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An evaluation of phosphine and carbene adducts of phosphite- and phosphinite-based palladacycles in the coupling of alkyl bromides with aryl boronic acids

Robin B. Bedford,[a,*] Michael Betham,[a] Simon J. Coles,[b] Robert M. Frost[c] and Michael B. Hursthouse[b]

[a]*School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK*
[b]*EPSRC National Crystallography Service, Department of Chemistry, University of Southampton, Highfield Road, Southampton, SO17 1BJ, UK*
[c]*Department of Chemistry, University of Exeter, Exeter, EX4 4QD, UK*

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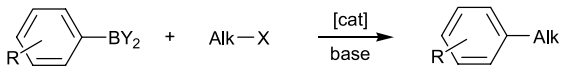
Abstract—A range of palladacyclic catalysts and their phosphine and carbene adducts were tested in the Suzuki coupling of an alkyl bromide with phenylboronic acid and showed modest activity in some cases. Unlike with aryl halide substrates it appears that there is no particular benefit in the use of palladacycles as the palladium source. Initial data indicate that the rate determining step is not the oxidative addition of the alkyl halide substrate, but rather lies later in the catalytic cycle.

1. Introduction

Coupling reactions leading to the formation of new C–C bonds, typically catalysed by ubiquitous palladium complexes, form the bedrock of many contemporary syntheses.[1] Despite the undoubted usefulness of such processes, there are still holes in the general methodologies currently available that limit their applicability. Much research is focused on addressing these shortcomings and the last few years have seen substantial advances. One area that has proved particularly problematic is the extension of Suzuki coupling of aryl boron nucleophiles to alkyl halides bearing β-hydrogens (Scheme 1).[2]



Scheme 1. Suzuki coupling of aryl boron nucleophiles with alkyl halides.

The problems associated with this process are two-fold. Firstly, the oxidative addition of the C–X bond is believed to be more difficult for alkyl halides as a result of the higher bond strength compared with aryl halides.[3] Secondly, β-elimination of the Pd–alkyl complex formed after oxidative addition can lead to competitive alkene formation rather than subsequent coupling, depending on the relative rates of the two processes (Scheme 2).

As long ago as 1992 Suzuki and co-workers showed that alkyl iodides could be coupled with alkyl- and aryl-(9-BBN) reagents (9-BBN = 9-borabicyclo[3.3.1]nonane) using $[Pd(PPh_3)_4]$ as catalyst and K_3PO_4 as base at 60 °C, giving the coupled products in reasonable yield.[4] By contrast, no activity was seen with alkyl bromides. Fu and co-workers have focused on the problem of using substrates other than alkyl iodides and found that primary alkyl bromides can be coupled with both alkyl- and vinyl-(9-BBN) reagents at rt in THF using palladium acetate/tricyclohexylphosphine as the catalyst and potassium phosphate as a mild base.[5] When the base is replaced with cesium hydroxide and the reactions performed in dioxane at 90 °C, then primary alkyl chlorides can be used as coupling partners with alkyl-(9-BBN) reagents.[6] Both alkyl- and aryl-(9-BBN) reagents can be coupled with alkyl tosylates at 50 °C in dioxane using sodium hydroxide as base employing a catalyst formed in situ from palladium acetate and $PMe(^tBu)_2$.[7] Caddick, Cloke and co-workers have shown that *N*-heterocyclic carbene adducts of palladium, formed in situ from palladium bis(dibenzylideneacetone) and the salt **1**, can

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* Corresponding author. Fax: +44 117 925 1295;
e-mail: r.bedford@bristol.ac.uk

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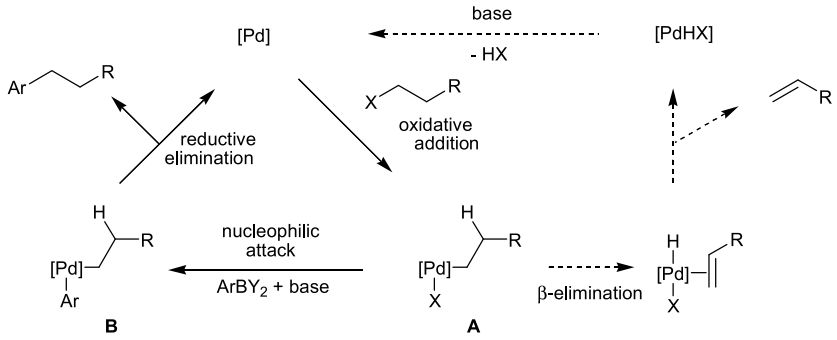
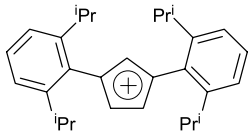
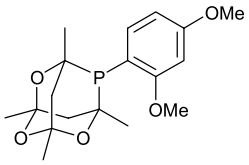


Scheme 2. Simplified catalytic cycles for competing coupling and β-elimination pathways.

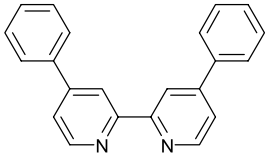
also be used to couple primary alkyl bromides with alkyl- and vinyl-(9-BBN) reagents, using potassium *tert*-butoxide as base at 40 °C in THF.[8]



1



2



3

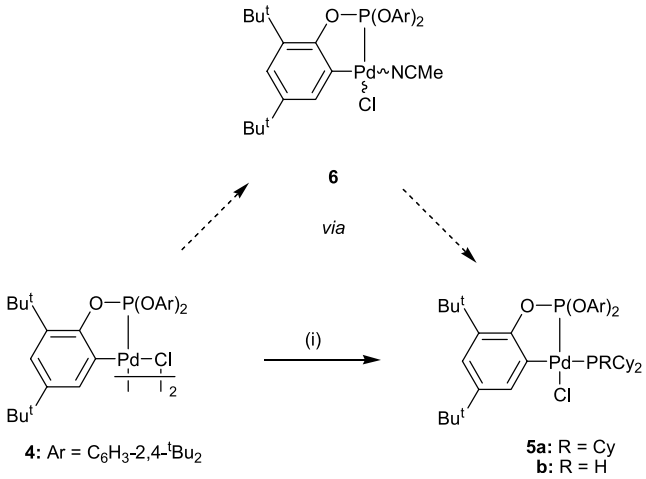
While such reactions are useful, the low commercial availability of alkyl- and aryl-(9-BBN) reagents and their air-sensitivity limits their appeal. In contrast aryl boronic acids reagents are widely available and easily handled. Therefore, Fu and co-workers investigated the possibility of using them as coupling partners with alkyl halides.[9] They found that the catalyst formed in situ from $Pd(OAc)_2$/$PMe(^tBu)_2$ couples primary alkyl bromides with aryl- and vinyl-boronic acids at rt when KO^tBu is used as the base in *tert*-amyl alcohol. Capretta and co-workers recently demonstrated that palladium catalysts containing the phosphaadamantyl ligand **2** can be used to good effect in the rt coupling of primary alkyl bromides and chlorides with aryl boronic acids, using potassium *tert*-butoxide in dioxane.[10] Interestingly, they even found that a moderate yield of coupled product results when the secondary alkyl bromide bromocyclohexane is used as a substrate. Zhou and Fu have also investigated the coupling of secondary alkyl halides with aryl- and vinyl-boronic acids and find that optimum activity is obtained with a nickel-based catalyst formed in situ from $[Ni(COD)_2]$ and bathophenanthroline, **3**, in *sec*-butanol using potassium *tert*-butoxide as base.[11]

We have been interested in the use phosphite- and phosphinite-based palladacyclic catalysts and their phosphine and carbene adducts in a range of Suzuki couplings of aryl halides with aryl and alkyl boronic acids.[12,13] Often the phosphines tested show far better activity when used in conjunction with palladacyclic precursors than classical palladium sources such as palladium acetate or palladium dibenzylideneacetone complexes.[14] We were interested to see whether this would hold true in the Suzuki coupling of alkyl halides with aryl boronic acids (Scheme 1, Y=OH), the results of an evaluative study are presented below.

2. Results and discussion

2.1. Synthesis and characterisation of catalysts

We have previously found that the reaction of the palladacyclic phosphite complex **4** with tricyclohexylphosphine at rt in dichloromethane leads to the formation of the phosphine adduct **5a**. However, under these conditions, the reaction does not go to completion, but rather gives a mixture of **4**, **5a** and PCy_3.[12b] Pure complex **5a** can be synthesized by the reaction of **4** with PCy_3CS_2, however, we wished to design a synthesis that exploits the free phosphine. This proves to be straightforward; the use of acetonitrile as solvent gives clean **5a** from **4** and PCy_3, presumably via the intermediate formation of a mono-nuclear acetonitrile complex **6** (Scheme 3).



Scheme 3. Synthesis of phosphine adducts of a phosphite palladacycle. Conditions: (i) $PRCy_2$, MeCN, rt, 18 h.

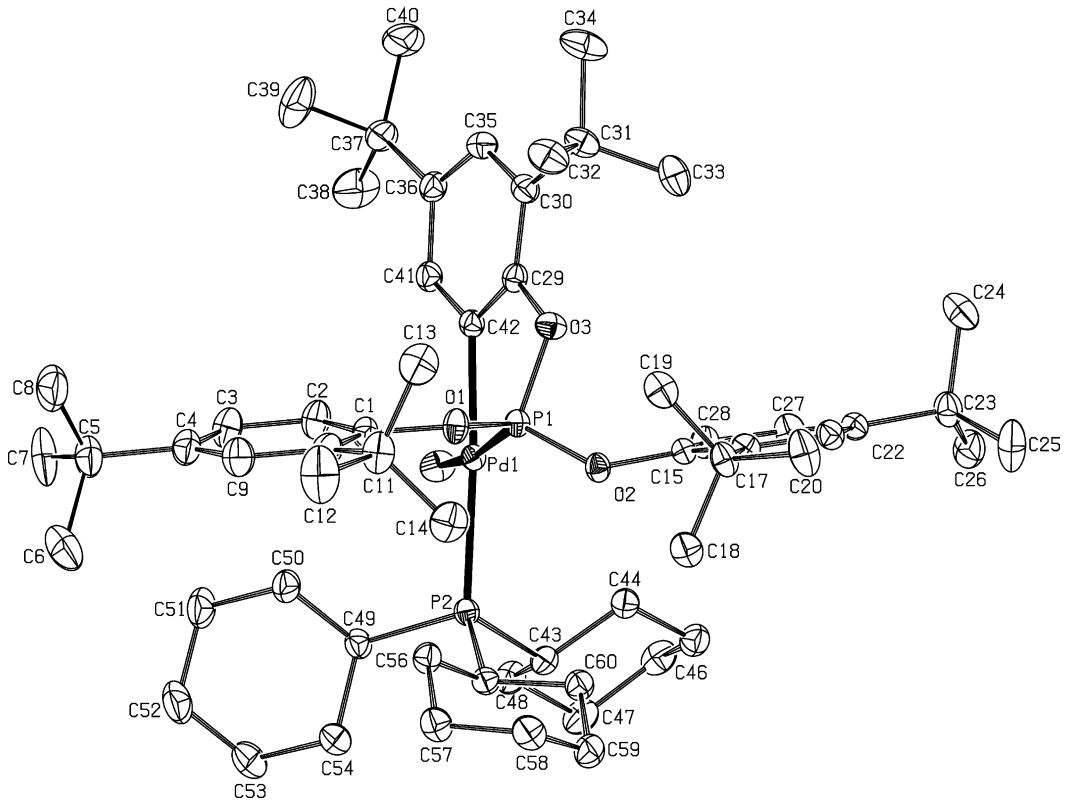
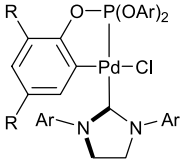


Figure 1. The molecular structure of **5a** with an ethanol solvate and disorder in two *tert*-butyl groups removed for clarity.

The ^{31}P spectrum of **5a** shows doublets at δ 136.0 and 26.2 ppm corresponding to the phosphite and phosphine donors, respectively, with a mutual coupling of 40.7 Hz. This relatively small coupling is indicative of a cis-disposition of the two phosphorus donors. Both this ^{31}P and the ^{1}H NMR spectral data are consistent with those obtained previously.[12b] The structure of complex **5a** was confirmed by single crystal X-ray analysis and the molecule is shown in Figure 1, whilst selected data are presented in Table 1. The structural analysis confirms the cis-disposition of the two P-donor groups. This is in marked contrast to the related carbene adducts **7**, which show the carbene ligand trans to the phosphite donor.[13]



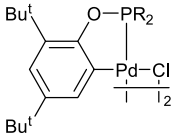
7a: R = ^{t}Bu; OAr = C_6H_3-2,4-$^{t}Bu_2$; Ar = mesityl
b: R = ^{t}Bu; OAr = C_6H_3-2,4-$^{t}Bu_2$; C_6H_3-2,6-$^{i}Pr_2$
c: R = H; OAr = OPh; Ar = mesityl

The synthetic methodology outlined above can also be applied to the synthesis of the novel secondary alkylphosphine adduct **5b**. The $^{31}P\{^{1}H\}$ NMR spectrum of **5b** shows doublets at δ 131.4 (phosphite) and 4.4 (phosphine) ppm with a mutual cis coupling of 46.2 Hz. These data are consistent with complex **5b** adopting a similar structure to **5a**. The proton-coupled ^{31}P spectrum shows a doublet of doublets at 134.2 ppm corresponding to the phosphite donor with a 47 Hz coupling to the phosphine phosphorus and a $^{3}J_{PH}$ of 14 Hz to the phosphine P–H and a doublet of doublets at 4.5 ppm with a large $^{1}J_{PH}$ of 312 Hz and a $^{2}J_{PP}$ of 41 Hz. The resonance for the P–H hydrogen is seen as a doublet of doublets of triplets in the ^{1}H NMR spectrum at 3.57 ppm with a large $^{1}J_{PH}$ of 310.5 Hz, a small $^{3}J_{PP}$ coupling of 15 Hz to the phosphite and a small $^{3}J_{HH}$ of 7 Hz to the two equivalent cyclohexyl PC*H*s. The $^{1}J_{PH}$ coupling is considerably larger than that of the free phosphine (170 Hz).

Table 1. Selected bond lengths and angles for complex **5a**

Bond lengths (Å)			
Pd1–P1	2.1770(5)	Pd1–P2	2.4052(5)
Pd1–C42	2.0842(18)	Pd1–Cl1	2.3488(5)
Bond angles (°)			
P1–Pd1–C42	77.83(5)	P1–Pd1–P2	106.044(17)
P2–Pd1–Cl1	84.946(17)	C42–Pd1–Cl1	91.37(5)
P1–Pd1–Cl1	168.029(18)	P2–Pd1–C42	175.64(5)

Attempts to produce phosphine adducts of **4** with the larger phosphines $P^{t}Bu_3$, PR_2(*o*-biphenyl) (R = Cy, ^{t}Bu), $PPh^{t}Bu_2$ using this method either failed or gave mixtures. The reaction of the two orthometallated phosphinite complexes **8a** and **8b** with PCy_3 again gave a mixture of products.

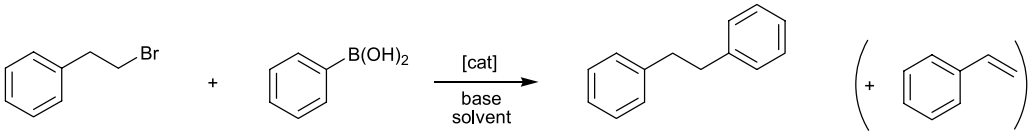


8a: R = Ph
b: R = ^{i}Pr

2.2. Catalysis

In the first instance we performed an optimisation study using the complex **5a** as catalyst in the coupling of

Table 2. Optimisation of solvents and bases[a]

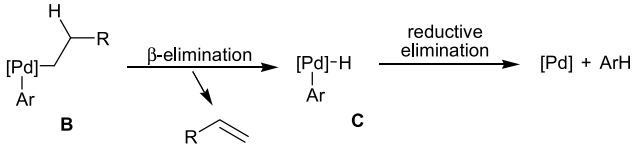


Entry	Solvent	Base	Conversion to 1,2-diphenyl ethane (%)[b]	Conversion to styrene (%)[b]
1	NMP	Cs_2CO_3	0	30
2	NMP	K_3PO_4	1	18
3	NMP	K_2CO_3	0	29
4	Toluene	Cs_2CO_3	2	6
5	Toluene	K_3PO_4	30	5
6	Toluene	K_2CO_3	5	4
7	Dioxane	Cs_2CO_3	6	13
8	Dioxane	K_3PO_4	31	4
9	Dioxane	K_2CO_3	36	1
10	Dioxane	KO^{t}Bu	0	64
11	Dioxane	KF	24	7
12	Dioxane	KF/K_3PO_4 1:1	11	6
13	DME	K_3PO_4	20	12
14	DME	K_2CO_3	4	2
15	DME	Cs_2CO_3	13	26
16	DME	KF	8	10
17	*sec*-Butanol	K_3PO_4	47	10
18	*sec*-Butanol	K_2CO_3	23	8
19	*sec*-Butanol	Cs_2CO_3	11	31
20	*sec*-Butanol	KO^{t}Bu	0	49
21	*tert*-Amyl alcohol	K_3PO_4	30	8
22	*tert*-Amyl alcohol	K_2CO_3	48	15
23	*tert*-Amyl alcohol	Cs_2CO_3	22	41
24	*tert*-Amyl alcohol	KO^{t}Bu	0	77

[a] Conditions: $BrCH_2CH_2Ph$ (5.0 mmol), $PhB(OH)_2$ (7.5 mmol), base (15.0 mmol), solvent (10 ml), 110 °C (external temperature).
[b] Conversion determined by GC (hexadecane internal standard).

(2-bromoethyl)benzene with phenylboronic acid with a range of solvents and bases; the results from this are summarized in Table 2. As can be seen, with respect to conversion to the desired 1,2-diphenylethane, the use of potassium phosphate in *sec*-butanol or potassium carbonate on *tert*-amyl alcohol gives the best activities (entries 17 and 22, respectively). However, in both cases substantial amounts of styrene are formed. While the use of potassium carbonate in 1,4-dioxane gives lower conversion to the desired product, the selectivity is much higher with very little styrene observed (entry 9). In stark contrast with the findings outlined in the introduction, potassium *tert*-butoxide proves to be a very poor choice of base with this catalyst (entries 10, 20, 24) giving little or no conversion to the desired product and substantial amounts of styrene via β-elimination, particularly when *tert*-amyl alcohol is used as the solvent.[8–11]

It is apparent from the relative conversions to the desired coupled product 1,2-diphenylethane and styrene that when the former is relatively low then the latter is relatively high. This is consistent with a manifold in which the rate determining step is not the oxidative addition of the alkyl bromide, but occurs after the formation of a palladium alkyl intermediate (Scheme 2, **A**). It is to be expected that the base plays an intimate role in the formation of the Pd-aryl intermediate (**B**) and if the rate-determining step is associated with this process a slow rate of formation of **B** from **A** would lead to greater amounts of β-eliminated product, in line with observation. Alternatively it is possible that the rate-determining step is reductive elimination, in which case β-elimination may also occur from the intermediate **B**. If this is true then an intermediate of the form **C** would be produced (Scheme 4), which would undergo reductive elimination to reform the active catalysts and an arene, in this case benzene. This certainly appears to be occurring; GC analysis of the product mixture formed in the reaction with cesium carbonate as base in *tert*-amyl alcohol (Table 2, entry 23) shows the presence of a substantial quantity of benzene, although at this stage we have not been able to determine the precise amount.



Scheme 4.

We next examined the effect of varying catalyst loading in the reaction in dioxane with K_2CO_3 acting as base and the results of this are shown in Figure 2. As can be seen the optimum conversion is achieved at 1.5 mol% catalyst loading but lowering the loading to 0.1 mol% leads to a maximum TON (turn-over number, mol product/mol catalyst) of 70. This is as expected since lowering the catalyst concentration would lead to a lower rate of catalyst decomposition by aggregation.

Then we examined the use of a range of catalysts, both

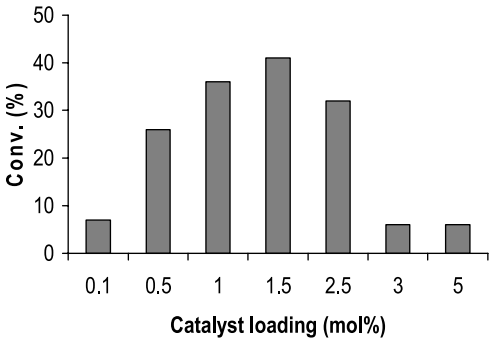


Figure 2. Variation in catalyst loading.

pre-formed or formed in situ, in the standard reaction. Dioxane was chosen as solvent and potassium carbonate as base for this study despite the fact that these conditions do not give the highest conversion, but rather because they show good selectivity for the desired product. The results from this study are presented in Table 3.

Table 3. Variation in catalyst[a]

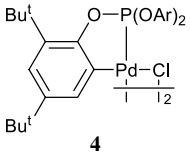
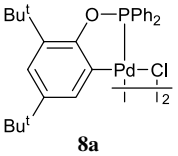
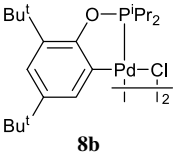
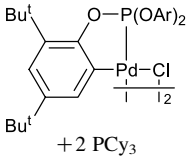
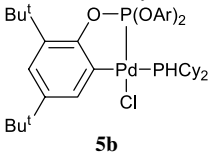
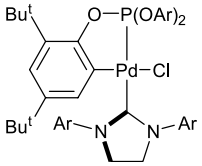
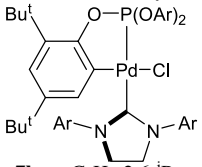
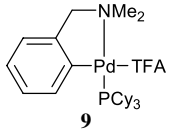
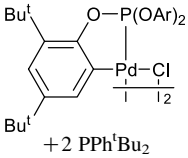
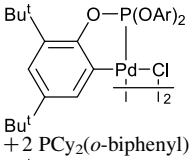
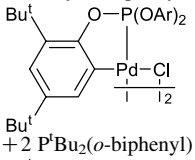
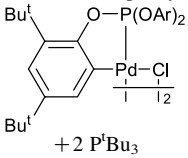
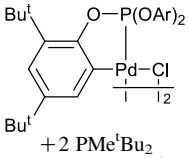
Entry	Catalyst	Conversion to 1,2-diphenylethane (%)[b]	Conversion to styrene (%)[b]
1	 **4**	2	8
2	 **8a**	0	6
3	 **8b**	0	10
4	 +2 PCy_3	17	6
5	**8a** +2 PCy_3	0	7
6	**8b** +2 PCy_3	6	7
7	 **5b**	6	4
8	 **7a**: Ar = mesityl	6	8
9	 **7b**: $=C_6H_3$-2,6-$^{i}Pr_2$	8	7

Table 3 (*continued*)

Entry	Catalyst	Conversion to 1,2-diphenylethane (%)[b]	Conversion to styrene (%)[b]
10	 **9**	11	4
11	 +2 $PPh^{t}Bu_2$	25	4
12	 +2 PCy_2(*o*-biphenyl)	26	11
13	 +2 $P^{t}Bu_2$(*o*-biphenyl)	3	6
14	 +2 $P^{t}Bu_3$	0	18
15	 +2 $PMe^{t}Bu_2$	16	7
16	$Pd(OAc)_2$ +2 $PMe^{t}Bu_2$	1	39
17	$Pd(OAc)_2$ +2 PCy_3	32	10
18	$Pd_2(dba)_3$ +4 PCy_3	15	7

[a] Conditions: $BrCH_2CH_2Ph$ (5.0 mmol), $PhB(OH)_2$ (7.5 mmol), K_2CO_3 (15.0 mmol), 1,4-dioxane (10 ml), 110 °C (external temperature).
[b] Conversion determined by GC (hexadecane internal standard).

The dimeric phosphite- and phosphinite-based palladacycles **4**, **8a** and **8b** all show little or no activity (entries 1–3). Comparing the activity of the catalysts formed in situ from dimer **4** and tricyclohexylphosphine (entry 4) with the preformed catalyst **5a** (Table 2, entry 9) indicates that it is important to pre-synthesise the catalysts, if possible. It is, therefore, perhaps not surprising that the catalysts formed in situ from the dimers **8** and PCy_3 show very poor activity (Table 3, entries 5 and 6). Indolese, Studer and co-workers have shown that palladacyclic catalysts with secondary alkylphosphine co-ligands are effective in the Suzuki biaryl coupling reaction of aryl chlorides.[15] Therefore, we were interested to see how the preformed catalyst **5b** would fare, unfortunately it proved to be disappointing (entry 7). It is perhaps not surprising that the carbene-containing complexes **7** did not prove to be any use (entries 8 and 9) since we have found them to be unimpressive in the Suzuki coupling of aryl chlorides.[13] In contrast, we have shown that

the preformed *N*-palladacyclic catalyst **9** shows good activity in the Suzuki biaryl coupling of aryl chlorides and were interested to see if it would work well in this instance.[16] Unfortunately it too proved essentially ineffective (entry 10).

Since we were unable to pre-form phosphine adducts of **5a** with bulkier phosphines, we tested the performance of catalysts produced in situ (entries 11–15). Both PPh^tBu_2 and PCy_2(*o*-biphenyl) (entries 11 and 12) show better conversions to product than the catalyst formed in situ with PCy_3 (entry 4), the latter at the expense of selectivity with respect to competitive styrene formation. Neither P(*o*-biphenyl)$^tBu_2$ or P^tBu_3 (entries 13 and 14) are promising. The phosphine ligand PMe^tBu_2 has been shown by Fu and co-workers to give optimum activity under their conditions in the Suzuki coupling of alkyl halides.[9] When it is used in conjunction with the palladacyclic complex **4** it shows poor activity (entry 15). However, the catalysts formed in situ from the phosphine and palladium acetate performed even worse with no conversion to coupled product and substantial styrene formation observed (entry 16). By contrast the catalyst formed in situ from tricyclohexylphosphine and palladium acetate shows similar activity (entry 17) to catalyst **5a** (Table 2, entry 9). Lower activity is seen when [Pd(dba)$_2$] is used as the palladium source (Table 3, entry 18).

We were surprised that PMe^tBu_2 performed so badly, given its good activity in the coupling of alkyl halides and tosylates with alkyl- and aryl-(9-BBN) or boronic acid reagents.[7,9] It is possible that the temperature of the reaction is too high and consequently the high relative rate of β-elimination precludes substantial coupling. In order to test this we performed the reaction again at 80 °C, at which temperature no product was observed despite the fact that the formation of styrene had been dramatically curtailed (4%). Similarly, when the reaction catalysed by **5a** was repeated at this temperature, very low (3%) conversion to product was observed. No conversion to product with either catalyst system is observed at rt or 50 °C.

3. Conclusions

In summary, unlike in the Suzuki biaryl coupling where the use of palladacyclic pre-catalysts can have a substantial benefit on activity compared with classical palladium precursors, when alkyl halides are used as substrates there is no discernible advantage in their use over palladium acetate. Preliminary data indicate that the rate-determining step in the coupling of alkyl bromides with aryl boronic acids is not oxidative addition, but rather lies later in the catalytic cycle. Mechanistic work is ongoing in our group to try to help optimize future catalyst structures.

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4. Experimental

4.1. General

All reactions and manipulations of air-sensitive materials were performed under nitrogen, either in a glove-box or using standard Schlenk techniques. Solvents were distilled from appropriate drying reagents prior to use. Complexes **4**, **7–9** were prepared according to literature procedures.[12b,13,16b,17] All other material were obtained commercially and used as received. GC analysis was performed on a Varian 3800 GC fitted with a 25 m CP Sil 5CB column and data were recorded on a Star workstation. All catalytic reactions were performed on a Radleys Carousel Reactor™. This consists of 12 ca. 45 ml tubes, which are fitted with screw-on Teflon caps that are equipped with valves for the introduction of inert gas and septa for the introduction of reagents. The 12 reaction tubes sit in two stacked aluminium blocks, the lower one fits on a hotplate-stirrer and can be maintained at a constant temperature with a thermostat, while the upper block has water circulating, which cools the top of the tubes, allowing reactions to be performed at reflux temperature.

4.1.1. Synthesis of [PdCl{κ^2-*P*,*C*-(OC_6H_2–2,4-$^tBu_2$)(OC_6H_3–2,4-$^tBu_2$)$_2$}PCy_3], 5a. A mixture of complex **4** (0.79 g, 0.50 mmol) and tricyclohexylphosphine (0.31 g, 1.10 mmol) in acetonitrile was stirred at rt overnight. The solvent was then removed in vacuo, the resulting solid was dissolved in dichloromethane (10 ml), ethanol (10 ml) was added and the solution was concentrated in vacuo to induce precipitation. The resultant precipitate was recrystallised (dichloromethane/ethanol) to give complex **5a** as a colourless solid (0.65 g, 61%). Anal. Calcd for $C_{60}H_{95}O_3P_2PdCl$: C, 67.5; H, 9.0. Found: C, 66.9; H, 8.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (br s, 30H, CH_2 of Cy); 1.30 (br s, 18H, ^{t}Bu of orthometallated ring); 1.48 (br s, 36H, ^{t}Bu of non-orthometallated rings); 2.32 (m, 3H, C*H* of Cy); 6.92 (d, 2H, $^3J_{HH}$=2.6 Hz, non-orthometallated ring H6); 6.94 (dd, 2H, $^3J_{HH}$=2.6 Hz, $^4J_{HH}$=2.45 Hz, non-orthometallated ring H5); 7.27 (br m, 2H, non-orthometallated ring H3); 7.59 (d, 1H, $^4J_{HH}$=3.0 Hz, orthometallated ring), 7.62 (d, 1H, $^4J_{HH}$=3.0 Hz, orthometallated ring). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 27.0 (d, J_{PP}=41.6 Hz, PCy_3); 136.6 (d, J_{PP}=41.6 Hz, P(OAr)$_3$).

4.2. Crystal structure determination for complex 5a

Data were collected at 120 K on an Nonius Kappa CCD area detector diffractometer located at the window of a Nonius FR591 rotating anode X-ray generator, equipped with a molybdenum target (λ Mo k$_\alpha$=0.71073 Å). Structures were solved and refined using the SHELX-97 suite of programs.[18] Data were corrected for absorption effects by means of comparison of equivalent reflections using the program SORTAV[19]. Non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were generally fixed in idealised positions with their thermal parameters riding on the values of their parent atoms. Positional disorder was found to be present in two tertiary butyl groups and the ethanol solvent molecule, which was modelled as 50% partial occupancy for each orientation. $C_{61}H_{98}ClO_{3.5}P_2Pd$, triclinic, *P*-1, a=12.4913(1), b=13.0629(1), c=20.7063(3) Å, α=99.150(1), β=99.642(1) γ=110.827(1)°, volume=3024.47(6) Å^3, Z=2, D_c=1.198 Mg/m^3, μ=0.445 mm^{-1}, 57,222 measured, 13,800 unique (R_{int}=0.0476) and 12,220 ($I>2\sigma(I)$) reflections, $R1$ (obs)=0.0345 and $wR2$ (all data)=0.08795

$\rho_{max}/\rho_{min}=0.847/-0.613$ eÅ^{-3}. Supplementary data have been deposited with the Cambridge Crystallographic Data Cente (Deposition number=CCDC270788).

4.2.1. Synthesis of [PdCl{κ^2-*P*,*C*-(OC_6H_3–2,4-^{t}Bu$_2$)(OC_6H_3–2,4-^{t}Bu$_2$)$_2$}$PHCy_2$], 5b. This as prepared using the same method for the synthesis of **5a**, with $PHCy_2$ in place of PCy_3. Complex **5b** was obtained as a colourless solid (0.304 g, 62%). Anal. Calcd for $C_{54}H_{85}O_3P_2PdCl\cdot(0.5\ CH_2Cl_2)$: C, 63.64; H, 8.43. Found: C, 63.61; H, 9.11. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.72 (br m, 2H Cy); 0.96 (br m, 4H, Cy); 1.07 (br s, 9H, ^{t}Bu of orthometallated ring); 1.16 (br m, 4H, Cy); 1.24 (br s, 18H, ^{t}Bu of non-orthometallated rings); 1.32 (br m, 4H, Cy); 1.39 (br s, 9H, ^{t}Bu of orthometallated ring); 1.46 (br m, 4H, Cy); 1.52 (br s, 18H, ^{t}Bu of non-orthometallated rings); 1.65 (br m, 2H, Cy); 1.80 (br m, 2H, Cy); 3.57 (ddt, 1H, $^1J_{PH}=310.5$ Hz, $^3J_{PH}=15.0$ Hz, $^3J_{HH}=7$ Hz P*H*Cy_2); 7.00 (dd, 2H, $^3J_{HH}=8.5$ Hz, $^4J_{HH}=2.4$ Hz, non-orthometallated ring H5); 7.12 (t, 2H, $^3J_{HH}=2.4$ Hz, non-orthometallated ring H6); 7.37 (br m, 2H, non-orthometallated ring H3); 7.39 (d, 1H, $^4J_{HH}=2.2$ Hz, orthometallated ring), 7.42 (d, 1H, $^4J_{HH}=2.2$ Hz, orthometallated ring). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 4.40 (d, $J_{PP}=46.2$ Hz, PCy_3); 134.1 (d, $J_{PP}=46.2$ Hz, $P(OAr)_3$).

4.3. Procedure for cross-coupling of (2-bromoethyl) benzene with phenylboronic acid

A Radleys Carousel tube was loaded with the appropriate amount of desired catalyst, then (2-bromoethyl)benzene (0.68 ml, 5.0 mmol) was added followed by the solvent (10 ml), base (15.0 mmol) and finally phenylboronic acid (7.5 mmol). The mixture was then heated to 110 °C (external temperature) for 18 h, allowed to cool to rt and then aqueous HCl (2 M, 10 ml) was added. The mixture was extracted with dichloromethane and the combined extracts dried ($MgSO_4$). Hexadecane (0.17 M in dichloromethane, 1.00 ml) was added and the product mixture analysed by GC. GC, GC–MS and ^{1}H spectroscopy of product mixtures were consistent with data obtained using commercial samples of styrene and 1,2-diphenylethane (Aldrich).

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