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The synthesis and characterisation of immobilised palladium carbene complexes and their application to heterogeneous catalysis

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ABSTRACT

Silica supported palladium NHC complexes have been prepared by two different routes: one involving the reaction of silica-supported imidazolium salts with palladium acetate and a direct immobilisation of a pre-formed complex by reacting a (trimethoxysilylpropyl)-*N*-aryl-imidazolylidene palladium complex with surface hydroxyl groups. A small range of catalysts of varying steric bulk were prepared in order to evaluate the effect on catalytic conversion. The activity of the palladium catalysts in Suzuki cross-coupling reactions has been established. The catalysts prepared by immobilising pre-formed palladium complexes gave superior results for the conversion of aryl bromides and aryl chlorides. In addition, use of sterically bulky NHCs (such as the *N*-2,6-(diisopropyl)phenyl-substituted ligand) resulted in increased catalytic activity, which is analogous to the trends noted in homogeneous catalysis.

1. Introduction

The immobilisation of metal catalysts onto insoluble supports is of great commercial interest because of the sustainable green chemistry applications it offers [1]. Although current homogeneous metal catalysts may have sufficient activity, heterogeneous analogues offer potential practical advantages of ease of product separation and the possibility of recycling as the catalysts can be filtered off from the product solution, washed and recycled.

Designing immobilised catalysts, in which dissociation or decomposition of immobilised ligands from the metal is minimised, is a significant challenge. Numerous reports of supported homogeneous catalysts have appeared in the literature, many of which involve phosphine donor groups [2]. We have previously reported the use of a novel silica-supported palladium phosphine catalyst and its use in a number of copper-free Sonogashira coupling reaction between aryl halides and alkynes [3].

More recently, attention has shifted to the use of *N*-heterocyclic carbene (NHC) ligands in binding transition metals to an insoluble support, because of their high activity for palladium catalysed cross-coupling reactions and ruthenium catalysed olefin metathesis [4a,b]. We have previously reported the use of novel NHCs in palladium and copper catalysed homogeneous reactions [4c,d]. The advantages of metal-NHC catalysts are that the ligands are less prone to dissociation from palladium than phosphine ligands and that the complexes are more thermally stable.

Of particular interest are the recent attempts at immobilising various NHC complexes of palladium for use in heterogeneous Suzuki couplings. Lee et al. [5] and Weck et al. [6] have synthesised polymer-bound palladium NHC catalysts which can catalyse the coupling of relatively unreactive aryl chlorides. Herrmann et al. [7] prepared an *N*-heterocyclic dicarbene complex tethered to Wang resin that catalysed Heck reactions of both activated and non-activated aryl bromides. In contrast to polymer-based tethers, the use of a silica-support requires no pre-swelling in organic solvents which thus reduces solvent usage and may reduce the propensity for catalyst leaching. As a result Sen et al. [8] and Lin et al. [9] have prepared silica-supported palladium NHC hybrid catalysts by reacting a metal salt with a tethered ligand. The disadvantage of this particular methodology is the difficulty in confirming the co-ordination around the metal centre. A more elegant route would be to synthesise a well-defined metal–carbene complex that may then be grafted directly to the silica surface. There have been a number of reports of trialkoxysilylpropyl functionalised palladium NHC complexes being immobilised on silica surfaces [10–12], however Lin et al. found that immobilisation of a pre-formed complexes was unsuccessful [9].

When designing palladium NHC complexes for tethering to a support medium via an organic linker, it is somewhat surprising

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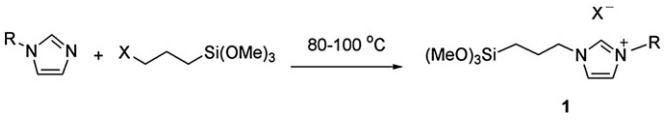
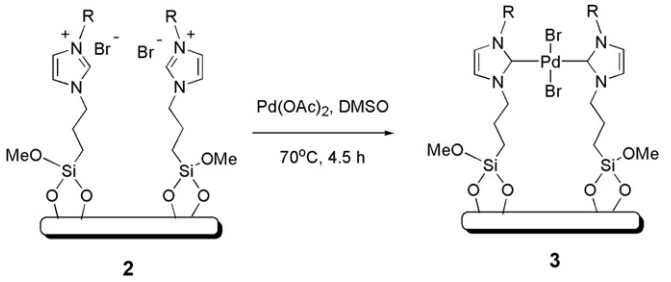
Table 1
Synthesis of imidazolium salts **1**.



1

Entry (name)	X	R	Temperature (°C)	% Yield
1a	Br	Benzyl-	80	79
1b	Br	Mesityl-	80	86
1c	Br	2,6-(Diisopropyl)phenyl-	100	76[a]
1d	I	2,6-(Diisopropyl)phenyl-	100	96

[a] Reaction carried out in acetonitrile.



2 **3**

Scheme 1. Formation of a palladium complex. R = benzyl (**3a**), mesityl (**3b**).

that the examples in the literature focus upon the use of *N*-alkyl substituted NHCs despite results from homogeneous catalysis that suggest that NHCs bearing bulky *N*-aryl substituents are more active towards C–C and C–N coupling reactions [12]. Artok et al. [10] did report the synthesis of an *N*-aryl substituted NHC palladium catalyst and its successful application in the Heck reaction.

Our aim was to synthesise palladium complexes of NHCs bearing bulky *N*-aryl or *N*-alkyl substituents and an alkoxysilylalkyl chain to enable tethering to a silica surface. This process would enable characterisation of the co-ordination geometry around the palladium metal prior to immobilisation of the catalyst onto the silica surface. It was anticipated that catalysts bearing bulky *N*-aryl substituents would have enhanced activity compared to those with simpler substituents. In this work we report the synthesis of bis (*N*-(trimethoxysilylpropyl)-*N*′-aryl)imidazolylidenepalladium complexes, their immobilisation onto a silica support and an evaluation of their activity for Suzuki coupling reactions. In addition, a similar catalyst was prepared by an alternative route involving the tethering of the imidazolium salt **2** (NHC ligand precursor) onto the silica support followed by reaction with palladium acetate, to afford **3**. This would enable a direct comparison of the two methodologies upon the catalytic activity.

2. Results and discussion

2.1. Synthesis of ligand precursors

N-Aryl imidazoles were prepared according to standard procedures [13]. The trialkoxysilyl group allows facile tethering to silica via condensation with surface silanol groups [14]. Imidazolium salts **1a–d** were prepared by heating a molten mixture of the *N*-substituted imidazole and 3-(bromo/iodopropyl)trimethoxysilane at 80–100 °C (Table 1). It was found that the diisopropylphenyl (dipp) derivative **1d** could be prepared in a more pure form by using acetonitrile as a solvent. Reactions were monitored by TLC and in all cases the imidazolium salt was detected on the baseline within 20 h accompanied by the complete disappearance of the imidazole starting material. The imidazolium salts were isolated in high yields after trituration of the reaction mixture with diethyl ether. The *N*-alkyl imidazolium bromides were isolated as viscous oils whilst the *N*-aryl derivatives were isolated as white solids which were not appreciably hygroscopic. A downfield signal between δ 9.5–10.5 ppm in the ^{1}H NMR spectra, characteristic of the C2 proton of an imidazolium salt, confirmed the successful formation of the imidazolium salts **1a–d** (Table 1).

2.2. Immobilisation of imidazolium salts and complexation with palladium

Imidazolium salts **1a–b** were immobilised by heating under reflux in toluene in the presence of silica according to the literature procedure [8]. The tethered imidazolium salts **2** were treated with palladium acetate to yield immobilised bis NHC palladium(II) complexes **3** (Scheme 1). The formation of a mono-NHC complex is also a possibility.

Elemental analysis of catalyst **3b** (R = mesityl) shows an excess of palladium (theory = 4.77%; found 6.88%), suggesting the presence of other palladium species. Formation of palladium black (palladium nanoparticles) at some stage in the synthesis is a strong possibility and would explain the dark colour of the catalyst. It appears the excess palladium (used to ensure complete reaction of all imidazolium salt moieties on the catalyst precursor) cannot be removed from the support material by simple washing steps alone (Fig. 1).

2.3. Screening of *3a–b* for Suzuki cross-coupling

Catalysts **3a–b** were screened for activity in a standard Suzuki coupling reaction between phenylboronic acid and 4-haloacetophenones (Table 2).

The catalytic activity of these complexes with aryl bromides is satisfactory, affecting the Suzuki coupling reaction at a low catalyst loading of 0.2 mol% and is comparable with contemporary silica-

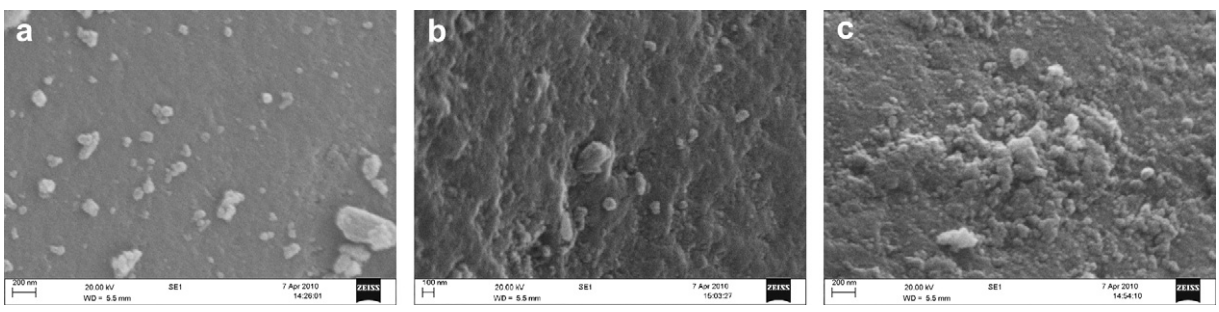
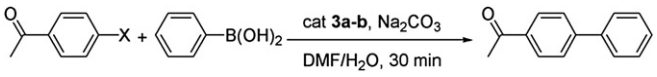


Fig. 1. SEM images of (a) Silica support medium, (b) Silica supported imidazolium salt **1b** (c) Silica supported NHC catalyst **3b** illustrating the presence of surface debris.

Table 2
Screening for activity in Suzuki reaction of 4-haloacetophenones and phenylboronic acid.



Entry	Catalyst (loading)	X	Temperature (°C)	Conversion (%)[a]
1	**3a** (0.2 mol%)	Br	80	79
2	**3b** (0.2 mol%)	Br	80	84
3	**3a** (2 mol%)	Cl	100	4[b]
4	**3b** (2 mol%)	Cl	100	7[b]

[a] % Conversion determined by GC using dodecane as an internal standard.
[b] Reaction time increased to 60 min.

supported NHC-Palladium catalysts. Significantly the use of a bulkier mesityl-derived NHC catalyst **3b** provides enhanced conversions compared to the corresponding benzyl-NHC complex **3a**. This provides some supporting evidence to the assertion that increased steric bulk around the metal centre has a positive effect upon the catalytic activity [20a]. However, the aryl chloride substrate is much less tolerated under these conditions. Conversions were low, even with increased catalyst loadings and temperature. This is not surprising as most silica-supported NHC catalysts tend to exhibit low conversions with aryl chloride substrates. As the activity of the catalysts was fairly modest and also because the catalysts did not appear to be composed of a pure immobilised complex (i.e. a mixture of *mono*- and *bis*-NHC species as well as uncoordinated Pd was likely to be present), an alternative approach to their synthesis was employed.

2.4. Synthesis of palladium NHC complexes

In order to synthesise the desired *bis*-NHC palladium dichloride complexes the imidazolium salts **1a**–**d** were deprotonated, using Ag_2O, to yield silver imidazol-2-ylidene complexes **4a**–**d** (not isolated), which were employed as carbene transfer reagents (Scheme 2).

Bis-(benzonitrile)palladium (II) dichloride was added to a solution of the silver NHC species **4a**–**d** and stirred at room temperature for 16 h. After filtration through celite the (*N*-(triethoxysilylpropyl)-*N*′-aryl)imidazolylidenepalladium complexes **5a**–**d** were isolated in moderate yields (35–57%). Interestingly, the imidazolium iodide **1d** did not furnish the corresponding *N*-(triethoxysilylpropyl)-*N*′-aryl) imidazolylidenepalladium dichloride complex **5d** (formed in 35% yield) as cleanly as the analogous bromide **1c** [15]. In our hands we found that all palladium species, prepared from imidazolium iodides, had significantly more complex NMR spectra, compared to the derivatives obtained from the corresponding bromides, and are not reported further here. It is possible that the iodide undergoes halide exchange with the palladium chloride ligands to afford palladium iodide complexes.

Palladium complexes **5a**–**c** were soluble in polar organic solvents and were characterised by mass spectrometry and ^{1}H & ^{13}C NMR spectroscopy. Chemical ionisation methods allowed the molecular ion of the *bis*-NHC palladium complexes **5a**–**c** to be measured. Satisfyingly the near-perfect match between the observed data and the theoretical isotope profiles (Fig. 2) and the high resolution mass spectral data provide overwhelming evidence for the presence of the *bis*-NHC complexes, as opposed to a variant such as a *mono*-NHC or dimeric species.

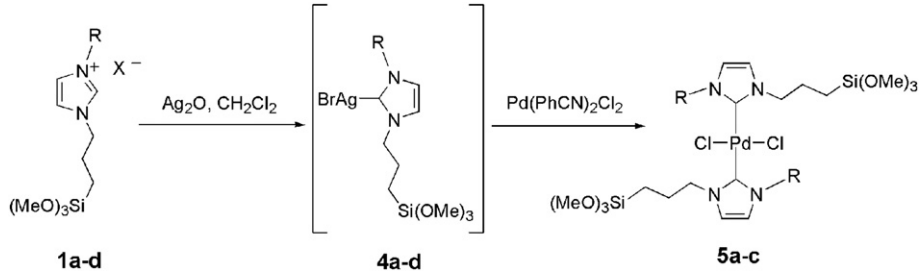
In the ^{1}H and ^{13}C NMR spectra most of the expected signals of a *bis*-NHC complex **5b** are duplicated. This duplication of resonances is often observed for two closely related species that are in equilibrium and such an observation has been previously reported with *N*-methyl imidazol-2-ylidene complexes where an explanation based upon the presence of *cis*- and *trans*-isomers was offered [11]. However, this seems less likely for bulkier NHC complexes such as **5b** due to steric crowding around the metal centre. A recent paper, however, described the synthesis and characterisation of a series of *bis*-NHC complexes of palladium also reported that the NMR resonances were duplicated [16]. The authors attributed this phenomenon to the presence of *trans-anti* and *trans-syn* rotameric isomers resulting from hindered rotation around the Pd–C bond. Support of this attribution was forthcoming from variable temperature NMR studies where the duplicated resonances were seen to coalesce as the temperature of the NMR study was increased (Fig. 3).

Extensive NMR analysis of complex **5b** enabled the resonances of both rotamers to be assigned unambiguously. The protons of the *N*-propyl chain experience some degree of shielding from the aromatic ring in the *trans-anti* rotamer, as a result the resonances attributed to this rotamer appear slightly upfield with respect to the corresponding *trans-syn* rotamer. In addition, *cis*- and *trans-bis*-NHC palladium complexes can be distinguished by the ^{13}C δ values for the carbene carbon resonances. *Trans*-carbene complexes usually have values in the range 168–172 ppm whilst *cis*-carbene complexes exhibit more high field shifts, typically 160–165 ppm [17]. In the ^{13}C NMR spectrum of **5b** two resonances for the carbene carbon atom are evident at a chemical shift δ 170.3 and 170.9 ppm respectively. These data coupled with the variable temperature NMR studies suggest the presence of two rotameric forms with a *trans*-arrangement consistent with *trans-anti* and *trans-syn* rotamers respectively.

Heteronuclear correlation experiments on **5b** revealed the presence of the alkyl $-CH_2$ groups which are obscured in the ^{1}H NMR spectrum by the *ortho*-methyl groups of the mesityl substituents. The ^{1}H NMR signals for **5b** (both rotamers) are assigned (Table 3).

2.5. Synthesis of silica-supported palladium NHC catalysts

Tethering of the palladium complexes **5a**–**c** to silica to form the supported palladium complexes **6a**–**c** was efficiently accomplished



Scheme 2. Synthesis of palladium complexes prior to immobilisation.

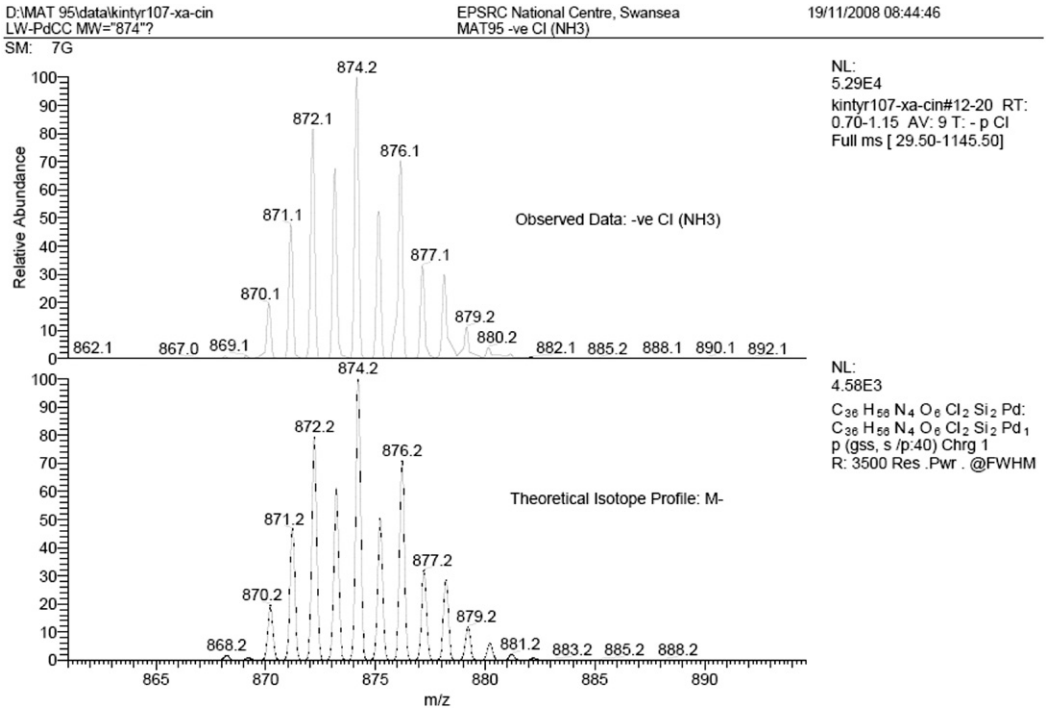


Fig. 2. Low-resolution mass spectrum of *bis*-[1-(mesityl)-3-(trimethoxysilyl)propylimidazole]palladium dichloride **5b** showing theoretical and observed isotope profiles.

by refluxing in chloroform overnight. The noteworthy feature of this reaction was that no trace of the bright yellow coloured palladium complex remained in the reaction mixture after filtration. The product, in the form of a pale yellow powder, was simply filtered off and washed with chloroform and dichloromethane. No trace of the complex was detected by NMR analysis of the washings, again indicating a highly efficient immobilisation process.

2.6. Suzuki coupling reactions

Initially catalysts **6a**–**c** were screened for activity in a series of Suzuki cross-coupling reactions (Table 4).

Our attempts to optimise the coupling reaction included an investigation into both the choice of base (Na_2CO_3, Cs_2CO_3 and morpholine) and solvent systems (DMF:H_2O [1:1], acetonitrile, DMF and DMF/H_2O [10:1]). We concluded that the use of Na_2CO_3 and DMF:H_2O (1:1) gave the best results and were used for the rest of the testing. At the 1 mol% level all three catalysts **6a**–**c** provided rapid and quantitative conversion of the substrates (entries 1–3). At a lower loading of 0.2 mol% catalyst **6c**, containing the most bulky *N*-substituent, readily outperformed **6a** and **6b** to again provide a rapid and quantitative conversion (Compare entries 4 & 5 with entry 6 as well as entry 3 with entry 6). This observation is consistent with our initial thesis that a more bulky *N*-substituent would result in a more active immobilised catalyst for Suzuki coupling, consistent with couplings performed in homogenously catalysed reactions. Early work by Nolan et al. [18] demonstrated that both *N*-mesityl and *N*-diisopropyl(phenyl) substituted imidazolylidenes were significantly more active (99% and 53% conversion respectively) than *N*-alkyl substituted imidazolylidenes (14–16% conversion) for the palladium catalysed Suzuki cross-coupling of aryl chlorides with an arylboronic acid. This work also indicated that when using $Pd_2(dba)_3$, as a palladium source, the diisopropyl(phenyl) substituted imidazolylidene ligand gave a slightly higher conversion (95%) than the *N*-mesityl substituted imidazolylidene (90%). Similar behaviour has been seen for other palladium catalysed cross-coupling reactions such as Negishi Coupling, Buchwald-Hartwig coupling and the arylation of ketones [19].

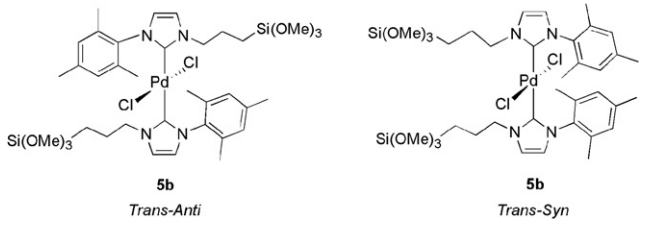
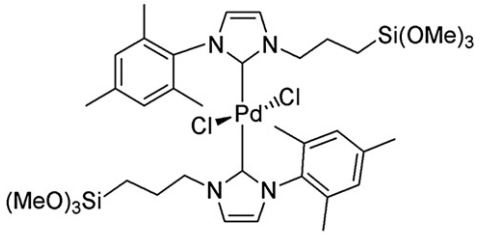


Fig. 3. Rotamers of palladium complexes.

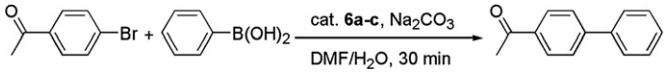
Table 3
^{1}H NMR assignments for NHC complex **5b**.



5b

Proton(s)	Resonance(s) (δ, ppm)	Integral, Multiplicity
Si-OC*H*$_3$	3.58	18H, s
SiC*H*$_2$	0.49, 0.78	4H, m
CH$_2$C*H*$_2$CH$_2$	1.90, 2.21	4H, m
N-C*H*$_2$	4.18, 4.62	4H, m
CH*=*CH	6.64, 6.70, 6.92, 6.97	4H, m
***o*-C*H*$_3$**	1.87, 2.19	12H, s
Ar-*H*	6.84, 6.98	4H, s
***p*-C*H*$_3$**	2.36, 2.46	6H, s

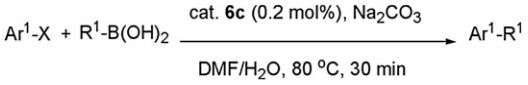
Table 4
Optimisation of Suzuki coupling reactions.



Entry	Catalyst[a]	Loading (mol%)	Temperature (°C)	Conversion (%)[b]
1	**6a**	1	80	>99
2	**6b**	1	80	>99
3	**6c**	1	80	>99
4	**6a**	0.2	80	81
5	**6b**	0.2	80	90
6	**6c**	0.2	80	>99
7	**6c**	0.2	60	28
8	**6c**	0.1	80	80
9	**6c**	1	RT	trace
10	**6c**	0.2	RT	12[c]

[a] Catalyst **6a** = *N*-benzyl, **6b** = *N*-mesityl and **6c** = *N*-2,6-(diisopropyl)phenyl.
[b] % Conversion based on the halide substrate, determined by GC using dodecane as an internal standard.
[c] Reaction time extended to 24 h.

Table 5
Testing of catalyst **6c** on a range of substrates.



Entry	Ar^1	X	R^1	Conversion (%)[a]
1	C_6H_5	I	C_6H_5	>99 (89)
2	2-(Me)C_6H_5	I	C_6H_5	67
3	3-C_5H_4N	I	C_6H_5	48
4	C_6H_5	Br	C_6H_5	>99
5	4-(MeCO)C_6H_4	Br	C_6H_5	98 (90)
6	C_6H_5	Br	3-C_5H_4N	<1
7	C_6H_5	Br	4-C_5H_4N	<1
8	4-(O_2N)C_6H_5	Br	C_6H_5	69
9	4-(MeO)C_6H_4	Br	C_6H_5	35 (29)
10	4-(MeCO)C_6H_5	Br	2-C_4H_3S	<1
11	C_6H_5	Cl	C_6H_5	52[b]
12	C_6H_5	Cl	$C_{10}H_7$	40[b]
13	4-(MeCO)C_6H_4	Cl	C_6H_5	30[b]
14	4-(O_2N)C_6H_5	Cl	C_6H_5	13[b]
15	4-(MeO)C_6H_4	Cl	C_6H_5	4[b]

[a] % conversion of the halide substrate was established by GC–MS using dodecane as an internal standard. Numbers in parentheses represent % yield isolated by column chromatography.
[b] Reaction temperature increased to 100 °C, catalyst loading increased to 2 mol %, reaction time increased to 60 min.

The established mechanism of Suzuki coupling involves three major steps: oxidative addition of the aryl halide, transmetallation followed by reductive elimination which yields the product and regenerates the active catalyst. It is well established that bulky, electron rich NHCs give the most active catalysts for cross-coupling reactions. The development of several different *mono*-NHC palladium catalysts also highlights that the palladium to ligand ratio is very important [20]. A number of mechanistic studies indicate that the active catalyst is in fact a *mono*-NHC species, similar observations have been made with phosphine ligands [21]. Mechanistic work by Cloke et al. [22] indicates that oxidative addition of an aryl halide is the rate determining step, an observation also supported by work by Nolan [18]. The greater activity of the sterically demanding ligands can then be attributed to their ability to stabilize such low co-ordinate palladium species which are then much more reactive towards oxidative addition due to their low valence electron count. Increased steric bulk is also likely to increase the rate of reductive elimination of the product as this step reduces steric crowding around the palladium centre. In our work we expect the prevalent species to be a *bis*-NHC species, this might explain its inability to catalyse coupling with the more demanding aryl chloride substrates. Nonetheless, it is possible that some ligand dissociation occurs in catalyst **6c** to give a low concentration of a more active *mono*-carbene species. The greater activity could then be attributed to this process being more likely for the more sterically demanding ligand. Another possible hypothesis is that with the use of aryl bromides the actual reductive elimination is the rate determining step. In this case the greater activity of the (diisopropyl)phenyl-substituted imidazolylidene catalyst **6c** may be explained by its steric bulk favouring reductive elimination.

Having identified the optimum grafted catalyst as well as the reaction conditions for effecting the Suzuki reaction we then studied the tolerance of catalyst **6c** to a range of electronically activated and deactivated substrates as well as functionally bulkier substrates. The data for these experiments, using 0.2 mol% of the catalyst, are summarised in Table 5 (Ar^1 is derived from the aryl halide component and R^1 is the boronic acid component). Several interesting conclusions may be drawn from these results. Firstly, it is apparent that sterically hindered substrates such as 2-iodotoluene (entry 2) experience lower conversion rates. Although heterocyclic aromatic halides exhibit a lower conversion (entry 3), heterocyclic boronic acids were not tolerated in these studies (entries 6, 7 and 10). This observation is perhaps not so surprising as nitrogen-containing heterocycles are difficult substrates for Suzuki coupling reactions as their basic nature can lead to co-ordination to palladium and inhibition of the active catalyst species [23,24]. Both Buchwald et al. [25] and Fu et al. [26] have reported some success with homogenous catalysts for these substrates and some success has also been reported recently with a hybrid catalyst [27]. Both electron-withdrawing and electron-donating substituents resulted in lower conversion rates. These data suggest that for the aryl bromides the rate determining step is unlikely to be the oxidative addition of the aryl halide.

Suzuki coupling of aryl chlorides continues to be a challenge for most existing hybrid catalysts [7,8,27], although exceptions to this rule do exist [28]. There are numerous examples of homogeneous catalysts, such as 'PEPPSI' [21a,b] and 'IBiox' [29] which are capable of coupling even sterically hindered and electronically deactivated substrates at room temperature. Catalyst **6c** does however, compare well with most hybrid NHC-palladium catalysts in the literature, in that it does convert aryl chloride substrates, but only slowly (entries 11–15) [7,8,27].

2.7. Recycling studies

Catalyst **6c** was tested for recyclability using the Suzuki coupling of 4-bromoacetophenone and phenylboronic acid. Although the catalyst is recyclable, the amount of conversion after 30 min drops off quickly. A similar reduction in catalytic activity was also reported by Artok et al. [10]. Catalyst **6c** exhibited activity over 4

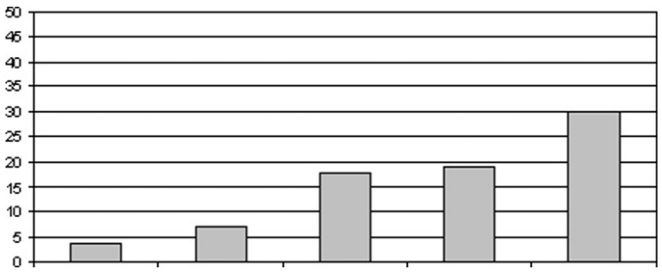


Fig. 4. The performance of the various NHC catalysts in the Suzuki reaction of 4-chloroacetophenone. Conditions: 100 °C, 60 min %Age conversion of the aryl chloride was determined by GC analysis.

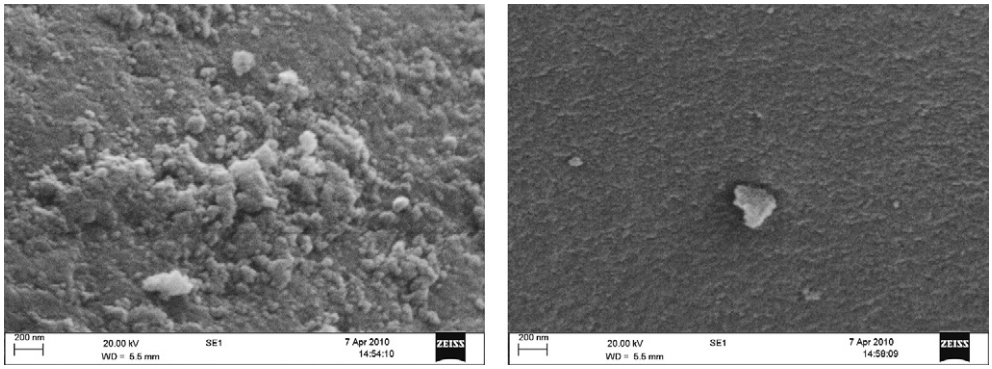


Fig. 5. SEM images of catalyst **3b** (left) and of catalyst **6b** (right). The consistent morphology demonstrated by the SEM of **6b** may correlate to the enhanced activity of this catalyst compared to **3b**.

consecutive cycles and, as we observed with the corresponding phosphine catalyst [3b] a steady reduction in activity was observed, In cycle 1, quantitative conversion was observed. This was reduced to 55% for the second cycle, 20% for the 3rd and 15% for the 4th cycle. These observations may be explained in terms of palladium leaching [30]; the changing colour of the catalyst suggests the formation of palladium metal particles with concomitant degradation of the tethered catalyst.

2.8. Comparison of catalysts *3b* and *6b*

Catalyst **3b**, prepared by the immobilisation of the imidazolium salt **2b** to silica before the formation of the NHC complex and catalyst **6b**, prepared by tethering the NHC complex **5b** directly to silica should in theory be reasonably similar in both structure and activity. A comparison of the data from Tables 2 and 4 (Suzuki reaction) reveals that catalyst **3b** provided an 84% yield of the coupled product at the 0.2 mol% loading of catalyst. In contrast NHC **6b** gave a 90% yield under the same conditions. These data suggest that **6b** is slightly more active in the Suzuki coupling of aryl bromides than **3b**. Furthermore the catalyst containing the bulkiest ligands, **6c**, demonstrated enhanced activity with conversions of >99% under the same reaction conditions.

In addition it was also observed that **6c** was able to affect the Suzuki coupling of aryl chlorides (30%) (Table 5, entry 13). In contrast NHC **3b** was only able to catalyse the same substrates with a yield of 7% performed at a higher reaction temperature. The data summarised (Fig. 4) serves as a comparison of activity between the 2 catalyst types; **3a**–**b**, prepared by formation of the NHC catalyst on the silica support and catalysts **6a**–**c**, produced in an alternative way that involved the immobilisation of the pre-formed NHC complex directly onto the silica support.

The corresponding SEM of the *N*-mesityl substituted NHC catalysts produced by the two routes are shown (Fig. 5) and serve to confirm the appearance of morphological differences between the two catalysts which may account for the difference in their catalytic activities.

3. Conclusion

Our investigations demonstrate that the immobilisation of a pre-formed palladium *N*-heterocyclic carbene complex to a silica support produces a well defined and more active catalyst for Suzuki cross-coupling reactions than the corresponding catalyst prepared by the reaction of palladium acetate with the tethered imidazolium salt. A range of catalysts with varying steric bulk were synthesised. The most active catalyst was the one prepared from the imidazolium salt bearing the bulkiest group suggesting that steric bulk plays an important role in controlling the catalytic activity of tethered palladium NHC catalysts. Although this has been documented for homogeneous reactions and reactions employing 'non-tethered' solid supported catalysts [2,31,32], this is the first time that the correlation between ligand size and activity has been reported for organically tethered NHC complexes. This is an important development as previous studies have been limited to methyl and benzyl derivatives. Our best prototype catalyst, **6c**, demonstrated an encouraging range of activities in the Suzuki coupling reactions of aryl bromides and chlorides. Further studies are currently underway in our laboratories and results will be disseminated in due course.

4. Experimental

4.1. General procedures

All NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) on a Jeol Eclipse$^+$ 400 NMR spectrometer using Jeol Delta version 4.3.6 control and processing software. Chemical shifts are reported in ppm, referenced to residual solvent peaks (acetone or chloroform). MS were recorded using a Varian CP-3800 Gas Chromatograph with Varian 1200L Quadrupole Mass Spectrometer controlled using Varian Saturn GC/MS System Control Version 6.41, Copyright 1989–2004 Varian Inc. Melting point determinations were recorded using a Stuart Scientific SMP3 digital melting point apparatus and are uncorrected.

4.2. Experimental procedures

4.2.1. 1-(Trimethoxysilyl)propyl-3-benzylimidazolium bromide (*1a*)

To a flame dried round-bottomed flask, containing a magnetic follower, was added *N*-benzylimidazole (316 mg, 2 mmol) and 3-(bromopropyl)trimethoxysilane (482 mg, 2 mmol) under a nitrogen atmosphere. The mixture was heated, with stirring, at 80 °C for about 6 h. The mixture was cooled to an ambient temperature and triturated with diethyl ether (3 × 50 mL) to afford the title compound **1a** as a viscous, colourless oil (630 mg, 79%). ^{1}H NMR (400 MHz, $CHCl_3$): 10.44–10.47 (s, 1H, Ar-H), 7.44–7.49 (m, 3H, Ar-H), 7.37–7.39 (m, 1H, Ar-H), 7.29–7.33 (m, 2H, Ar-H), 5.56–5.59 (s, 2H, benzyl-H), 4.22–4.27 (t, J = 7.32 Hz, 2H, alkyl-CH_2), 3.47–3.50 (s, 9H, $-OCH_3$), 1.89–1.99 (p, J = 7.87 Hz, 2H, alkyl-CH_2), 0.53–0.59 (t, J = 7.87 Hz, 2H, alkyl-CH_2). ^{13}C NMR (100 MHz, $CHCl_3$): 136.9, 133.2, 129.5, 129.1, 122.2, 65.9, 53.2, 51.9, 50.7, 24.1, 15.3, 5.9. MS (ES): 321 m/z (M^+ − Br).

4.2.2. 1-(Trimethoxysilyl)propyl-3-mesitylimidazolium bromide (**1b**)

This was synthesised as described for **1a** using *N*-mesitylimidazole (0.930 g, 5 mmol). Trituration in diethyl ether (3 × 50 mL) provided the title compound as an off-white solid (MP: 120–123 °C, 1.846 g, 86%). ^{1}H NMR (400 MHz, $CHCl_3$): 10.05–10.09 (s, 1H, Ar-H), 7.88–7.91 (m, 1H, Ar-H), 7.19–7.21 (m, 1H, Ar-H), 6.82–6.85 (s, 2H, Ar-H), 4.50–4.56 (t, J = 6.96 Hz, 2H, alkyl-CH_2), 3.38–3.42 (s, 9H, O–CH_3), 2.16–2.19 (s, 3H, –CH_3), 1.88–1.99 (m, 8H, alkyl-CH_2 and Ar-CH_3 overlapping), 0.48–0.55 (t, J = 8.06 Hz, 2H, alkyl-CH_2). ^{13}C NMR (100 MHz, $CHCl_3$): 141.1, 137.6, 134.1, 130.7, 129.8, 123.6, 123.5, 51.9, 50.7, 24.3, 21.1, 17.6, 5.6. MS (ES): 349 m/z (M^+ – Br). HRMS (EI): calculated for $C_{18}H_{29}O_3N_2Si$; 349.1942, found: 349.1939.

4.2.3. 1-(Trimethoxysilyl)propyl-3-(2′,6′-diisopropylphenyl) imidazolium bromide (**1c**)

N-(2,6-diisopropylphenyl)imidazole (764 mg, 3.2 mmol) in acetonitrile (20 mL) was added to a dry, round-bottomed flask under an atmosphere of nitrogen. 3-(bromopropyl)trimethoxysilane (684 mg, 3.2 mmol) was added and the mixture heated to 100 °C for 7 h. After cooling to room temperature, the solvent was removed *in vacuo* and the crude product (now solid) was triturated in diethyl ether (3 × 50 mL) to yield the title compound **1c** as an off-white solid (MP: 116–118 °C, 1.17 g, 76%). ^{1}H NMR (400 MHz, $CHCl_3$): 10.30–10.36 (s, 1H, Ar-H), 7.91–7.94 (s, 1H, Ar-H), 7.47–7.55 (m, 1H, Ar-H), 7.25–7.30 (m, 2H, Ar-H), 7.19–7.22 (m, 1H, Ar-H), 4.74–4.81 (t, J = 6.96 Hz, 2H, alkyl-CH_2), 3.52–3.57 (s, 9H, O–CH_3), 2.19–2.30 (septet, J = 6.96 Hz, 2H, alkyl-CH), 2.04–2.14 (quintet, J = 8.06 Hz, 2H, alkyl-CH_2), 0.63–0.69 (t, J = 8.06 Hz, 2H, alkyl-CH_2). ^{13}C NMR (100 MHz, $CHCl_3$): 145.4, 138.4, 132.0, 130.2, 124.8, 124.2, 123.2, 52.1, 50.8, 28.8, 24.5, 24.2, 5.6. MS (ES): 391 m/z (M^+ – Br). HRMS (EI): calculated for $C_{19}H_{35}O_3N_2Si$; 391.2411, found: 391.2401.

4.2.4. 1-(Trimethoxysilyl)propyl-3-(2′,6′-diisopropylphenyl) imidazolium iodide (**1d**)

The procedure was carried out as described for **1c** using *N*-(2,6-diisopropylphenyl)imidazole (764 mg, 3.2 mmol) and 3-iodopropyltrimethoxysilane (3.2 mmol). The title compound **1d** was isolated as an orange oil (1.38 g, 96%). ^{1}H NMR (400 MHz, $CHCl_3$): 9.87–9.91 (s, 1H, Ar-H), 8.01–8.05 (s, 1H, Ar-H), 7.43–7.51 (m, 1H, Ar-H), 7.20–7.27 (m, 3H, Ar-H), 4.64–4.71 (t, J = 6.96 Hz, 2H, alkyl-CH_2), 3.46–3.54 (s, 9H, O–CH_3), 2.14–2.26 (septet, J = 6.77 Hz, 2H, alkyl-CH), 1.99–2.09 (quintet, J = 8.06 Hz, 2H, alkyl-CH_2), 1.05–1.17 (dd, J = 6.77 Hz, 12H, –CH_3), 0.57–0.65 (t, J = 8.06 Hz, 2H, alkyl-CH_2). ^{13}C NMR (100 MHz, $CHCl_3$): 145.1, 137.0, 131.7, 129.7, 124.4, 124.3, 123.6, 51.8, 50.6, 28.4, 24.3, 24.2, 24.0, 5.2. MS (ES): 391 m/z (M^+ – I).

4.2.5. Bis-1-(trimethoxysilyl)-3-mesitylimidazol-2-ylidene palladium dichloride (**5b**)

1-(Trimethoxysilyl)propyl-3-mesitylimidazolium bromide **1b** (1.287 g, 3 mmol) was added to a dry, light-protected Schlenk tube under a nitrogen atmosphere. To this was added silver (I) oxide (0.348 g, 1.5 mmol) and anhydrous chloroform (7.5 mL) and the resulting mixture was stirred at room temperature overnight. The mixture was carefully removed under continuous nitrogen flow, by pipette and filtered through celite directly into another dry, light-protected Schlenk tube under nitrogen (an extra 2.5 mL of anhydrous chloroform was used to dissolve any product remaining in the original vessel). The white precipitate was discarded. *Bis*-(benzonitrile)palladium (II) dichloride (0.504 g, 1.3 mmol) was added gradually and the mixture was stirred overnight. The mixture (bright-yellow) was again filtered through celite and the solvent removed *in vacuo* to yield the crude product. Purification was accomplished by trituration with anhydrous diethyl ether (3 × 20 mL), yielding the title compound **6b** as a yellow solid (0.530 g, 47%, as a mixture of *trans-syn-* and *trans-anti*-rotamers). ^{1}H NMR (400 MHz, $CHCl_3$): 6.95–7.00 (m, 3H, Ar-H), 6.91–6.93 (m, 1H, Ar-H imid.), 6.81–6.86 (m, 2H, Ar-H), 6.69–6.72 (m, 1H, Ar-H), 6.62–6.66 (m, 1H, Ar-H), 4.54–4.70 (m, 2H, alkyl-CH_2, syn-isomer), 4.11–4.26 (m, 2H, alkyl-CH_2, anti-isomer), 3.56–3.60 (s, 18H, OCH_3), 2.41–2.48 (s, 3H, p-CH_3, syn-isomer), 2.34–2.38 (s, 3H, p-CH_3, anti-isomer), 2.15–2.30 (m, 8H, alkyl-CH_2, syn-isomer and o-CH_3, syn-isomer overlapping), 1.85–1.94 (m, 8H, alkyl-CH_2, anti-isomer and o-CH_3, anti-isomer overlapping), 0.79–0.95 (m, 2H, alkyl-CH_2, syn-isomer), 0.45–0.53 (m, 2H, alkyl-CH_2, anti-isomer). ^{13}C NMR (100 MHz, $CHCl_3$): 170.9, 170.5, 138.4, 137.5, 137.4, 136.9, 136.8, 136.5, 136.2, 136.0, 135.7, 135.6, 128.88, 128.83, 128.79, 128.75, 122.65, 122.55, 122.4, 122.25, 121.0, 120.9, 120.85, 120.75, 53.28, 53.1, 53.03, 52.87, 50.7, 24.45, 24.3, 24.1, 24.0, 21.35, 21.08, 19.65, 19.23, 19.13, 19.0, 18.95, 18.88, 18.7, 18.55, 6.44, 6.39, 6.1, 6.07. Note: duplication of all signals observed as a result of syn- and anti-isomerism. MS (EI): m/z 835 (M^+ – Cl). HRMS (EI): calculated for $C_{36}H_{56}O_6N_4Si_2Pd$; 870.2161, found: 870.2161.

4.2.6. Bis-1-(trimethoxysilyl)-3-benzylimidazol-2-ylidene palladium dichloride (**5a**)

As described using 1-(trimethoxysilyl)propyl-3-benzylimidazolium bromide **1a** (0.399g, 1 mmol) was used as the imidazolium salt (adjusting the quantities of the other reagents according to this stoichiometry). The title compound was obtained as a bright yellow solid (0.205 g, 56%). ^{1}H NMR (400 MHz, $CHCl_3$): 7.15–7.50 (m, 14H, Ar-H), 5.49–5.82 (m, 4H, benzyl-CH_2, syn- and anti-isomers), 4.32–4.49 (m, 4H, alkyl-CH_2, syn- and anti-isomers), 3.39–3.55 (m, 18H, –OCH_3, several overlapping signals), 2.02–2.35 (m, 4H, alkyl-CH_2, syn- and anti-isomers), 0.63–0.89 (m, 4H, alkyl-CH_2, syn- and anti-isomers). ^{13}C NMR (100 MHz, $CHCl_3$):Not reported due to overlapping signals originating from syn- and anti-isomers. HRMS (EI): calculated for $C_{32}H_{48}O_6N_4Si_2Pd$; 814.1535, found: 814.1537.

4.2.7. Bis-1-(trimethoxysilyl)-3-(2′,6′-diisopropylphenyl)imidazol-2-ylidene palladium dichloride (**5c**)

As described using 1-(trimethoxysilyl)propyl-3-(2′,6′-diisopropylphenyl) imidazolium bromide (0.235 g, 0.5 mmol) was used as the imidazolium salt (adjusting the quantities of the other reagents according to this stoichiometry). The title compound was obtained as a dull-yellow solid (0.112 g, 47%). ^{1}H NMR (400 MHz, $CHCl_3$): 7.26–7.36 (m, 6H, Ar-H), 6.89–7.08 (m, 2H, Ar-H), 6.65–6.81 (m, 2H, Ar-H), 4.67–4.89 (m, 2H, alkyl-CH_2, syn-isomer), 4.05–4.39 (m, 2H, alkyl-CH_2, anti-isomer), 3.43–3.63 (m, 18H, –OCH_3), 2.80–3.01 (m, 2H, alkyl-CH_2, syn-isomer), 2.52–2.73 (m, 2H, alkyl-CH_2, anti-isomer), 2.20–2.38 (m, 2H, alkyl-CH, syn-isomer), 1.73–1.84 (m, 2H, alkyl-CH, syn-isomer), 0.75–1.41 (m, 28H, alkyl–CH_3 and alkyl-CH_2). ^{13}C NMR (100 MHz, $CHCl_3$) Not reported due to overlapping signals originating from syn- and anti-isomers. HRMS (EI): calculated for $C_{42}H_{68}O_6N_4Si_2Pd$; 954.3089, found: 954.3090.

4.2.8. General procedure for immobilisation of imidazolium salts **1a–c**

Under nitrogen, a dry round-bottomed flask was charged with imidazolium salt (1 mmol), anhydrous toluene (60 mL) and silica gel (1.00 g, pre-dried). The mixture was fitted with a Dean–Stark trap and refluxed for 24 h. After cooling to room temperature, the mixture was filtered and washed with anhydrous dichoromethane (3 × 50 mL). The resulting white solid was dried *in vacuo* at 60 °C over phosphorous pentoxide (24 h) to yield the modified support material (>95% by weight). ^{1}H NMR analysis of the dichloromethane washings showed no trace of the imidazolium salt starting

material, indicating near-quantitative immobilisation. The imidazolium salt loading was determined by TGA analysis.

4.2.9. Complexation of immobilised imidazolium salt **2b** (Synthesis of **3b**)

The immobilised imidazolium salt (1.00 g, 1 mmol) was suspended in dimethylsulfoxide (4.5 mL) and to this was added palladium (II) acetate (0.11 g, 0.5 mmol). This mixture was stirred at 60 °C for 4 h, then the temperature was increased to 100 °C for a further 30 min, then the mixture was allowed to cool to room temperature. The mixture was filtered, washed with dichloromethane (4 × 50 mL) and finally dried *in vacuo* at 60 °C over phosphorous pentoxide (48 h) to yield a light-brown solid (99% by weight). ICP-AES analysis: calculated 4.77% Pd, found 6.88% Pd.

4.2.10. Immobilisation of complex **5c** (Synthesis of **6c**)

A solution of the *bis*-NHC complex **5c** (0.1 mmol) in anhydrous chloroform (20 mL) was added to a dry Shlenk tube under nitrogen. Silica gel (1.00 g, pre-dried) was added and the mixture was refluxed for 20 h. After cooling to room temperature, the mixture was filtered under a cone of nitrogen and washed with anhydrous chloroform (3 × 50 mL) and anhydrous dichloromethane (4 × 50 mL). The yellow solid was dried under reduced pressure and stored under nitrogen at −4 °C. The washings were concentrated under reduced pressure and analysed by ^{1}H NMR, which showed no trace of the complex. ICP-AES analysis: calculated 0.98% Pd, found 0.89% Pd.

4.2.11. General procedure for Suzuki coupling reactions

The haloarene (1 mmol) and catalyst (0.2 mol%) were added to a dry Shlenk tube equipped with a magnetic stirring bar under nitrogen. To this was added DMF/H_2O (1:1, 2 mL), sodium carbonate (2 mmol) and the boronic acid (1.4 mmol). The mixture was heated at 80 °C for 30 min, then cooled to room temperature, diluted with acetone (3 mL) and filtered to remove the catalyst, base and unwanted salts. The % conversion was established using gas chromatography with reference to dodecane as an internal standard. Recycling was accomplished by washing the used catalyst with water (10 mL) then with DMF/H_2O (1:1, 10 mL). The catalyst, usually somewhat discoloured, may then be used directly in the next coupling reaction with a substantial decrease in activity being observed.

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