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Journal of Organometallic Chemistry 633 (2001) 173–181

Journal of Organo metallic Chemistry

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Silica-supported imine palladacycles—recyclable catalysts for the Suzuki reaction?

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Received 18 May 2001; accepted 20 June 2001

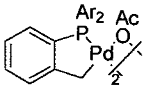
Abstract

Silica-supported, imine-based palladacyclic catalysts have been synthesised and the crystal structure of complex **9**, the triphenylphosphine adduct of the pre-supported precursor complex **8**, has been determined. The solid-supported catalysts show considerably lower activity in the Suzuki reaction than their homogeneous counterparts. Poor recyclability of the silica-immobilised catalysts and the presence of active catalysts in solution indicate that imine-based palladacyclic catalysts are unstable with respect to liberation of zero-valent palladium species. Whilst the solid-supported complexes are not useful as catalysts, they do function as excellent mechanistic probes. Studies on model complexes give further information on the processes that cause the liberation of zero-valent species not only from the solid-supported catalysts, but also from homogeneous systems. In all cases it appears that a reductive-elimination event occurs to generate the active catalyst. © 2001 Published by Elsevier Science B.V.

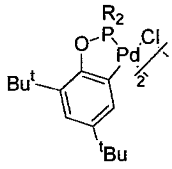
Keywords: Suzuki reaction; Palladacycles; Catalysis; Silica supported

1. Introduction

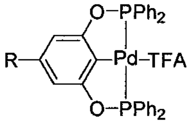
There has recently been considerable interest in the synthesis of new, high-activity palladium-based catalysts that can be used in low concentration in the Suzuki reaction (Scheme 1) since such catalysts have the potential to be used in industrial systems. In particular, palladacyclic catalysts in which a ligand coordinates to the metal centre through both a donor atom and metallated carbon have shown considerable promise. Beller et al. demonstrated that complex **1** shows good activity [1] whilst we have shown that the palladated triarylphosphite complex **2**, the phosphinite complexes **3** and the bis(phosphinite) PCP-pincer complexes **4** show excellent activity [2–4]. High activity is not limited to metallated phosphorus donor systems—Weissman and Milstein have shown that the metallated imine complex **5a** shows excellent activity [5], whilst Zim et al. have shown that the metallated thioether complexes **6** can also be used [6].



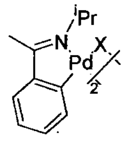
1: Ar = 2-MeC$_6$H$_4$



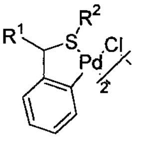
2: R = C$_6$H$_3$-2,4-^{t}Bu$_2$
3: R = Ph, ^{i}Pr



4: R = H, Me



5a: X = TFA



6: R^1 = H, Me;
R^2 = Me, ^{t}Bu

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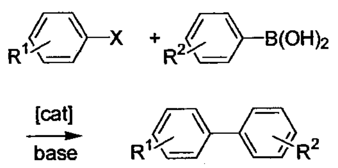
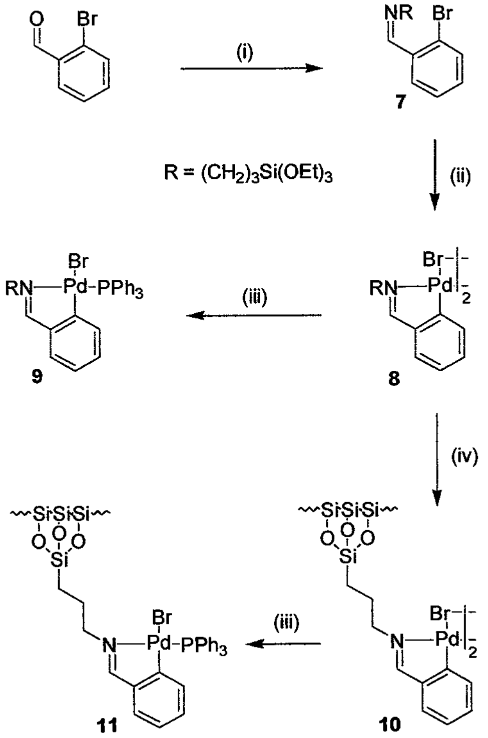
0022-328X/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0022-328X(01)01080-4



Scheme 1. The Suzuki biaryl coupling reaction.



Scheme 2. (i) $H_2N(CH_2)_3Si(OEt)_3$, EtOH, molecular sieves; (ii) $[Pd(dba)_2]$, toluene, 60 °C; (iii) PPh_3, CH_2Cl_2; (iv) silica, toluene, reflux temperature.

Given the high activity and longevity of palladacyclic complexes, they would appear to be ideal candidates for recycling protocols. In particular the imine palladacyclic complexes are reported as having high stability and they should be easily modified to incorporate functionalities that will allow them to be supported [7,5]. For these reasons we wished to investigate the immobilisation of analogues of **5a** on mesoporous silica and see whether the resultant species are viable as recyclable catalysts in the Suzuki reaction.

2. Results and discussion

2.1. Synthesis and catalytic activity of silica-supported palladacyclic complexes

Silica-immobilised imine ligands have been reported previously in the synthesis of recyclable chromium-based oxidation catalysts by Clark and co-workers [8] and their methodology was adapted for this work. The triethoxysilyl-modified imine **7** was synthesised in 91% yield by the reaction of 3-aminopropyltriethoxysilane with 2-bromobenzaldehyde (Scheme 2). Imine **7** reacts with $[Pd(dba)_2]$ in toluene to give the dimeric palladacycle **8** in good yield. Complex **8** readily reacts with triphenylphosphine to give the mononuclear adduct **9**, the structure of which was determined by single crystal X-ray analysis. There are two molecules in the asymmetric unit that differ significantly in the conformation of the triethoxysilyl group. One of the two independent molecules (molecule A) is shown in Fig. 1 and selected data are given in Table 1. The palladium adopts an approximately square planar geometry with the triphenylphosphine ligand *cis* to the metallated carbon. Both the average Pd–C and Pd–N bond lengths are significantly higher than those reported for complex **5a** [5], presumably as a result of differences in the *trans* influence of the co-ligands.

The $^{31}P\{^1H\}$-NMR spectrum of **9** shows a single peak at δ 43 ppm confirming that only one isomer is present in solution. The $^{31}P\{^1H\}$-MAS NMR spectrum of **9** shows a singlet at δ 39 ppm with a slight broadening on the low frequency side. This broadening is likely to be due to imperfect crystallisation and/or polymorphism.

The immobilisation of **8** was performed by heating it with mesoporous silica (Merck Kieselgel, 100 Å) in a ratio of ca. 0.60 mmol Pd per gram of silica in toluene for 17 h, to give the modified silica product **10**. Pd analysis was performed on a sample of **10** which showed a palladium loading of 0.31 mmol g^{-1} indicating that ca. 52% of complex **8** has been immobilised, the rest was recovered from the combined supernatant solution and washings. In order to establish that the structure of the complex had not altered on immobilisation, **10** was treated with a solution of triphenylphosphine to generate the immobilised complex **11**. The $^{31}P\{^1H\}$-MAS NMR spectrum of **11** shows a singlet at δ 42 ppm with a distinct shoulder to low frequency. The shift of the main peak is very similar to those obtained in the ^{31}P spectra of **9** both in solution and in the solid state. This indicates that the immobilisation has not perturbed the coordination sphere of the palladium to any great extent.

In order to evaluate the extent to which structural features other than immobilisation affect the activity of the catalyst **10** compared with the reported complex **5a**, the model complex **5b** was synthesised in 89% yield by the reaction of the imine **12** with $[Pd(dba)_2]$ (Scheme 3).

The activity of the supported catalysts **10** and **11** and the model complex **5b** in the Suzuki reaction (Scheme 1) was then investigated and the results are summarised in Table 2. The model complex **5b** shows excellent activity; only slightly lower than that reported with **5a** [5], indicating that a change in the structure of the

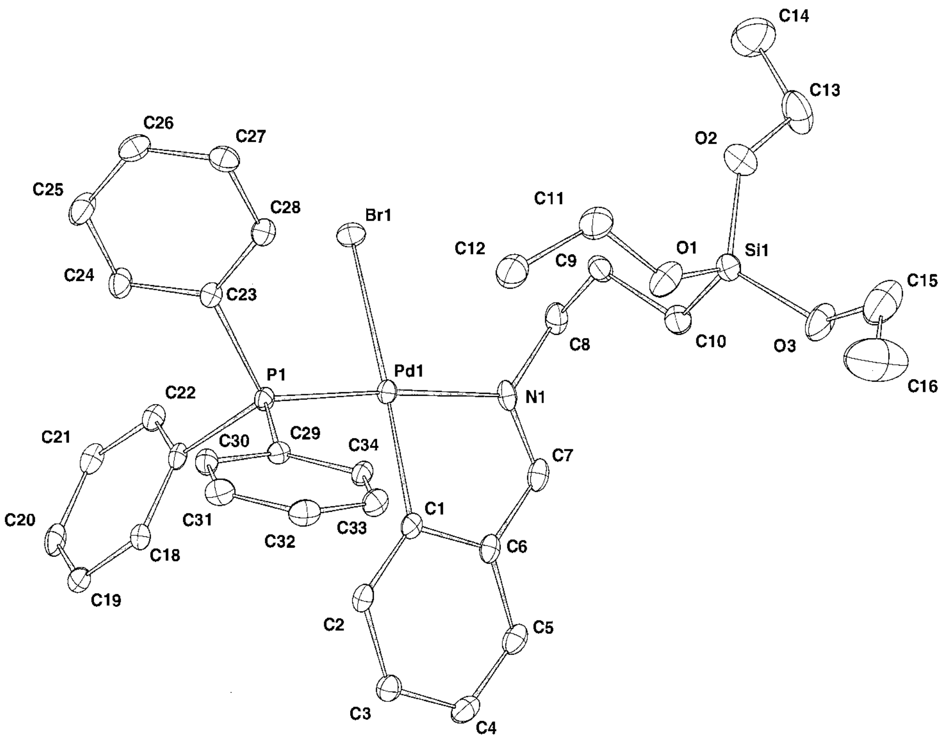


Fig. 1. One of the two independent molecules of **9** (molecule A). Selected bond lengths (Å) and angles (°) for molecule A (shown): N1–Pd1 2.102(3); C1–Pd1 2.036(4); Pd1–P1 2.2567(10); Br1–Pd1 2.5001(5); C7–N1 1.282(5); C1–C6 1.424(5); C6–C7 1.439(6); and molecule B (not shown): N1′–Pd1′ 2.102(3); C1′–Pd1′ 2.036(4); Pd1′–P1′ 2.2567(10); Br1′–Pd1′ 2.5001(5); C7–N1 1.282(5); C1–C6 1.424(5); C6–C7 1.439(6).

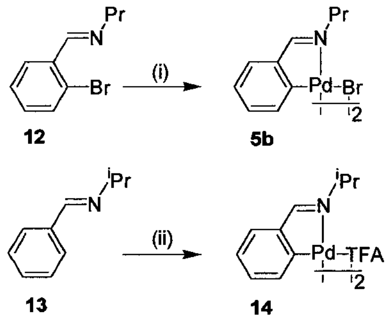
imine ligand and/or replacement of the TFA ligand with bromide has only a small effect on the activity. By contrast, when the immobilised catalyst **10** is used considerably lower activity is observed on the first catalytic run.

In all cases where recycling of **10** was attempted a decrease in activity was observed from one run to the next. Looking more closely at the coupling of 4-bromoanisole (entry 3) it can be seen that a fairly steady fall in activity occurs during runs 1–7 after which a more substantial drop in activity is observed. Interestingly, this coincides with a marked colour change of the silica. During runs 1–6 the silica has a deep brown–red colouration compared with unused **10** which is pale yellow. By the end of run 7, the silica was grey–black, suggesting the presence of a substantial quantity of bulk palladium metal. One plausible explanation for the drop in activity between runs that agrees with the observed colour changes is that palladium nanoparticles are being formed, which are deep red–brown, and it is these that are the true catalytically active species. At the end of the useful life of these nanoparticles they decompose to finely divided palladium metal, which is black. Palladium nanoparticles have previously been shown to be highly active catalysts in the Heck reaction [9], and a similar decomposition of a polystyrene-supported imine palladacycle to generate active palladium colloids in the Heck reaction has very recently been reported, although no mechanism for the liberation of the palladium nanoparticles was given [10].

By contrast with the findings that the polystyrene-supported systems show little or no activity after the first run [10], we find that when mesoporous silica is used as a support considerable activity is observed over several runs. Whether the silica in some way stabilises the putative palladium nanoparticles, thus increasing their longevity and hence their recyclability, or whether it acts merely as a gradual-release supply of colloidal palladium is not clear. Either way, some active catalyst, regardless of its precise nature, is removed from the

Table 1
Selected bond lengths (Å) and bond angles (°) for **9**

	Molecule A	Molecule B
Bond lengths		
C1–Pd1	2.036(4)	2.030(4)
N1–Pd1	2.102(3)	2.096(3)
Br1–Pd1	2.5001(5)	2.4905(6)
Pd1–P1	2.2567(10)	2.2528(11)
Bond angles		
C1–Pd1–N1	81.05(14)	80.67(15)
C1–Pd1–P1	94.33(11)	94.75(11)
N1–Pd1–P1	174.12(10)	174.54(10)
C1–Pd1–Br1	165.71(11)	167.67(10)
N1–Pd1–Br1	93.44(10)	93.04(10)
P1–Pd1–Br1	91.88(3)	92.00(3)



Scheme 3. (i) [Pd(dba)$_2$], toluene, 70 °C; (ii) [Pd(TFA)$_2$], THF, 50 °C.

silica, demonstrated by the observation that filtered solutions of reactions catalysed by **10** still show considerable activity. For instance when the coupling of 4-bromoanisole with phenylboronic acid catalysed by **10** is stopped after 6 h, 69% conversion to 4-methoxybiphenyl is observed; removal of the silica by filtration, addition of more phenylboronic acid and base and heating for a further 19 h gives an extra 11% of the coupled product. The fact that active catalytic species are removed from the silica support demonstrates that far from being stable, the metallated imine function is highly reactive and labile.

Initially the catalyst **11** shows much higher activity than **10**. However, in contrast to the results obtained with **10**, attempts to recycle the triphenylphosphine-modified catalyst **11** were unsuccessful with essentially complete loss of activity being observed between the first and second runs (entry 7). This implies that the active catalyst in this process is completely removed from the silica in the first catalytic run, whereas the silica **10** seems to show a gradual release of active catalyst over several runs. One explanation for this is that very low coordinate, homogeneous species are liberated from **11**, stabilised by the coordination of triphenylphosphine. Very low coordinate palladium phosphine complexes have previously been implicated as highly active homogeneous catalysts in the Suzuki reaction and in catalytic aminations [11,12].

Obviously the solid-supported catalysts **10** and **11** show neither high enough activity nor recyclability for them to be of any practical use in catalytic processes, but a study of their modes of decomposition may give vital information on the nature of the true active species when high activity, palladacyclic species are used in homogeneous catalysis and this is addressed below.

2.2. Mechanistic studies

In order to establish the mechanism by which zero-valent palladium species can be released from imine palladacycles, the reactions of the model complexes **14** and **15** with the individual substrates of the Suzuki reaction were examined. Whilst it showed no reactivity with 4-bromoacetophenone, heating **14** with excess phenylboronic acid and potassium carbonate in toluene for 18 h led to substantial deposition of palladium black. Hydrolysis of the product mixture followed by GC and GC–MS analysis showed the formation of 2-phenylbenzaldehyde **16**, and its decarbonylation product, biphenyl, in a combined yield of ~18% [13]. By contrast, when the same reaction was performed with the triphenylphosphine adduct **15**, substantial deposition of palladium was observed even at room temperature and the combined yield of **16** and biphenyl at the end of the reaction was ~51%. A plausible mechanism that accounts for the presence of **16** in these two reactions is shown in Scheme 4. Nucleophilic attack by the phenyl group from the boronate species on the palladium centres of **14** and **15** in a manner essentially identical to that invoked in a 'classical' Suzuki mechanism [14], generates the putative intermediates **17**. Reductive elimination of the metallated imine ligand with the phenyl group generates the coupled imine **18**–which

Table 2
Suzuki coupling of aryl bromides with phenylboronic acid catalysed by imine palladacycles

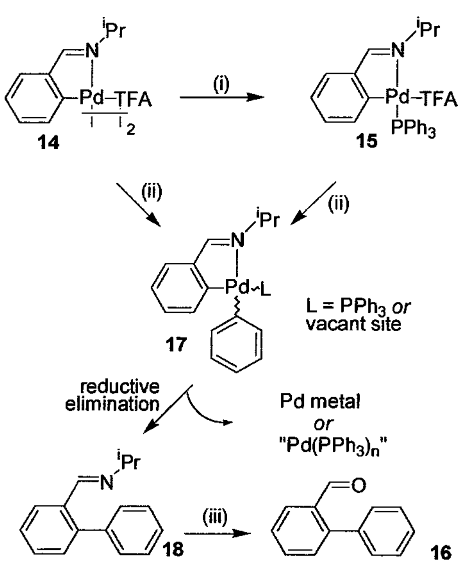
Entry	Substrate	Catalyst (mol% Pd)	Method	[run] Conversion (%) [a]	TON (mol product/mol Pd)
1	4-Bromoacetophenone	**5b** (0.0001)	A	54	540 000
2	4-Bromoacetophenone	**10** (0.0017) [b]	A	[1] 47, [2] 8, [3] 12, [4] 5, [5] 15, [6] 3, [7] 2	Run 1: 27 650; total: 54 100
3	4-Bromoanisole	**10** (0.31)	A	[1] 85, [2] 66, [3] 58, [4] 38, [5] 27, [6] 24, [7] 17, [8] 4	Run 1: 274; total: 1029
4	4-Bromoacetophenone	**10** (0.031) [c]	B	91	2935
5	4-Bromoacetophenone	**11** (0.0013) [b]	B	100	75 400
6	4-Bromoanisole	**11** (0.0013) [b]	A	[1] 63, [2] <0.5	Run 1: 48 500

Reaction conditions, method A: 2 mmol aryl bromide, 3 mmol PhB(OH)$_2$, 4 mmol K$_2$CO$_3$, 20 ml toluene, 130 °C, 17 h. Method B: 10 mmol aryl bromide, 11.5 mmol PhB(OH)$_2$, 15 mmol K$_2$CO$_3$, 30 ml toluene, 130 °C, 17 h.

[a] Determined by GC, based on aryl bromide.

[b] Catalyst diluted with silica-total mass 0.05 g.

[c] Catalyst diluted with silica-total mass 1.00 g.



Scheme 4. (i) PPh_3, CH_2Cl_2; (ii) five equivalents $PhB(OH)_2$, 7.5 equivalents K_2CO_3, toluene, reflux temperature; (iii) HCl(aq), reflux temperature.

subsequently undergoes hydrolysis during work–up and palladium(0) species.

It is highly likely that the phenylation and reductive-elimination steps outlined in Scheme 4 also occur as initiation steps in the catalytic cycles of Suzuki reactions catalysed by imine palladacycles and that the substantial quantities of palladium(0) species generated during this process act as the true active catalysts. One consequence of such a process acting as an initiation step would be that the eliminated imine ligand would be left on the silica wall. Subsequent hydrolysis of these imines in the presence of adventitious water [15] would result in 'dangling' amines which could quaternarise to give ammonium salts that may help to stabilise palladium nanoparticles in the silica, since alkylammonium salts are known to stabilise catalytically active palladium colloids [9].

Whilst they may be active, the putative silica-stabilised nanoparticles cannot be the only active catalysts as activity is observed in filtered solutions of reactions stopped part way through a catalytic run. The possibility also exists that any palladium nanoparticles formed are not stabilised by the silica, but instead are produced directly as a colloidal suspension at a steady rate by the decomposition route outlined above, however, this does not account for the observed colour of the silica **10** during recycling.

By contrast when **11** is used, it is far more likely that very low-coordinate palladium–phosphine species enter solution after reductive elimination of the organic functions from the metal centre. Such species have been implicated previously as catalysts in coupling reactions [12]. The liberation of active catalysts from **11** would be expected to be fast compared with **10** due to the enhancement of the rate of reductive elimination brought about by the phosphine ligand, as seen in the reactions of the model complexes **14** and **15** with Ph-$B(OH)_2$. This helps explain why catalyst **11** shows no recyclability—all of the active catalyst species are liberated into homogeneous solution during the first run.

3. Conclusions

In summary, whilst the silica-supported catalysts **10** and **11** show only poor recyclability, their modes of decomposition give vital information on the likely nature of the true active catalysts in the Suzuki reaction catalysed by all high-activity imine palladacyles. In all cases it seems that Pd(0) species are formed via a reductive-elimination process, preceded by nucleophilic attack of the phenyl boronate complex at the palladium centre [14]. We would expect this to be favoured by increased steric bulk around the metal centre and this is indeed observed. The presence of large amounts of reductively eliminated organic by-products indicates the concomitant production of an equal amount of palladium(0) species which almost certainly act as the true active catalyst(s). This mechanism obviously applies equally well to the previously reported complex **5a** [5]. Preliminary findings in our group indicate that the orthopalladated phosphinite complexes **3** may also undergo a similar initiation process [4], whilst Hartwig has shown a related process probably operates in Stille and amination reactions catalysed by **1** [16]. Combined, these results suggest that all high-activity palladacyclic complexes may in fact act as precursors to either low-coordinate palladium species or palladium nanoparticles, depending on the coordination strength of the donor group left after reductive elimination of the aryl function. These results go some way to resolving the current debate as to whether C–C coupling reactions catalysed by palladacycles proceed via a Pd(0)/Pd(II) or a Pd(II)/Pd(IV) pathway [17].

4. Experimental

4.1. General

All procedures were performed under an atmosphere of dry nitrogen unless stated otherwise using standard Schlenk line techniques. Solvents were distilled from appropriate drying reagents before use. NMR spectra were recorded on a Bruker AC300 or on a Bruker DRX400 Avance spectrometer. $^{31}P\{^1H\}$-MAS NMR spectra were recorded on Bruker MSL400. GC analysis was performed on a Varian GC 3800 fitted with a 25 m CP-SIL 5CB column. GC–MS was performed on a ThermoQuest trace GC–MS fitted with 15 m Restek

RTX-5MS column, operating in EI mode. [Pd(dba)$_2$] [18], [Pd(TFA)$_2$] [19], *N*-(2-bromo)benzylidene propylamine (**12**) [20], *N*-benzylidene isopropylamine (**13**) [21], were prepared according to literature methods. All other materials were purchased and used as received.

4.2. Syntheses

4.2.1. N-(2-Bromo)benzylidene(3-triethoxysilyl)-propylamine (7)

To a mixture of 3-aminopropyltriethoxysilane (10.0 ml, 42.73 mmol) in EtOH (30 ml), 2-bromobenzaldehyde (4.96 ml, 42.81 mmol) and 4 Å molecular sieves (5 g) were added. The reaction mixture was stirred at room temperature (r.t.) overnight and then filtered through a plug of celite. The solvent was removed in vacuo giving **7** as a pale yellow oil which was sufficiently pure for subsequent reactions (15.06 g, 91%). ^{1}H-NMR (CDCl$_3$): $\delta = 0.68$ (m, 2H, Si–CH$_2$), 1.22 (t, ^3J(HH) = 7.0 Hz, 9H, CH$_3$), 1.83 (m, 2H, CH$_2$–C*H*$_2$–CH$_2$), 3.66 (dt, ^3J(HH) = 6.9 Hz, ^4J(HH) = 1.1 Hz, 2H, N–CH$_2$), 3.82 (q, ^3J(HH) = 7.0 Hz, 6H, O–CH$_2$), 7.21 (ddd, ^3J(H^{4}H^3) = 8.0 Hz, ^3J(H^{4}H^5) = 7.6 Hz, ^4J(H^{4}H^6) = 2.0 Hz, 1H, H^4), 7.31 (m, 1H, H^5), 7.54 (dd, ^3J(H^{3}H^4) = 8.0 Hz, ^4J(H^{3}H^5) = 1.4 Hz, 1H, H^3), 7.99 (dd, ^3J(H^{6}H^5) = 7.7 Hz, ^4J(H^{6}H^4) = 2.0 Hz, 1H, H^6), 8.62 (br s, 1H, N=CH). Anal. Found: C, 49.0; H, 6.7; N, 3.5. Calc. for $C_{16}H_{26}BrNO_3Si$: C, 49.5; H, 6.75; N, 3.6%.

4.2.2. [{Pd(μ-Br){κ^2-C,N–C$_6$H$_4$-2-(CH=NC$_3$H$_6$Si-(OEt)$_3$)}}$_2$] (8)

A solution of [Pd(dba)$_2$] (1.314 g, 2.28 mmol) and **7** (1.552 g, 4.00 mmol) in 40 ml of toluene (40 ml) was stirred at 60 °C for 17 h, allowed to cool to r.t. and then filtered through celite. The solvent was removed in vacuo and the residue was recrystallised from CH$_2$Cl$_2$–hexane to give **8** in ~80% yield contaminated with dba (~20%). Exhaustive washing with hexane yielded pure **8** (0.169 g, 15%). ^{1}H-NMR (CDCl$_3$): $\delta = 0.64$ (br m, 2H, Si–CH$_2$), 1.23 (t, ^3J(HH) = 7.0 Hz, 9H, CH$_3$), 2.00 (m, 2H, CH$_2$–C*H*$_2$–CH$_2$), 3.69 (t, ^3J(HH) = 6.8 Hz, 2H, N–CH$_2$), 3.84 (q, ^3J(HH) = 7.0 Hz, 6H, O–CH$_2$), 7.04 (m, 2H, H^4, H^5), 7.21 (dd, ^3J(H^{6}H^5) = 6.9 Hz, ^4J(H^{6}H^4) = 2.0 Hz, 1H, H^6), 7.56 (br d, 1H, H^3), 7.86 (s, 1H, N=CH). Anal. Found: C, 38.2; H, 5.2; N, 2.6. Calc. for $C_{32}H_{52}Br_2N_2O_6Pd_2Si_2$: C, 38.8; H, 5.3; N, 2.8%.

4.2.3. [{PdBr{κ^2-C,N–C$_6$H$_4$-2-(CH=NC$_3$H$_6$Si-(OEt)$_3$)}(PPh$_3$)] (9)

A solution of **8** (0.425 g, 0.43 mmol) and triphenylphosphine (0.229 g, 0.87 mmol) in CH$_2$Cl$_2$ (25 ml) was stirred at r.t. for 16 h. Concentration of the solution and addition of EtOH, followed by cooling to −10 °C led to the precipitation of complex **9** as a yellow powder, which was then recrystallised from CH$_2$Cl$_2$–EtOH (0.362 g, 56%). ^{1}H-NMR (CDCl$_3$): $\delta = 0.60$ (br m, 2H, Si–CH$_2$), 1.23 (t, ^3J(HH) = 7.0 Hz, 9H, CH$_3$), 2.03 (br m, 2H, CH$_2$–C*H*$_2$–CH$_2$), 3.84 (q, ^3J(HH) = 7.0 Hz, 6H, O–CH$_2$), 4.09 (br m, 2H, N–CH$_2$), 6.37 (br dd, 1H, H^3), 6.53 (ddd, ^3J(H^{4}H^3) = 7.6 Hz, ^3J(H^{4}H^5) = 7.5 Hz, ^4J(H^{4}H^6) = 1.5 Hz, 1H, H^4), 6.91 (ddd, ^3J(H^{5}H^4) = 7.5 Hz, ^3J(H^{5}H^6) = 7.4 Hz, ^4J(H^{5}H^3) = 1.1 Hz, 1H, H^5), 7.26 (dd, ^3J(H^{6}H^5) = 7.4 Hz, ^4J(H^{6}H^4) = 1.5 Hz, 1H, H^6), 7.35, 7.74 (m, 15H, PPh$_3$), 8.13 (br d, ^4J(PH) = 7.5 Hz, 1H, N=CH). ^{31}P{^{1}H}-NMR (CDCl$_3$): $\delta = 43.3$ (s). ^{31}P{^{1}H}-NMR MAS: $\delta = 39$ (br s). Anal. Found: C, 53.4; H, 5.4; N, 1.7. Calc. for $C_{34}H_{41}BrNO_3PPdSi$: C, 53.9; H, 5.5; N, 1.85%.

4.2.4. Silica-immobilised catalyst (10)

A mixture of **8** (0.594 g, 0.60 mmol) and mesoporous silica (Merck Kieselgel, 100 Å, 2.002 g) was heated in toluene (25 ml) at reflux temperature for 17 h. The solution was allowed to cool to r.t. and the supernatant liquid was removed with a syringe. The pale yellow, modified silica product **10** was washed with toluene (7 × 20 ml) and CH$_2$Cl$_2$ (2 × 20 ml) and dried in vacuo. (Palladium analysis found: 3.30% *m*/*m* Pd, RSD = 5.77%.)

4.2.5. Silica-immobilised catalyst (11)

A mixture of **10** (0.935 g, 0.290 mmol Pd) and triphenylphosphine (0.127 g, 0.48 mmol) in CH$_2$Cl$_2$ (30 ml) was stirred at r.t. for 14 h. The supernatant liquid was removed with a syringe and the resultant pale yellow silica **11** was washed with CH$_2$Cl$_2$ (5 × 20 ml) and then dried in vacuo. (Palladium analysis found: 2.79% *m*/*m* Pd, RSD = 2.64%); ^{31}P{^{1}H}-NMR MAS: $\delta = 42$ (br s).

4.2.6. [{Pd(μ-Br){κ^2-C,N–C$_6$H$_4$-2-(CH=NPr)}$_2$] (5b)

A mixture of *N*-(2-bromo)benzylidene propylamine (0.978 g, 4.32 mmol) and [Pd(dba)$_2$] (2.258 g, 3.93 mmol) in toluene (60 ml) was warmed to 70 °C for 5 h, the resultant solution was filtered through celite and then the solvent was removed in vacuo. The resultant solid was purified by column chromatography (silica, hexane–EtOAc 3:1) to give **5b** as a pale yellow solid (1.167 g, 89%). ^{1}H-NMR (CDCl$_3$): $\delta = 0.95$ (t, ^3J(HH) = 7.5 Hz, 3H, CH$_3$), 1.89 (m, 2H, CH$_3$–C*H*$_2$), 3.65 (t, ^3J(HH) = 7.0 Hz, 2H, N–CH$_2$), 7.04 (br m, 2 H, H^4, H^5), 7.22 (br m, 1H, H^6), 7.56 (br m, 1H, H^3), 7.84 (br s, 1H, N=CH). Anal. Found: C, 36.3; H, 3.6; N, 3.9. Calc. for $C_{20}H_{24}Br_2N_2Pd_2$: C, 36.1; H, 3.6; N, 4.2%.

4.2.7. [{Pd(μ-TFA){κ^2-C,N-C_6H_4-2-(CH=N^{i}Pr)}$_2$] (**14**)

A solution of *N*-benzylidene isopropylamine (1.316 g, 8.93 mmol) and [Pd(TFA)$_2$] (2.125 g, 6.39 mmol) in THF (80 ml) was stirred at 50 °C for 20 min, allowed to cool to r.t. and then filtered through celite. The solvent was removed on rotary evaporator and the residue was recrystallised from CH_2Cl_2–EtOH to give **14** as a green solid (1.762 g, 75%). ^{1}H-NMR ($CDCl_3$): $\delta = 0.70$ (d, $^3J(HH) = 6.6$ Hz, 3H, CH_3), 1.24 (d, $^3J(HH) = 6.6$ Hz, 3H, CH_3), 3.30 (m, 1H, C*H*–CH_3), 6.92 (m, 1H, aromatic proton), 7.08 (m, 3H, aromatic protons), 7.39 (s, 1H, N=CH). Anal. Found: C, 39.25; H, 3.2; N, 3.7. Calc. for $C_{24}H_{24}F_6N_2O_4Pd_2$: C, 39.4; H, 3.3; N, 3.8%.

4.2.8. [{Pd(TFA){κ^2-C,N-C_6H_4-2-(CH=N^{i}Pr)}(PPh_3)] (**15**)

A solution of **14** (0.500 g, 0.68 mmol) and triphenylphosphine (0.398 g, 1.5 mmol) in CH_2Cl_2 (30 ml) was stirred at r.t. for 30 min and then filtered through celite. Addition of EtOH (50 ml) and concentration on rotary evaporator gave a solid which was recrystallised from CH_2Cl_2–EtOH to give **15** as a pale yellow solid (0.712 g, 83%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.37$ (d, $^3J(HH) = 6.6$ Hz, 6H, CH_3), 4.07 (br m, 1H, C*H*–CH_3), 6.45 (br dd, 1H, H^3), 6.56 (ddd, $^3J(H^4H^3) = 7.7$ Hz, $^3J(H^4H^5) = 7.5$ Hz, $^4J(H^4H^6) = 1.1$ Hz, 1H, H^4), 6.94 (ddd, $^3J(H^5H^4) = 7.5$ Hz, $^3J(H^5H^6) = 7.4$, $^4J(H^5H^3) = 0.8$ Hz, 1H, H^5), 7.29 (dd, $^3J(H^6H^5) = 7.4$ Hz, $^4J(H^6H^4) = 1.1$ Hz, 1H, H^6), 7.43 (m, 9H, PPh_3), 7.79 (m, 6H, PPh_3), 8.15 (dd, $J = 0.9$ Hz, $J = 7.9$ Hz, 1H, N=CH). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 41.15$ (s). Anal. Found: C, 56.7; H, 4.2; N, 2.1. Calc. for $C_{30}H_{27}F_3NO_2PPd$: C, 57.4; H, 4.3; N, 2.2%.

4.3. Catalysis

4.3.1. Catalysis with **5b**

A solution of **5b** (2.0×10^{-6} mmol) in toluene (2 ml), obtained by multiple dilutions, was put into a Schlenk tube, the solvent removed in vacuo and the tube was evacuated and then flushed with nitrogen three times. Then 4-bromoacetophenone (0.398 g, 2.00 mmol), phenylboronic acid (0.366 g, 3.00 mmol), K_2CO_3 (0.553 g, 4.00 mmol) and toluene (20 ml) were added. The mixture was then heated at 130 °C (external temperature) under nitrogen for 17 h, then cooled in an ice-bath and poured into brine (40 ml) and toluene (30 ml) was added. The two phases were separated and the organic layer was washed with brine (2 × 40 ml). The aqueous phase was extracted with CH_2Cl_2 (3 × 30 ml). The organic phases were combined, dried over $MgSO_4$, filtered through celite and the solvent removed on a rotary evaporator. Toluene (10 ml) was added and the conversion was determined by GC analysis (hexadecane standard).

4.3.2. Catalysis with **10** and **11**

4.3.2.1. *Method A*. The reactions were performed in a modified three-necked round bottom flask where one of the side necks had the female joint removed and replaced by a fritted male joint. The modified flask was charged with the appropriate amount of **10** or **11** either undiluted, or mixed with an appropriate amount of silica (Merck Kieselgel, 100 Å — see Table 2 for dilutions). The flask was flushed with nitrogen, then the appropriate aryl bromide (2.00 mmol), phenylboronic acid (0.366 g, 3.00 mmol), K_2CO_3 (0.553 g, 4.00 mmol) and toluene (20 ml) were added. The mixture was heated at 130 °C (external temperature) under nitrogen for 17 h. The reaction mixture was cooled in an ice-bath, then filtered off through the frit and the catalyst-containing residue washed with CH_2Cl_2 (20 ml), distilled water (3 × 20 ml), acetone (3 × 20 ml), CH_2Cl_2 (20 ml) and then dried in vacuo to give the catalyst ready for re-use. The solvent was removed from the combined organic extracts on a rotary evaporator and then toluene (10 ml) was added and the conversion was determined by GC analysis (hexadecane standard).

4.3.2.2. *Method B*. A Schlenk tube was charged with the appropriate amount of either **10** or **11** mixed with an appropriate amount of silica (Merck Kieselgel, 100 Å — see Table 2 for dilutions). The tube was evacuated and then flushed with nitrogen three times, then 4-bromoacetophenone (1.990 g, 10.00 mmol), phenylboronic acid (1.402 g, 11.50 mmol), K_2CO_3 (2.764 g, 20.00 mmol) and toluene (30 ml) were added. The mixture was then heated at 130 °C (external temperature) under nitrogen for 17 h. The reaction mixture was cooled in an ice-bath and then filtered through celite which was washed with toluene (5 × 20 ml) and EtOAc (2 × 20 ml). The solvents were removed on a rotary evaporator. To the resulting solid, water was added (100 ml) and the mixture was stirred for 30 min. Then, the solid was collected by filtration, washed with water (5 × 20 ml) and dissolved in toluene (40 ml). The solution was dried over $MgSO_4$ and then analysed by GC (hexadecane standard).

4.3.3. Demonstration of presence of active catalyst removal from silica **10**

A mixture of **10** (0.020 g, 0.0062 mmol Pd), 4-bromoanisole (0.25 ml, 2.00 mmol), phenylboronic acid (0.366 g, 3.00 mmol) and K_2CO_3 (0.553 g, 4.00 mmol) were heated at 130 °C (external temperature) in toluene (20 ml) for 6 h. The solution was cooled with an ice-bath, filtered through celite which was washed with toluene (30 ml) and hexadecane (2 ml, internal standard) was added to the combined solution and washings. GC analysis of the solution showed a 68% conversion of the 4-bromoanisole to 4-methoxybiphenyl. To the solution more phenylboronic acid (0.366 g, 3.00 mmol) and K_2CO_3 (0.553 g, 4.00 mmol) were added and the solution was heated at 130 °C (external temperature) for a further 19 h. The solution was cooled in an ice-bath and then poured into HCl (1.18 sg, 40 ml). The organic layer was separated, washed with water (3 × 40 ml), dried over $MgSO_4$ and then filtered through celite. GC analysis revealed an 80% conversion of 4-bromoanisole to 4-methoxybiphenyl.

4.3.4. Decomposition studies

A mixture of either complex **14** or **15** (0.31 mmol Pd), phenylboronic acid (0.194 g, 1.59 mmol) and K_2CO_3 (0.330 g, 2.39 mmol) in toluene (25 ml) was heated at 130 °C (external temperature) for 18 h. The solution was cooled in an ice-bath, poured in HCl (1.18 sg, 30 ml) and then stirred vigorously at 70 °C for 3 h. The two phases were separated and the organic layer was washed with water (3 × 30 ml), dried over $MgSO_4$, filtered through celite and the solvent was removed on rotary evaporator. Toluene (4 ml) and mesitylene (1 ml, internal standard) were added and the mixture analysed by GC–MS and GC. Both techniques indicated the presence of 2-phenylbenzaldehyde and biphenyl by comparison with authentic samples. The combined yields of 2-phenylbenzaldehyde and biphenyl were ca. 18% (for **12**) and 51% (for **13**).

4.4. Crystal structure determination of complex 9

Suitable crystals of **9** were grown from CH_2Cl_2–EtOH. Cell dimensions and intensity data were recorded at 150 K, using a Nonius KappaCCD area detector diffractometer mounted at the window of a rotating anode operating at 50 kV, 90 mA with a molybdenum anode (λ (Mo–K_α) = 0.71073 Å). The crystal-to-detector distance was 30 mm and ϕ- and Ω-scans with a κ offset were employed to access a complete set of unique reflections (2° increments, 10 s exposure time). Data collection and processing were carried out using DIRAX [22], DENZO [23] and MAXUS [24] run from within Nonius COLLECT [25] program and an empirical absorption correction was applied using SORTAV [26,27]. The structure was solved via direct methods [28] and refined by full-matrix least-squares [29] on F^2. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated using a riding model. Crystal data: $C_{34}H_{41}BrNO_3PPdSi$, $M = 757.05$, monoclinic, $a = 26.5989(6)$, $b = 14.9407(3)$, $c = 17.5024(5)$ Å, $\beta = 102.531(4)°$, $U = 6789.9(3)$ Å^3, $T = 150$ K, space group $P2_1/c$ (no. 14), $Z = 8$ (the two molecules in the asymmetric unit differ significantly in the conformation of the triethoxysilyl group), μ (Mo–K_α) = 1.84 mm^{-1}, 32 235 reflections measured, 11 859 unique ($R_{\text{int}} = 0.0529$) which were used in all calculations. The final $R1(F^2)$ was 0.0419 [$F^2 > 2\sigma(F^2)$] and $wR(F^2)$ was 0.1045 (all data).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153753 for compound **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the University of Exeter for a student bursary (C.S.J.C.) and Johnson Matthey Chemicals for palladium analysis. The MAS NMR measurements were supported by EPSRC grant no. GR/M12209.

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[13] Shorter reaction times led to higher **16**:biphenyl ratios, demonstrating that the presence of biphenyl was due to a palladium-mediated decarbonylation of **16**. Further, heating **16** with a catalytic amount of palladium acetate led to catalytic decarbonylation giving biphenyl.

[14] This step is usually, misleadingly described as 'trans-metallation'.

[15] Removal of all the water from the silica without destruction of the supported complex is not possible. In addition, substantial quantities of water are introduced during washing after each catalytic run.

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