conversion for a number of substrate pairs. Catalysts 3e and 4e with particle diameters of 315–500  $\mu\text{m}$  and pore sizes of 150 Å were utilised in this study (Table 4).

Conversions using these more challenging substrate pairs were promising and especially noteworthy is the considerable improvement in the conversion of the chloride substrate.

### 3. Conclusion

The well-known sterically demanding phosphatridioxadamanane ligand has been covalently attached to silica via an ethyl linker group using radical coupling chemistry to form the surface immobilising trialkoxysilyl precursor. Very low loadings ( $0.01\text{--}0.02\text{ mmol g}^{-1}$ ) of palladium from dichlorobis(triphenylphosphino)palladium(II) or bis(dibenzylideneacetone)palladium(0) afforded highly active catalytic materials, as evidenced by the observed high percentage conversion for a wide range of Suzuki substrate pairs with 0.1 mol% Pd catalyst. No specific effect of pore size, particle size or catalyst precursor oxidation state, on the extent of conversion was observed for the conditions explored.

### 4. Experimental

#### 4.1. General information

All reagents used were purchased from Aldrich, Avocado or Lancaster and were used without further purification, unless otherwise stated. 2,4,8-Trioxa-1,3,5,7-tetramethyl-6-phosphaadamantane obtained from Cytec.

#### 4.1.1. Instruments

Solid state NMR, Bruker AMX 400 MHz ( $^{29}\text{Si}$  MAS, frequency 79.5 MHz, spinning speed 12 kHz; 30 s recycle delay, with  $2\ \mu\text{s}$  ~45° pulse;  $^{13}\text{C}$  CP MAS; frequency 100.65 MHz, spinning speed 10 kHz, 2 ms contact time, 10 s delay, 90° pulse for 3.5  $\mu\text{s}$ ).  $^{31}\text{P}$  CP MAS, fre-

quency 162.02 MHz, spinning speed 12 kHz, 2 ms contact time, 30 s delay 90° pulse for 3.5  $\mu$ s). Surface areas were measured using a Micromeritics Flowsorb II 2300 single point surface area analyser.

HPLC Agilent Technologies 1100 Series. Phenomenex C18 column.

LC-MS Shimadzu LCMS-2010EV Mass Spectrometer.

#### 4.2. Typical procedure for supported silicaethylphosphaadamantane 2

Into a 500 mL round-bottomed flask fitted with reflux condenser, over-head stirrer and thermometer was added 2,4,8-trioxa-1,3,5,7-tetramethyl-6-phosphaadamantane (12.97 g, 0.060 mol,  $M_w$  216.243). Vinyltrimethoxysilane (7.7 mL, 0.050 mol,  $M_w$  148.23,  $\rho$  0.968) was added and the mixture was heated to reflux. The solid was dissolved at about 80 °C. Di-*tert*-butyl peroxide (20 drops) was added. The mixture was heated for a further 2 h at this temperature and then cooled. The progress of the addition reaction was monitored by the consumption of vinyltrimethoxysilane by the disappearance of the peak at 5.8–6.0 ppm. The reaction was deemed complete when the vinyl peaks were no longer present. The mixture is essentially 6-ethyltrimethoxysilyl-2,4,8-trioxa-1,3,5,7-tetramethyl-6-phosphaadamantane **1** at this point.

Selected NMR data for sample of reaction mixture:

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.65–0.77 (2H, m,  $\text{CH}_2\text{Si}$ ), 1.19–1.88 (18H, m,  $\text{PCH}_2$ ,  $\text{PCCH}_2$ ,  $\text{PCCH}_3$ ,  $\text{OCCH}_3$ ), 3.47 (9H, s,  $\text{SiOCH}_3$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.7 ( $\text{SiCH}_2$ ,  $^2J_{\text{PC}}$  19 Hz), 13.0 ( $\text{PCH}_2$ ,  $J_{\text{PC}}$  24 Hz), 26.9 ( $\text{OCCH}_3$ ) 27.9 ( $\text{PCCH}_3$ ), 37 ( $\text{PCCH}_2$ ), 44.4 ( $\text{PCCH}_2$   $^2J_{\text{PC}}$  15 Hz), 50.5 ( $\text{SiOCH}_3$ ), 72.2 ( $\text{PCCH}_3$ ), 95.6 ( $\text{OCCH}_3$ ), 96.4 ( $\text{OCCH}_3$ ) (assignments based on those reported [7] for the related methylphosphine cage).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  –21.3.

#### 4.3. 2,4,8-Trioxa-1,3,5,7-tetramethyl-6-phosphaadamantane-6-ethylsilica2

Without further purification the compound **1** as formed above (18.2 g, 0.050 mol) was combined with toluene (100 mL) and agitated while silica (40 g, 60–200  $\mu\text{m}$ , 110 Å) was added slowly. Distilled water (3 mL) was added to the stirred mixture and it was then refluxed for 4 h. Once cool the solid was filtered off washed with toluene (75 mL) then methanol (2  $\times$  75 mL) before being dried under reduced pressure.

Solid state NMR data for **2c**:

$^{13}\text{C}$  CPMAS NMR 97(s,  $\text{OCCH}_3$ ), 71(s,  $\text{PCCH}_3$ ), 45( $\text{PCCH}_2$ ), 37(s,  $\text{PCCH}_2$ ), 28(s,  $\text{OCCH}_3$ ), 13( $\text{PCH}_2$ ,  $\text{SiCH}_2$ );

$^{29}\text{Si}$  MAS NMR: –65, –108, –115 ppm;

$^{31}\text{P}$  CPMAS NMR –22 ppm.

#### 4.4. Triphenylphosphine palladium(II) dichloride phosphaadamantane ethyl silica 3

$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (175.5 mg, 0.25 mmol) was dissolved in dichloromethane (200 mL). This yellow solution was added into a Nalgene bottle containing phosphaadamantane ethyl silica (5 g). The mixture was rolled for 5 h until the colour of the solution has turned into pale yellow. The mixture was then filtered and the yellow solid was washed with dichloromethane (2  $\times$  50 mL) and dried under reduced pressure. A small amount of triphenylphosphine palladium(II) dichloride phosphaadamantane ethyl silica (~20–25 mg) was digested with concentrated nitric acid (3 mL). The mixture was filtered off and the filtrate was diluted up to

10 mL. The amount of palladium in this solution was analysed by ICP-OES.

#### 4.5. Bis(dibenzylideneacetone)palladium(0) phosphaadamantane ethyl silica 4

Bis(dibenzylideneacetone)palladium(0) (114 mg, 0.25 mmol) was dissolved in dichloromethane (200 mL). This dark purple solution was added into a Nalgene bottle containing phosphaadamantane ethyl silicas **2** (5 g). The mixture was rolled for 5 h until the colour of the solution turned into pale yellow. The mixture was then filtered and the yellow solid was washed with dichloromethane (2  $\times$  50 mL) and dried under reduced pressure. A small amount of bis(dibenzylideneacetone)palladium(0) phosphaadamantane ethyl silica (~20–25 mg) was digested with concentrated nitric acid (3 mL). The mixture was filtered and the filtrate was diluted to 10 mL. The amount of palladium in this solution was analysed by ICP-OES.

#### 4.6. Suzuki reactions

- (i) An aryl halide (1 mmol), a boronic acid (1.5 mmol),  $\text{K}_2\text{CO}_3$  (2 mmol) and the corresponding catalyst (0.1–0.2 mol%) were heated at 120 °C in xylene (4 mL) for 2 h. The reaction was followed by HPLC. The catalyst was filtered off, washed with water and methanol and dried under vacuum prior to reuse.
- (ii) An aryl halide (1 mmol), a boronic acid (1.5 mmol),  $\text{K}_2\text{CO}_3$  (2 mmol) the corresponding catalyst (0.1–0.2 mol%) were stirred in a mixture of EtOH:H<sub>2</sub>O:DME (1:2:4) (2.5 mL) at 130 °C for 30 min in a Biotage microwave reactor. The conversion was measured by HPLC. The catalyst was washed with water and methanol and dried under vacuum prior to reuse.

#### 4.7. Leaching test

A sample from the Suzuki reaction with 3-bromopyridine was taken after 2 min and the remainder of the hot supernatant syringe filtered into a clean reaction flask. Further solvent and base was added to the filtrate and the reaction was continued in the absence of the catalyst for a further 2 h. Conversion was found to be 9% in the case of triphenylphosphine palladium(II) dichloride phosphaadamantane ethyl silica **3c** and 12% conversion in the case of bis(dibenzylideneacetone)palladium(0) phosphaadamantane ethyl silica **4c** after 2 min. No further conversion in the filtrate was observed after 2 h. The two filtrates were concentrated and the two white residues were digested and analysed by ICP-OES. The residues were Pd free within the detection limits of the instrument (~60 ppb).

The metal content of digested **3c** and **4c** was analysed by ICP-OES after they had been recycled twice in the Suzuki reaction above. Results showed that the palladium content of neither catalyst changed significantly after two recycles.

#### Acknowledgements

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#### References

- [1] J.M. Frechet, M.J. Farrall, *J. Org. Chem.* 41 (1976) 3877–3882.
- [2] (a) Y. Uozomi, *Top. Curr. Chem.* 242 (2004) 77–112;  
(b) N.E. Leadbeater, M. Marco, *Chem. Rev.* 102 (2002) 3217–3273, references cited therein.
- [3] L. Yin, J. Liebscher, *Chem. Rev.* 107 (2007) 133–173.
- [4] (a) G. Adjabeng, T. Brenstrum, J. Wilson, C. Frampton, A. Robertson, J. Hillhouse, J. McNulty, A. Capretta, *Org. Lett.* 5 (2003) 953–955;

- (b) S.A. Ohnmacht, T. Brenstrum, K.H. Bleicher, J. McNulty, A. Capretta A, *Tetrahedron Lett.* 45 (2004) 5661–5663;  
(c) T. Brenstrum, D.A. Gerristma, G.M. Adjabeng, C.S. Frampton, J. Britten, A.J. Robertson, J. McNulty, A. Capretta, *J. Org. Chem.* 69 (2004) 7635–7639.
- [5] G. Adjabeng, T. Brenstrum, C.S. Frampton, A.J. Robertson, J. Hillhouse, J. McNulty, A. Capretta, *J. Org. Chem.* 69 (2004) 5082–5086.
- [6] D. Gerristma, T. Brenstrum, J. McNulty, A. Capretta, *Tetrahedron Lett.* 45 (2004) 8319–8832.
- [7] (a) R.A. Baber, M.L. Clarke, K.M. Heslop, A.C. Marr, A.G. Orpen, P.G. Pringle, A. Ward, E. Damaris, D.E. Zambrano-Williams, *Dalton Trans.* (2005) 1079–1085;  
(b) M.L. Clarke, G.J. Roff, *Chem. Eur. J.* 12 (2006) 7078–7986.
- [8] R. Sayah, K. Glegoia, E. Framery, V. Dufauda, *Adv. Synth. Catal.* 349 (2007) 373–381.
- [9] M. Cai, M.J. Junchao Sha, Q. Xu, *J. Mol. Catal. A: Chem.* 268 (2007) 82–86.
- [10] G. Singh, S. Bali, K. Ajai, A.K. Singh, *Polyhedron* 26 (2007) 897–903.
- [11] (a) M. Al-Hashimi, A.C. Sullivan, J.R.H. Wilson, *J. Mol. Catal. A: Chem.* 273 (2007) 298–302;  
(b) M. Al-Hashimi, A. Qazi, A.C. Sullivan, J.R.H. Wilson, *J. Mol. Catal. A: Chem.* 278 (2007) 160–164.
- [12] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, *Magn. Reson. Chem.* 40 (2002) 70–76.