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Phosphine and arsine adducts of *N*-donor palladacycles as catalysts in the Suzuki coupling of aryl bromides

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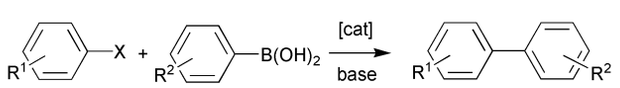
Triarylphosphine and arsine adducts of imine- and amine-based palladacycles have been produced and the crystal structures of three examples have been determined, as has the structure of a parent imine-based palladacycle. The complexes were tested in the Suzuki coupling of an electronically deactivated aryl bromide and the phosphine adducts were found to show much greater activity than the parent palladacycles. Triarylphosphine adducts are preferable to trialkylphosphine adducts as they not only show higher activity but they are also more easily synthesised.

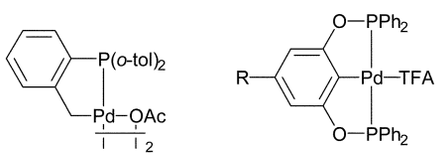
Introduction

The coupling of aryl halides with aryl boronic acids, the Suzuki reaction (Scheme 1), is one of the most powerful and versatile methods for the synthesis of biaryls.[1] There has recently been considerable interest in the development of new, high-activity catalysts that can be used in low loadings in such reactions, and palladacyclic complexes have played a significant role in this regard. The area was initiated by Beller, Herrmann and co-workers, who demonstrated that the palladacyclic complex **1** acts as a good catalyst in the coupling of aryl bromide substrates.[2] We demonstrated that the pincer complexes **2** and the orthopalladated triarylphosphite and phosphinite complexes **3** show good to excellent activity in such couplings,[3] whilst Cole-Hamilton and co-workers showed that the phosphine-based complexes **4** can also be used.[4] Activity is not limited to ortho-metallated phosphorus donor systems. We,[5] and later others,[6] showed that the *N*-donor palladacycle **5a** can also be used in aryl bromide coupling reactions. Of particular note, Milstein and co-workers demonstrated that the orthometallated imine complex **6a** shows excellent activity,[7] while Nájera has shown that the related oxime-containing complexes **7** can even activate deactivated aryl chlorides in the presence of water and tetra-butylammonium bromide.[8] Dupont and Monteiro have shown that orthometallated thioether complexes of the type **8** can also be used.[9] Tricyclohexylphosphine adducts of both imine- and amine-based palladacycles, complexes **9a** and **10a**, show very good activity when aryl chlorides are used as substrates.[10] Very recently we have found that similar adducts formed between complexes of the types **3** and **11** with tricyclohexylphosphine, as well as other di- and tri-alkylphosphines, show amongst the highest activities yet reported in aryl chloride coupling reactions.[11]



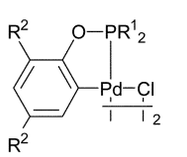
Scheme 1 The Suzuki biaryl coupling reaction.

We have previously investigated the possibility of using silica-supported analogues of the imine-based complex **5a** as recyclable catalysts for the Suzuki reaction.[12] During the course of that study we noticed that addition of a triphenylphosphine ligand to a solid-supported imine-based palladacycle substantially increases the catalytic activity of the complex. We therefore decided to explore further the effect of phosphine ligands on the activity of palladated imine and amine catalysts in the Suzuki coupling of aryl bromides and the results of this study are presented below.

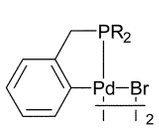


1

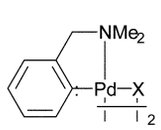
2: R = H, Me



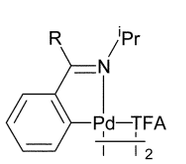
3a: R^1 = OC_6H_3-2,4-$^tBu_2$; R^2 = ^{t}Bu
b: R^1 = Ph; R^2 = H
c: R^1 = Ph; R^2 = ^{t}Bu
d: R^1 = ^{i}Pr; R^2 = ^{t}Bu



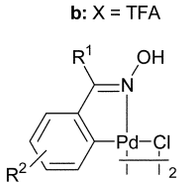
4: R = Ph, ^{t}Bu



5a: X = Cl
b: X = TFA



6a: R = Me
b: R = H



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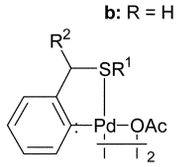
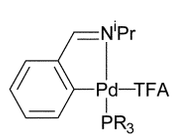
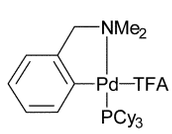


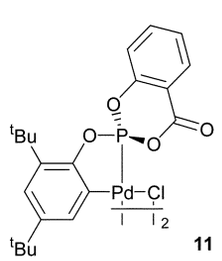
8: R^1 = Me, ^{t}Bu: R^2 = H, Me



9a: R = Cy
b: R = Ph



10a



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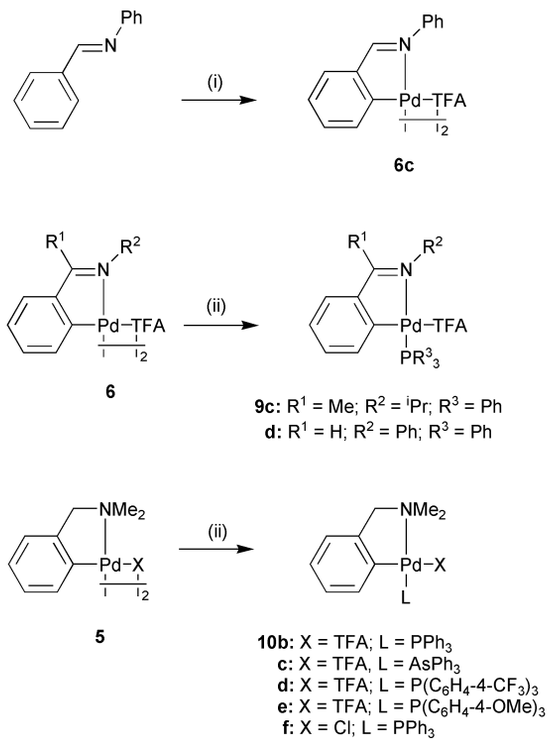
Results and discussion

Synthesis and characterisation of the complexes

The literature methods for the production of **6a** and **b**[12,13] were extended to the synthesis of the analogous complex [{Pd(μ-TFA)(κ²-*N*,*C*-C_6H_4CH=NPh)}$_2$], **6c**, from $Pd(TFA)_2$ and *N*-benzylidene aniline in 57% yield (Scheme 2). The crystal structure of **6c** was determined and the molecule is shown in Fig. 1, while selected data are given in Table 1. The palladium centres adopt approximately square planar coordination geometries, with only one of the two possible isomers, the *trans* isomer, evident. The structure is very similar to those reported previously for the complexes **6a** and **b**,[13,10b] with essentially identical Pd–C, Pd–N, and Pd–O bonds to **6a** and only slightly shorter Pd–O (*trans* to C) compared with **6b**.



Scheme 2 Conditions: (i) $Pd(TFA)_2$, THF, 60 °C, 4 h. (ii) 2.2 PR_3 or $AsPh_3$, CH_2Cl_2, r.t., 20 min.

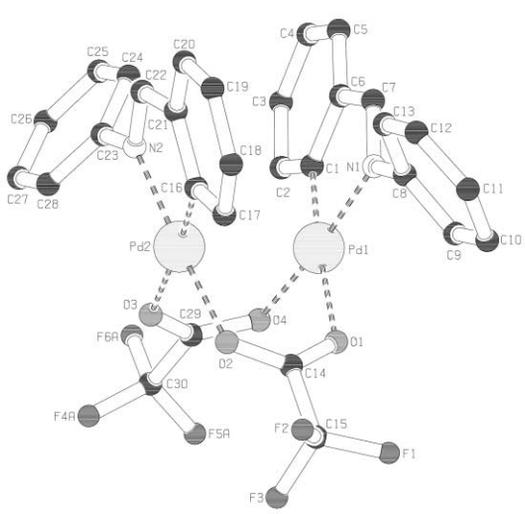


Fig. 1 The molecular structure of [{Pd(μ-TFA)(κ²-*N*,*C*-C_6H_4CH=NPh)}$_2$], **6c**. One of the CF_3 groups exhibits rotational disorder over two sites around C30, one of which is omitted for clarity.

The triphenylphosphine adducts of the complexes **6**, complexes **9c** and **d**, are synthesised in good yields by reaction of the parent dimers with triphenylphosphine in dichloromethane (Scheme 2), according to the method used previously for the synthesis of **9b**.[12] Similarly the phosphine and arsine adducts **10b**–**e** were prepared by reaction of the dimeric complexes **5** with the appropriate ligands in dichloromethane. The ^{31}P NMR spectra of complexes **9c** and **d** show singlets at δ 42.3 and 42.2 ppm, respectively, very similar to that reported for **9b**.[12] The spectra of the complexes **10b**, **d**–**f** show singlets in the range δ 39.9–43.0 ppm. The ^1H NMR spectra of the adducts **10b**–**f** reveal that the proton on the carbon ortho to the palladated carbon always appears at the low field end of the peaks associated with the metallated ring, in the range 6.18–6.44 ppm. This range is at higher field compared with those reported for the analogous complexes with PCy_2(*o*-biphenyl), PCy_3 and P^tBu_3 ligands (δ 6.89, 7.11 and 7.42 ppm, respectively).[10b] The complexes **10b**, **d**–**f** show a doublet in the range δ 4.00–4.10 ppm for the methylene protons of the orthometallated *N*,*N*-dimethylbenzylamine with J_{PH} couplings in the range 1.5 to 2.2 Hz and a doublet in the range δ 2.72–2.88 ppm with J_{PH}s in the range 2.4 to 2.75 Hz corresponding to the *N*-methyl groups. By comparison complex **10c** shows singlets at δ 4.08 and 2.80 ppm, respectively, for these two environments. Further evidence that the observed couplings to the methylene and methyl protons of **10f** are due to phosphorus was obtained by running a ^1H-{^{31}P} NMR spectrum which showed the two environments as singlets. The similarities in the NMR data indicate that the stereochemistries must be essentially identical in all cases. The structures of three of the phosphine adducts, namely complexes **9d**, **10d** and **f**, were determined unequivocally by single crystal X-ray analysis and the molecules are shown in Figs. 2–4 while selected data are given in Table 2. The crystal structure of **10f** shows poor *R*-factors as a result of stacking faults and twinning. In all cases it can be seen that only the isomer in which the phosphorus is *trans* to the *N*-donor is obtained. The Pd–C bond lengths are essentially identical while the Pd–P are very similar. Comparing the imine- and amine-containing complexes **9d** and **10d** it can be seen that the Pd–N bond length of the latter is marginally longer.

Table 1 Selected bond lengths (Å) and angles (°) for the complex [{Pd(μ-TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)}$_2$], **6c**

Pd1–C1	1.948(4)	Pd2–C16	1.956(4)
Pd1–N1	2.030(3)	Pd2–N2	2.021(3)
Pd1–O1	2.175(3)	Pd2–O2	2.055(3)
Pd1–O4	2.049(3)	Pd2–O3	2.165(3)
C1–Pd1–N1	81.19(15)	C16–Pd2–N2	80.89(15)
C1–Pd1–O1	175.26(13)	C16–Pd2–O2	92.08(14)
C1–Pd1–O4	92.04(14)	C16–Pd2–O3	174.95(13)
N1–Pd1–O1	98.24(12)	N2–Pd2–O3	99.12(12)
N1–Pd1–O4	173.01(13)	N2–Pd2–O2	172.97(12)
O1–Pd1–O4	88.65(11)	O2–Pd–O3	87.87(12)

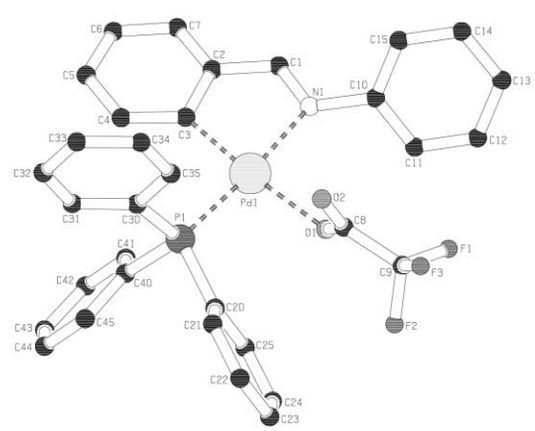


Fig. 2 The molecular structure of [Pd(TFA)(κ²-*N*,*C*-C_6H_4CH=NPh)-(PPh_3)], **9d**.

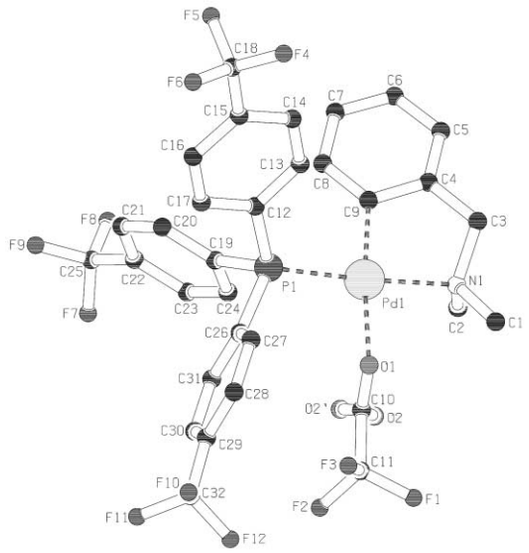


Fig. 3 The molecular structure of [Pd(TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)-{$P(C_6H_4$-4-$CF_3)_3$}], **10d**.

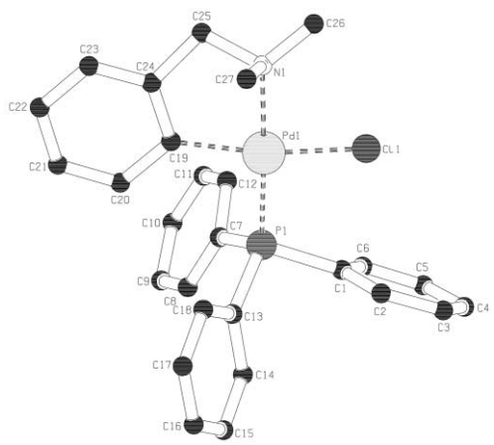


Fig. 4 The molecular structure of [PdCl(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)-(PPh_3)], **10f**.

Table 2 Selected bond lengths (Å) and angles (°) for the complex [Pd(TFA)(κ²-*N*,*C*-C_6H_4CH=NPh)(PPh_3)], **9d** and [Pd(X)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)(PR_3)], **10d**·(0.5MeOH) (X = TFA, R = C_6H_4-4-CF_3) and **10f** (X = Cl, R = Ph)

	9d	**10d**·(0.5MeOH)	**10f**
Pd–C	2.003(3)	1.999(2)	1.972(9)
Pd–P	2.2489(9)	2.2495(5)	2.268(3)
Pd–N	2.122(3)	2.1457(18)	2.106(10)
Pd–X	2.124(2)	2.1417(15)	2.153(8)
C–Pd–N	81.67(12)	82.48(8)	82.9(4)
C–Pd–P	93.41(10)	94.12(7)	94.8(3)
C–Pd–X	172.80(11)	174.64(7)	170.4(4)
P–Pd–N	175.00(8)	176.32(5)	176.8(3)
P–Pd–X	92.85(7)	91.13(5)	94.1(2)
N–Pd–X	92.12(10)	92.25(7)	88.0(4)

Catalytic studies

In order to standardise the catalytic studies, all of the catalyst systems were tested in the same reaction, namely the Suzuki coupling of phenylboronic acid with 4-bromoanisole. This bromide was chosen since catalysts that show very high turnover numbers (TONs) with more easy to couple bromides such as 4-bromoacetophenone often show quite poor activity with this bromide. This is because the *para*-methoxy function electronically deactivates the substrate. Therefore this substrate is a good indicator of optimal catalyst performance. The reaction conditions were not optimised, but rather toluene was used a solvent and K_2CO_3 as base in order to allow comparison with previous studies in the literature. The results from the catalytic studies are summarised in Table 3.

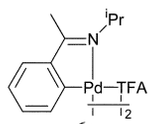
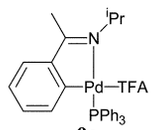
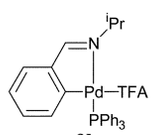
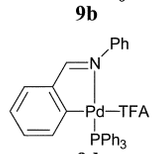
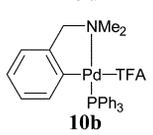
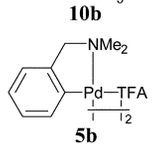
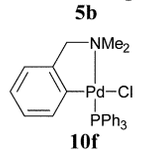
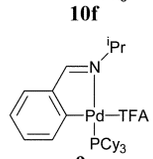
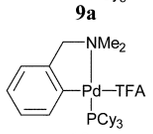
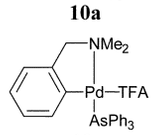
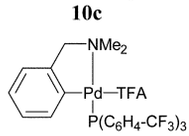
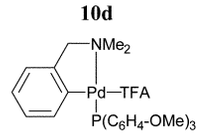
As can be seen (Table 3, entry 1) complex **6a** shows good activity, with the TON obtained being somewhat higher than those recorded previously under similar conditions (102 000–136 000).[7] By contrast, the highest TON reported in this reaction is 8.75 million with **3c** acting as catalyst under essentially identical conditions.[3c] The addition of triphenylphosphine is clearly beneficial, with a jump in TON to 480 000 (entry 2). Interestingly, changing from an orthometallated ketimine to aldimine precursor (compare entries 2 and 3) leads to an even greater enhancement in activity. Similarly when the imine is replaced with an orthometallated *N*,*N*-dimethylbenzylamine ligand then greater activity results (entry 5). This system also has the advantage that the orthometallated ligand is commercially available and inexpensive. Again it is obvious that the triphenylphosphine ligand is necessary to maintain optimum activity, with the parent dimer **5b** showing substantially lower conversion (entry 6). The nature of the anionic 'X' ligand also seems to play an important role in catalyst performance: changing from TFA to Cl appears to be highly deleterious as exemplified by comparing the result obtained with **10b** with that with **10f** (entries 5 and 7). While counter-ion effects are observed when related PCy_3-containing adducts are used in the coupling of aryl chlorides, they are nowhere near as pronounced.[10b]

Since the incorporation of a phosphine ligand leads to substantial enhancement in activity, we next examined the effect on performance of changing this ligand. The results are summarised in entries 8–12. As can be seen the PCy_3 complexes **9a** and **10a** show somewhat poorer activity than their triphenylphosphine counterparts, despite the fact that both of these complexes are excellent pre-catalysts for the coupling of aryl chlorides.[10] One explanation for this is that the rate-determining step in the aryl bromide coupling may not be oxidative addition of the aryl halide, as is the case at least with deactivated aryl chlorides, but rather either nucleophilic attack of the base-activated boronate at the palladium centre,[14] or reductive elimination of the product. If this is the case then far from being advantageous, the presence of good σ-donor but poor π-acid ligands such as PCy_3 would be expected to be deleterious to the rate. Triphenylarsine is a significantly better π-acid than PPh_3 and therefore may be expected to show good activity, however the activity observed is somewhat lower (entry 10).

In order to examine more subtle variations in electronic effects we investigated the use of the palladacyclic adducts **10d** and **e** which contain $P(C_6H_4$-4-$CF_3)_3$ and $P(C_6H_4$-4-$OMe)_3$ ligands, respectively (entries 11 and 12). Interestingly both show poorer activity than the PPh_3-containing analogue **10b** under these conditions, with the more electron-deficient complex **10d** proving the least effective. In order to perform a more accurate comparison we next followed the course of the coupling of 4-bromoanisole with phenylboronic acid catalysed by **10b**, **d** and **e** at 0.1 mol% Pd and 80 °C. The plots of conversion against time obtained are shown in Fig. 5. As can be seen, under these conditions the most-electron rich system, complex **10e**, shows the lowest overall conversion, the PPh_3-containing complex **10b** is slightly better and the most electron-deficient pre-catalyst, complex **10d**, gives by far the highest performance. Interestingly this system seems to have the lowest initial rates of conversion, but the highest lifetime. It is this slightly increased longevity that leads to the greatest conversion under these conditions.

Fig. 6 shows the effect on the reaction of increasing the ratio of the triarylphosphines to Pd in the coupling of 4-bromoanisole with phenylboronic acid. As can be seen there is not a particularly large effect with the optimum ratio of P : Pd varying depending on the phosphine. This is in marked contrast to the application of PCy_3 adducts of amine- or phosphite-

Table 3 Suzuki coupling of 4-bromoanisole with phenylboronic acid[a]

Entry	Catalyst	Conversion (%)	TON (mol product/mol cat)
1	 **6a**	64	320 000
2	 **9c**	48	480 000
3	 **9b**	82	820 000
4	 **9d**	70	700 000
5	 **10b**	73	730 000
6	 **5b**	10	100 000
7	 **10f**	15	150 000
8	 **9a**	40	400 000
9	 **10a**	65	650 000
10	 **10c**	48	480 000
11	 **10d**	35	350 000
12	 **10e**	51	510 000

[a] Conditions: 4-bromoanisole (2.0 mmol), phenylboronic acid (3.0 mmol), K_2CO_3 (4.0 mmol), toluene (20 mL), reflux, 17 h.

based palladacycles in the coupling of 4-chloroanisole with phenylboronic acid.[10b,15] In these cases the addition of greater than 2 : 1 or 1 : 1 of PCy_3 : Pd, respectively, is highly deleterious. This suggests that while a low-coordinate active catalyst is required for chloride coupling reactions, this is less important with aryl bromides.

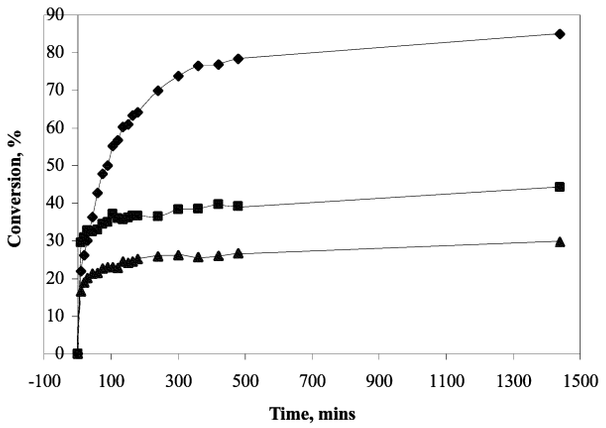


Fig. 5 Plots of conversion against time for the Suzuki coupling of 4-bromoanisole with phenylboronic acid at 80 °C. Catalysts: ◆ = [Pd(TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$){P(C_6H_4-4-CF_3)$_3$}], **10d**; ■ = [Pd(TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)(PPh_3)], **10b**; ▲ = [Pd(TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$){P(C_6H_4-4-OMe)$_3$}], **10e**. Conditions: 4-bromoanisole (10 mmol), phenylboronic acid (15 mmol), K_2CO_3 (20 mmol), toluene (30 mL), hexadecane (internal standard, 0.20 mL), 80 °C.

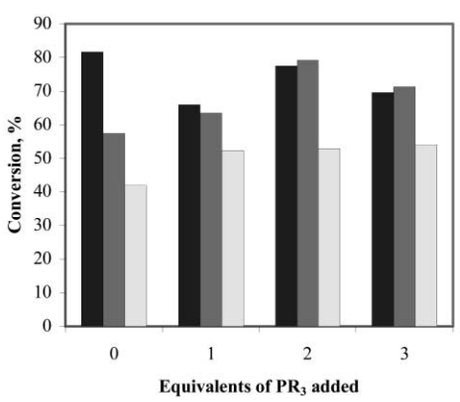


Fig. 6 Effect of adding extra PR_3 to the catalysts [Pd(TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)(PR_3)] in the coupling of 4-bromoanisole with phenylboronic acid, conditions as in Fig. 5, 17 h. R = C_6H_4-4-CF_3, dark; C_6H_4-4-OMe, mid; Ph, light.

Why do the phosphine adducts **9** and **10** show higher catalytic activity than the parent dimeric complexes **5** and **6**? We have previously demonstrated that while complex **9b** shows no reaction with aryl bromides, stoichiometric reaction with excess $PhB(OH)_2$ and base leads to the loss of the orthometallated imine ligand *via* reductive elimination with a phenyl ligand.[12] We postulated that this process probably generates low coordinate, monophosphine species 'Pd(PR_3)'. Such species would presumably be partially stabilised by the reversible coordination of weak ligands such as the eliminated imine or solvent. A similar loss of a 'coupled' ligand is seen in the reaction of complex **10a** with $PhB(OH)_2$ and base under catalytic conditions.[10] Low coordinate monophosphine complexes have been demonstrated to be active in coupling reactions,[16] in particular Beller has recently shown that zerovalent diene monophosphine complexes [Pd(diene)(PR_3)] act as high activity catalysts in the Suzuki coupling of aryl chlorides.[17] Therefore it seems likely that the true role of the orthometallated amine and imine ligands is a sacrificial one which leads to the liberation of low coordinate, high-activity catalysts.

Conclusions

In summary triarylphosphine adducts of amine- and imine-based palladacycles show much greater activity than the parent dimers in the Suzuki coupling of a deactivated aryl bromide. While tricyclohexylphosphine-containing adducts perform well in the Suzuki coupling of aryl chlorides,[10] they show no advantage compared with far more inexpensive triphenylphosphine analogues with bromide substrates. In addition, the much lower air-sensitivity of triphenylphosphine compared with tricyclohexylphosphine makes adducts with this ligand far more attractive catalysts in aryl bromide couplings.

Experimental

General

All reactions and manipulations of air-sensitive materials were carried out under nitrogen either in a glove-box or using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. $Pd(TFA)_2$,[18] *N*-benzylidene aniline[19] and complexes **6a**,[13] **b**,[12] **9a**,[10b] **b**[12] and **10a**,[10b] **f**[20] were prepared according to literature methods. GC analyses were performed on a Varian 3800 GC fitted with a 25m CP Sil 5CB column and data were recorded on a Star workstation.

Syntheses

Synthesis of [{Pd(μ-TFA)(κ²-*N*,*C*-C_6H_4CH=NPh)}$_2$], 6c. A solution of $Pd(TFA)_2$ (1.346 g, 4.05 mmol) and *N*-benzylidene aniline (0.961 g, 5.30 mmol) in THF (80 mL) was warmed at 60 °C for 4 h. The resultant solution was filtered through celite, the solvent removed on a rotary evaporator and the crude product recrystallised from CH_2Cl_2/EtOH. Yellow solid, 0.92 g, 57%.

General method for the synthesis of triarylphosphine/arsine adducts. A solution of the appropriate dimeric complex (0.13–0.66 mmol) and triarylphosphine/arsine (2.2 equivalents) in dichloromethane (20–30 mL) was stirred at room temperature for 20 min. The solution was filtered through celite, ethanol (30 mL) was added and the solution concentrated on a rotary evaporator to induce precipitation. The product was collected by filtration and recrystallised from either CH_2Cl_2/EtOH or CH_2Cl_2/MeOH.

[Pd(TFA)(κ²-*N*,*C*-C_6H_4CMe=N^{i}Pr)(PPh_3)], 9c. Yield 66% (CH_2Cl_2/EtOH). Found: C, 58.05; H, 4.4; N, 2.0. Calc. for $C_{33}H_{25}F_3NO_5PPd$: C, 58.00; H, 4.55; N, 2.18%. NMR ($CDCl_3$): δ_H (300 MHz) 7.78 (m, 6H, PPh_3), 7.39 (m, 9H, PPh_3), 7.23 (d, br, 1H, metallated ring), 6.88 (m, 1H, metallated ring), 6.48 (m, 2H, metallated ring), 4.31 (m, 1H, C*H*(CH_3)$_2$), 2.42 (s, 3H, CH_3), 1.40 (d, br, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$) ppm. δ_P (121 MHz) 42.3 ppm.

[Pd(TFA)(κ²-*N*,*C*-C_6H_4CH=NPh)(PPh_3)], 9d. Yield 90% (CH_2Cl_2/EtOH). Found: C, 59.9; H, 3.6; N, 2.0. Calc. for $C_{33}H_{25}F_3NO_5PPd$: C, 59.88; H, 3.81; N, 2.12%. NMR ($CDCl_3$): δ_H (300 MHz) 8.21 (d, br, 1H, J_{PH} = 6.3 Hz, N=CH), 7.79 (m, 6H), 7.35 (m, 15H), 6.99 (m, 1H, metallated ring), 6.65 (ddd, br, metallated ring), 6.53 (ddd, br, 1H, metallated ring) ppm. δ_P (121 MHz) 42.2 ppm.

[Pd(TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)(PPh_3)], 10b. Yield 56% (CH_2Cl_2/EtOH). Found: C, 56.5; H, 4.2; N, 2.1. Calc. for $C_{29}H_{27}F_3NO_2PPd$: C, 56.55; H, 4.42; N, 2.27%. NMR ($CDCl_3$): δ_H (300 MHz) 7.73 (m, 6H, PPh_3), 7.42 (m, 9H, PPh_3), 7.01 (d, br, 1H, metallated ring), 6.87 (ddd, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.9 Hz, metallated ring), 6.42 (m, 1H, metallated ring), 6.35 (m, 1H, metallated ring), 4.06 (d, br, 2H, CH_2), 2.76 (d, 6H, $^4J_{PH}$ = 2.6 Hz, Me) ppm. δ_P (121 MHz) 42.6 ppm.

[Pd(TFA)(κ²-*N*,*C*-$C_6H_4CH_2NMe_2$)($AsPh_3$)], 10c. Yield 50% (CH_2Cl_2/MeOH). Found: C, 52.6; H, 4.05; N, 1.9. Calc. for $C_{29}H_{27}AsF_3NO_2Pd$: C, 52.78; H, 4.12; N, 2.12%. NMR ($CDCl_3$): δ_H (300 MHz) 7.62 (d, 6H, $^3J_{HH}$ = 6.9 Hz, ortho H of $AsPh_3$), 7.38 (m, 9H, $AsPh_3$), 7.05 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.9 Hz,

Table 4 Crystal data and refinement parameters for complexes **6c**, **9d**, **10d** and **10f**

	6c	9d	10d	10f
Empirical formula	$C_{30}H_{20}F_6N_2O_4Pd_2$	$C_{33}H_{25}F_3NO_2PPd$	$C_{32.50}H_{24}F_{12}NO_{2.50}PPd$	$C_{27.35}H_{27}Cl_{1.30}NO_{0.25}PPd$
Formula weight	799.28	661.91	833.90	557.15
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.6340(2)	9.911(2)	10.08040(10)	9.4871(19)
b/Å	11.3047(3)	29.932(6)	11.74440(10)	13.833(3)
c/Å	14.3380(3)	9.907(2)	14.4457(2)	15.203(4)
α/°	68.0360(15)	90	74.0690(10)	64.56(2)
β/°	85.2730(15)	104.20(3)	83.9980(10)	86.38(3)
γ/°	88.4090(9)	90	83.5620(10)	73.77(3)
Volume/Å^3	1443.27(6)	2849.3(10)	1629.27(3)	1726.2(7)
Z	2	4	2	2
Density (calc)/Mg m^{-3}	1.839	1.543	1.700	1.072
Absorption coefficient/mm^{-1}	1.324	0.759	0.721	0.696
Reflections	17171	14475	33547	8990
Independent reflections	5041	5317	7436	5746
R(int)	0.0904	0.0868	0.1007	0.0753
Final R_1, wR_2 [$F^2 > 2\sigma(F^2)$]	0.0404, 0.1069	0.0429, 0.1154	0.0366, 0.0955	0.1043, 0.2581

metallated ring), 6.87 (ddd, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.9 Hz, metallated ring), 6.44 (m, 2H, metallated ring), 4.08 (s, 2H, CH_2), 2.80 (s, 6H, CH_3) ppm.

[Pd(TFA)(κ^2-*N*,*C*-$C_6H_4CH_2NMe_2$){P(C_6H_4-4-CF_3)$_3$}], 10d. Yield 60% (CH_2Cl_2/MeOH). Found: C, 46.0; H, 2.9; N, 1.5. Calc. for $C_{31}H_{24}F_{12}NO_2PPd$: C, 46.88; H, 2.95; N, 1.71%. NMR ($CDCl_3$): δ_H (300 MHz) 7.84 (dd, 6H, $^3J_{HH}$ = 8.2 Hz, $^3J_{PH}$ = 11.4 Hz, ortho H of PR_3), 7.67 (dd, 6H, $^3J_{HH}$ = 8.2 Hz, $^4J_{PH}$ = 1.5 Hz, meta H of PR_3), 7.05 (dd, 1H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, metallated ring), 6.92 (dd, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.6 Hz, metallated ring), 6.46 (ddd, 1H, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.5 Hz, metallated ring), 6.18 (ddd, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 0.6 Hz, *J* = 6.1 Hz, metallated ring), 4.09 (d, 2H, $^4J_{PH}$ = 2.1 Hz, CH_2), 2.75 (d, 6H, $^4J_{PH}$ = 2.5 Hz, CH_3) ppm. δ_P (121 MHz) 42.4 ppm. δ_F (282 MHz) −75.7 (s, 3F, TFA), −63.8 (s, 9F, $ArCF_3$) ppm.

[Pd(TFA)(κ^2-*N*,*C*-$C_6H_4CH_2NMe_2$){P(C_6H_4-4-OMe)$_3$}], 10e. Yield, 86% (CH_2Cl_2/MeOH). Found: C, 54.8; H, 4.6; N, 1.65. Calc. for $C_{32}H_{33}F_3NO_5PPd$: C, 54.44; H, 4.71; N, 1.98%. NMR ($CDCl_3$): δ_H (300 MHz) 7.61 (dd, 6H, $^3J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 8.9 Hz, ortho H of PR_3), 6.99 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, metallated ring), 6.87 (dd, 7H, $^3J_{HH}$ = 8.9 Hz, $^4J_{PH}$ = 1.7 Hz, meta H of PR_3 and 1 H of metallated ring (obscured)), 6.45 (ddd, br, 1H, $^3J_{HH}$ = 7.5 Hz, metallated ring), 6.37 (ddd, br, 1H, $^3J_{HH}$ = 6.97 Hz, $^4J_{HH}$ = 1.1 Hz, metallated ring), 4.00 (d, 2H, $^2J_{HH}$ = 1.5 Hz, CH_2), 3.80 (s, 9H, OCH_3), 2.72 (d, 6H, $^4J_{PH}$ = 2.4 Hz, CH_3) ppm. δ_P (121 MHz) 40.1 ppm.

Catalysis

General method for the Suzuki coupling of 4-bromoanisole with phenylboronic acid (Table 3). To a mixture of 4-bromoanisole (0.358 g, 2.0 mmol), $PhB(OH)_2$ (0.366 g, 3.0 mmol) and K_2CO_3 (0.524 g, 4.0 mmol) in toluene (19 mL) was added the catalyst as a toluene solution (1.00 mL) made up to the correct concentration by multiple volumetric dilutions of a stock solution. The resultant mixture was then heated at 110 °C for 17 h, cooled and quenched with HCl(aq) (2 M, 40 mL). The organic layer was removed and the aqueous layer was extracted with toluene (3 × 50 mL), the combined organic layers were washed with water, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residue was dissolved in toluene (6 mL), hexadecane (0.068 M in CH_2Cl_2, 1.00 mL, internal standard) was added and the conversion to product determined by GC.

Time-dependent studies on the coupling of phenylboronic acid with 4-bromoanisole (Fig. 5). In a three-necked flask under an atmosphere of nitrogen were placed 4-bromoanisole (1.87 g, 10.0 mmol), phenylboronic acid (1.83 g, 15.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol), hexadecane (0.20 mL, 0.68 mmol, internal standard) and toluene (30 mL). The mixture was heated to 80 °C and then the appropriate catalyst was added as a solution in toluene (1.00 mL), prepared by volumetric dilution. The temperature was maintained at 80 °C for 24 h and aliquots (0.2 mL) were taken at regular intervals. These samples were quenched in aqueous HCl (2 M, 0.5 mL), the mixture extracted with toluene (3 × 1 mL), the combined organic extracts dried over $MgSO_4$ and then the conversion to coupled product was determined by GC.

X-Ray structure determinations

Data were collected by means of combined phi and omega scans on a Bruker-Nonius Kappa CCD area detector situated at the window of a rotating anode (λMo Kα = 0.71073 Å). The structures were solved by direct methods, SHELXS-97 and refined using SHELXL-97.[21] Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded. The data were corrected for absorption effects using SORTAV.[22] Crystal data for the structures are given in Table 4.

CCDC reference numbers 208239–208242.

See http://www.rsc.org/suppdata/dt/b3/b304053d/ for crystallographic data in CIF or other electronic format.

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