Orthopalladated and -platinated Bulky Triarylphosphite Complexes: Synthesis, Reactivity and Application as High-Activity Catalysts for Suzuki and Stille Coupling Reactions

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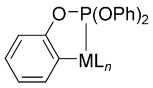
Abstract: Bulky triarylphosphite ligands undergo facile orthometallation reactions with palladium and platinum precursors. The crystal structure of an example of the resultant palladacycles has been determined. The reactivity of some of the metallacycles with HCl, monodentate and bidentate phosphines and sodium diethyldithiocarbamate has been investigated, and the crystal structure of a diethyldithiocarbamate adduct of a palladacycle is presented. The palladacyclic complexes prove to be extremely active catalysts for the Suzuki coupling of aryl bromides with aryl boronic acids. They can also be used as catalysts for the coupling of alkylboronic acids. Meanwhile di- and trialkyl phosphine adducts of one of the palladacycles shows very high activity in the Suzuki coupling of aryl chlorides and can also be used to good effect for the Stille coupling of these substrates. The role of the phosphite ligand in the Suzuki coupling of aryl chlorides seems to be one of increasing catalyst longevity by stabilisation of the Pd^0 resting state.

Keywords: cross-coupling · homogeneous catalysis · metallacycles · palladium · platinum

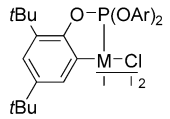
Introduction

The fact that triarylphosphite ligands, $P(OAr)_3$, often undergo facile orthometallation reactions with late transition metals has almost certainly led to the perception that they would not be as useful as the ubiquitous triarylphosphine ligands in catalysis. However, in some cases it appears that the apparently deleterious metallation of a triarylphosphite ligand can actually increase the catalytic activity of a complex. For instance while the complexes **1**–**3** all show reasonable catalytic activity in alkene hydrogenation, no activity was observed with the non-orthometallated analogues $[RuHCl\{P(OPh)_3\}_4]$, $[CoH\{P(OPh)_3\}_4]$ or $[PdCl_2\{P(OPh)_3\}_2]$.[1] Lewis has shown that reversible orthometallation of triarylphosphites at ruthenium can be exploited as a means of catalytically activating the *ortho*-position of phenol to give *ortho*-specific deuteration and alkylation.[2, 3] These orthometallated ruthenium phosphite catalyst systems are also able to catalyse styrene oligomerisation.[2]



1: $ML_n = RuCl\{P(OPh)_3\}_3$
2: $ML_n = Co\{P(OPh)_3\}_3$
3: $ML_n = PdCl\{P(OPh)_3\}$

The use of highly sterically encumbered orthometallated triarylphosphite complexes in catalysis has only fairly recently been addressed. For instance, an orthometallated complex of the bulky triarylphosphite ligand tris(2,4-di-*tert*-butylphenyl)-phosphite, **4a**, proves to be an active catalyst for imine hydrogenation.[4]



Ar = C_6H_3-2,4-tBu_2

5a: M = Pd
6: M = Pt

We have shown that **5a**, an orthopalladated complex of the ligand **4a**, shows high activity in biaryl coupling reactions under both Suzuki and Stille conditions (Scheme 1)[5] and in the Heck arylation of alkenes,[6] while related phosphinite complexes show extremely high activity in the Suzuki coupling of aryl bromides.[7] Surprisingly we also found that the *platinum* complex **6** shows good activity in Suzuki coupling reactions.[8] While complex **5a** shows no activity in the Suzuki coupling of deactivated (electron-rich)

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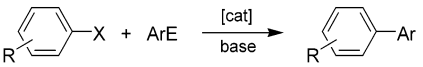
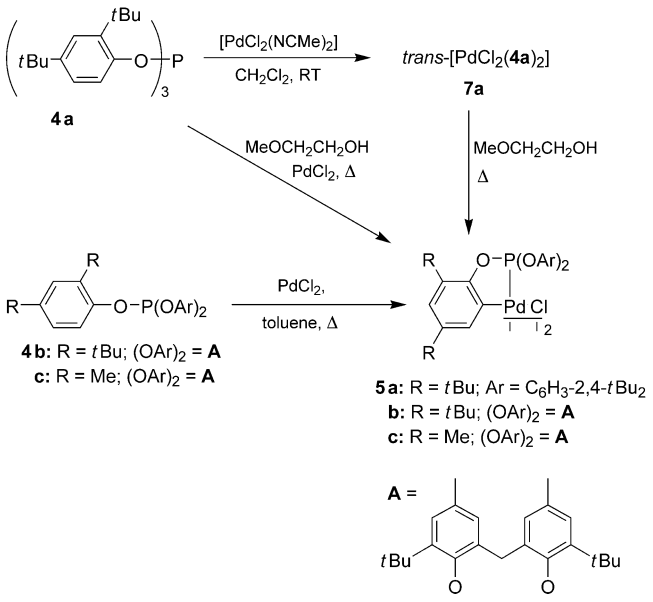


Scheme 1. Suzuki (E = $B(OH)_2$) and Stille (E = SnR_3) biaryl coupling reactions.

aryl chlorides, the addition of tricyclohexylphosphine gives a catalyst that shows one of the highest activities yet reported to date in such reactions.[9] This PCy_3-containing adduct also shows good activity in the Stille coupling of aryl chlorides.[10] We now report in full the synthesis of the bulky orthometallated phosphite complexes of palladium and platinum, an exploration of their reactivity and their application as catalysts in Suzuki and Stille coupling reactions.

Results and Discussion

Synthesis of orthometallated complexes: The reaction of $[PdCl_2(NCMe)_2]$ with two equivalents of the bulky phosphite **4a** gives the complex $[PdCl_2(\mathbf{4a})_2]$, **7a**, exclusively in the *trans* configuration (Scheme 2) as indicated by the presence of only



Scheme 2. Synthesis of orthopalladated complexes.

one Pd–Cl stretch in the IR spectrum at 373 cm^{-1}. By contrast analogous complexes with smaller triarylphosphite ligands tend to give all *cis*, or a mixture of *cis* and *trans* isomers.[11] Presumably the high steric profile of **4a** over-rides the electronic advantages associated with the *cis* arrangement, in which the π-acidic triarylphosphite ligands would be *trans* to the π-basic chlorides. The analogous platinum complex, $[PtCl_2(\mathbf{4a})_2]$, **8**, also exists exclusively as the *trans* isomer,[8] while $[PtCl_2\{P(OPh)_3\}_2]$ is *cis*.[11] This indicates that the stereochemistry of both the palladium and platinum complexes is determined by the bulk of the ligands.

Heating **7a** in 2-methoxyethanol at reflux leads to the formation of the dimeric orthometallated complex **5a** and one equivalent of free ligand **4a** (Scheme 2). A more convenient synthesis of **5a** and the analogous complexes **5b** and **c** was effected by the reaction of one equivalent of the appropriate phosphite with palladium dichloride in 2-methoxyethanol or toluene at reflux temperature. Surprisingly we found that the room-temperature reaction of palladium dichloride with exactly one equivalent of **4a** in a dichloromethane/ethanol mixture also led predominantly to the formation of **5a** after 24 hours. Presumably the facile nature of this reaction is due to the steric bulk of **4a**. Interestingly the non-orthometallated bis-phosphite adduct **7a**, does not give **5a** under the same conditions. This indicates that the rate of formation of **5a** from **7a** at elevated temperature is limited by the dissociation of one equivalent of the ligand **4a** and suggests that orthometallation occurs after phosphite dissociation has given a monophosphite intermediate.

The ^{31}P NMR spectra in $CDCl_3$ at 25 °C show both **5a** and **b** to be a mixtures of the *trans* and *cis* isomers. Both ^{31}P and ^{1}H NMR spectra of complex **5c** show very broad peaks at 25 °C. This is presumably due to the facile interchange of a) the *cis* and *trans* isomers and b) the interconversion of two atropisomers of the eight-membered rings on the phosphite ligands. This gives a total of six possible isomers. Indeed when the ^{31}P NMR spectrum is recorded at −90 °C, eight peaks are observed. Six of these fall in the range $\delta = 114$ to 119 ppm; this is consistent with their corresponding to orthopalladated triarylphosphite ligands. In addition, two substantially broader peaks are observed at $\delta = 129$ and 109 ppm. The latter peak is consistent with an orthometallated phosphite ligand, while the former has a very similar shift to the free phosphite ligand. It has previously been shown that orthopalladated and -platinated triarylphosphite complexes undergo an intramolecular *cis*–*trans* interconversion, although the precise mechanism by which this occurs was not established.[12] The phosphorus NMR data given above is consistent with a mechanism whereby the P donor decoordinates allowing rotation about the Pd–C bond.

The crystal structure of complex **5c** has been determined, and the molecule is shown in Figure 1, while selected data are given in Table 1. As can be seen, the molecule adopts the *trans*-configuration in the solid state, as observed previously with **5a**.[5] The bond lengths about the Pd atoms are very

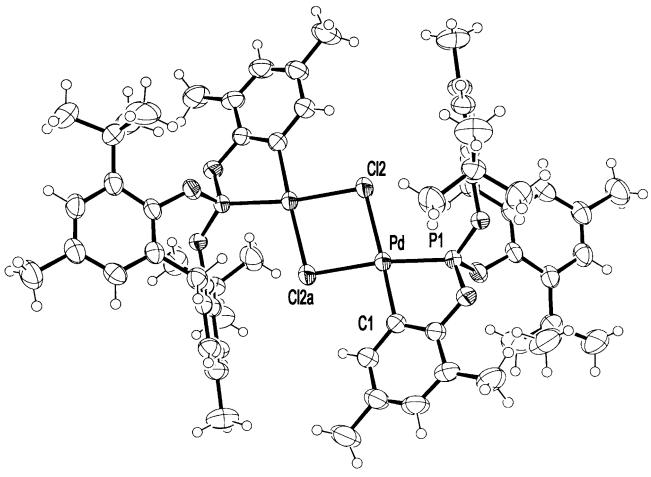


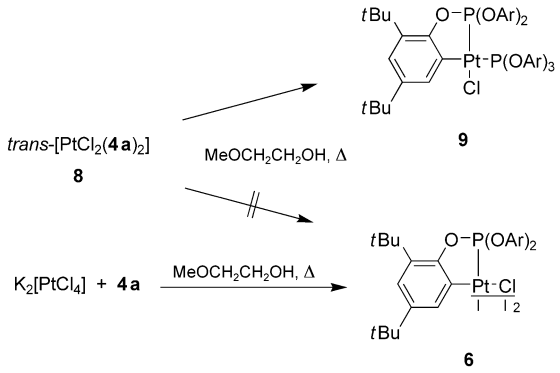
Figure 1. The molecular structure of complex **5c**. Selected bond lengths and angles are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for complex **5c**.

Pd–C1	2.014(3)	Pd–Cl2	2.390(1)
Pd–P1	2.1585(9)	Pd–Cl2a	2.408(1)
C1-Pd-P1	78.06 (10)	C1-Pd-Cl2	94.38(10)
P1-Pd-Cl2a	102.39(4)	Cl2-Pd-Cl2a	85.38(4)
C1-Pd-Cl2a	171.94(11)	P1-Pd-Cl2	172.17(3)

similar to those of complex **5a**, as are those associated with the metallated ring. The P-Pd-Cl(*cis*) angle of **5c** is slightly larger than that in **5a** possibly due to the increased steric profile of the proximate aryloxide residues.

The attempted synthesis of a platinum analogue of complex **5a** by heating complex **8** in 2-methoxyethanol did not generate the dimeric complex **6** but rather gave the monomeric species [PtCl{κ^2-*P,C*-P(OC$_6$H$_2$-*t*Bu$_2$)(OC$_6$H$_3$-*t*Bu$_2$)$_2$}{P(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_3$}], **9** (Scheme 3). The magnitude of the $^2J_{PP}$ coupling in the ^{31}P NMR spectrum, 24 Hz, is indicative of a *cis* arrangement of the P donors.[12] Complex **6** is readily synthesised by heating one equivalent of **4a** with $K_2[PtCl_4]$ in 2-methoxyethanol.[8]



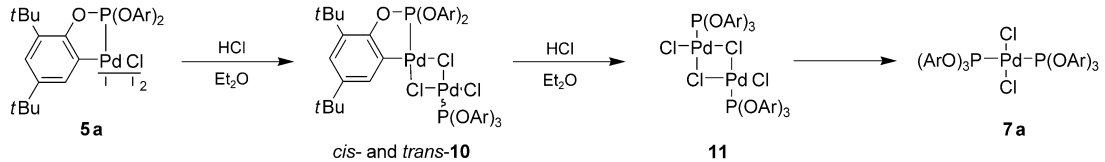
Scheme 3. Synthesis of orthoplatinated complexes. Ar = C$_6$H$_3$-2,4-*t*Bu$_2$.

De-orthometallation reactions: The reaction of **5a** with two equivalents of anhydrous hydrochloric acid in diethyl ether was followed by ^{31}P NMR spectroscopy. After about 3 hours, a mixture was formed of small amounts of the two isomers of **5a** (~8.5% combined, based on percentage of P), the two isomers of what we believe to be the mono-de-metallated dimer **10** (~37.5% combined), a species we assign as the non-orthometallated dimer **11** (~52%) and the non-orthometallated monomeric complex **7a** (~2%) (Scheme 4). The assignment of the structures of the two isomers of the complex **10** is based on the appearance of two peaks of equal intensity at $\delta = 117.5$ and 61 ppm (major isomer) and two further peaks of equal intensity at δ 120.8 and 58.0 ppm (minor isomer, ratio of isomers ~ 4.8:1). In both cases the low-field signals are very similar to those of **5a**; this indicates the presence of an orthopalladated triarylphosphite. The ~60 ppm difference between these signals and the high-field signals is consistent with the latter peaks being due to non-orthometallated triarylphosphites coordinated to Pd^{II} centres. The peaks assigned to the isomers of **10** were observed within 10 minutes of addition. Within 30 minutes a peak appeared at $\delta =$ 55.5 ppm. We assigned this peak to the non-orthometallated dimer **11** on the basis of the similarity of its shift to those of the non-orthometallated phosphites in the two isomers of **10** and related [{PdCl(μ-Cl){P(OAr)$_3$}}$_2$] complexes reported previously,[13, 14] and the fact that it appeared after the formation of **10**. The appearance of only one peak when it could be imagined that two isomers should be present may be due to coincidental overlap of the two signals, or the presence of only one isomer. Either way this observation is in accord with literature precedents.[13, 14] The only other peak observed in the spectrum is a singlet at $\delta = 85.5$, which is consistent with the formation of **7a**.

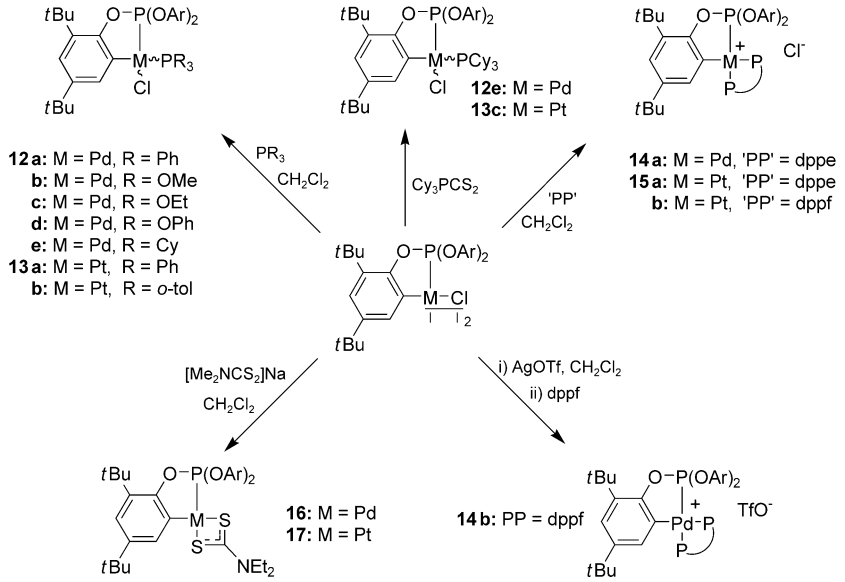
Synthesis of adducts of the orthopalladated and -platinated complexes: The dimeric complexes **5a** and **6** both react smoothly with triphenylphosphine to generate the complexes **12a** and **13a** (Scheme 5). The palladium complex also reacts with P(OMe)$_3$, P(OEt)$_3$ and P(OPh)$_3$ to give the adducts **12b**, **c** and **d**. By contrast complex **6** does not react with P(OMe)$_3$. While complex **6** reacts with tri-*o*-tolylphosphine to give the complex **13b**, the analogous reaction with the Pd analogue **5a** does not proceed. The explanation of this may not be simply due to steric factors since the tricyclohexylphosphine adduct **12e** can be synthesised by simple reaction between **5a** and PCy$_3$, whereas the analogous reaction with complex **6** fails. In this case the complex **12e** is obtained impure with both the dimer **5a** and PCy$_3$ seen in the product mixture. Both **12e** and **13c** can be made cleanly by treatment of the complexes **5a** and **6** respectively with Cy$_3$PCS$_2$, with loss of CS$_2$.

^{31}P NMR spectroscopy reveals that the platinum phosphine adducts are formed as a mixture of the two possible isomers in which the P donors are *cis* or *trans*. The palladium phosphite adducts are obtained purely with the isomer with the P donors *cis*, presumably this is preferred as it places the π-donor ligands *trans* to the π-acidic ligands. The triphenylphosphine complex **12a** is obtained as a mixture of both possible isomers, while the tricyclohexylphosphine adduct **12e** is isolated either solely or predominantly (depending on exact reaction time) as the isomer in which the P donors are *cis*.

Both complexes **5a** and **6** undergo facile reactions with the chelating bisphosphine 1,2-bis(diphenylphosphino)ethane (DPPE) to generate the cationic complexes **14a** and **15a** (Scheme 5). While complex **6** also reacts cleanly with 1,1′-bis(diphenylphosphino)ferrocene (DPPF) to give the complex **15b**, the analogous reaction of **5a** leads to a complex mixture of products. However, treatment of **5a** with silver



Scheme 4. De-orthometallation with HCl. Ar = C$_6$H$_3$-2,4-*t*Bu$_2$.



Scheme 5. Adduct formation. Ar = C_6H_3-2,4-tBu$_2$.

triflate in acetonitrile followed by addition of DPPF gives the complex **14b** in good yield.

The complexes **5a** and **6** also react with anionic chelating ligands. Thus their reactions with sodium diethyldithiocarbamate give the neutral complexes **16** and **17** (Scheme 5). Single crystal structure analysis of **16** was performed, and the molecular structure is shown in Figure 2 while selected data are given in Table 2. The Pd–C and Pd–P bonds are both significantly longer than the equivalent bonds in **5a**[6] and **5c**.

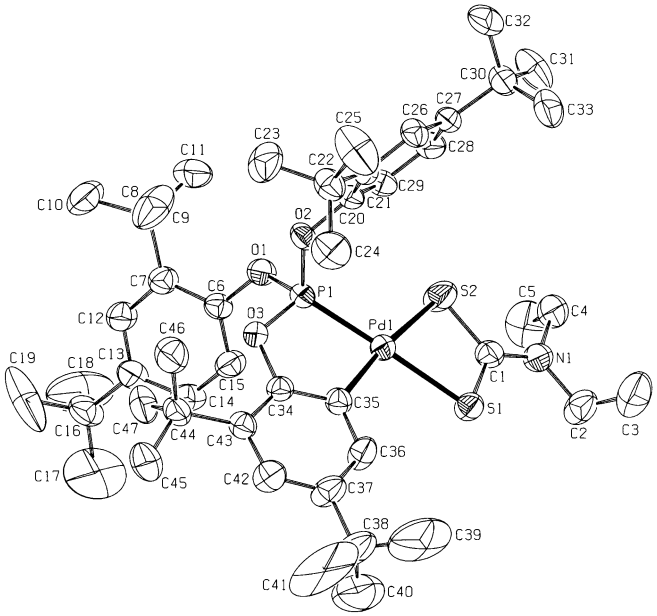


Figure 2. The molecular structure of complex **16**. Selected bond lengths and angles are given in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] for complex **16**.

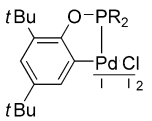
Pd1–P1	2.1820(14)	Pd1–C35	2.047(5)
Pd1–S1	2.3739(14)	Pd1–S2	2.3719(15)
P1-Pd1-C35	79.77(14)	S1-Pd-S2	74.36(5)
P1-Pd1-S2	106.72(5)	C35-Pd1-S1	99.04(14)
C35-Pd1-S2	172.46(15)	P1-Pd1-S1	178.04(5)

Catalysis

a) The Suzuki reaction: The results of a study of the Suzuki coupling of aryl bromides with phenylboronic acid are summarised in Table 3. The conditions for the biaryl coupling reactions were not optimised, rather toluene and potassium carbonate were chosen in order to be able to perform a comparison with results obtained previously with the related orthometallated phosphinite complexes **18**.[7]

The catalysts investigated were complexes **5a**,**b** and the triphenylphosphite analogue [{Pd(μ-Cl){κ^2-*P*,*C*-P(OC$_6$H$_4$)(OPh)$_2$}}$_2$], **5d**,[12] the triphenylphosphine adduct, **12a**, the complexes [PdCl$_2${P(OAr)$_3$}$_2$] (**7a**: Ar = C_6H_3-2,4-tBu$_2$; **7b**: Ar = Ph) and catalysts formed in situ from palladium acetate or palladium bis(dibenzylidine acetone) and appropriate phosphite ligands.

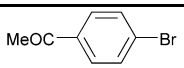
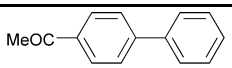
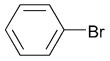
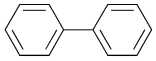
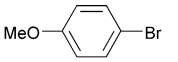
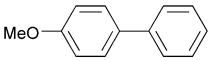
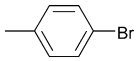
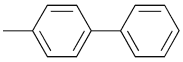
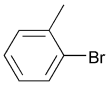
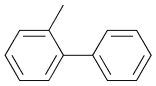
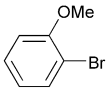
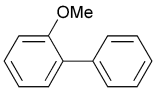
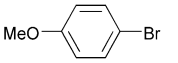
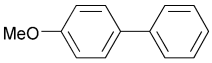
As can be seen, when 4-bromoacetophenone is used as the substrate in the Suzuki coupling reaction with phenylboronic acid (entries 1 and 2), extremely high turn-over numbers (TONs, mol product per mol catalyst) of up to 58.5 million are observed. This is one of the highest TONs yet observed in this reaction, the highest (up to nearly half a billion) being obtained when the closely related phosphinite analogues **18** are used as catalysts.[7] This aryl bromide is electronically activated (electron-deficient) and consequently not an ideal indicator of catalyst performance. Indeed palladium acetate on its own shows TONs of up to 100000 in this reaction.[15] When the nonactivated substrate bromobenzene is employed then the maximum TON observed is reduced to 635000, and with the deactivated bromide 4-bromoanisole the TON is reduced further to a maximum of 300000 (entry 5). By contrast the phosphinite complexes **18** give a TON that is up to an order of magnitude higher.[7] The disparity in activity between the phosphite complex **5a** and the phosphinite complexes **18** indicates that, under limiting conditions, subtle changes to precatalyst structure can have a profound influence on performance. The activity shown, while lower than that of the related phosphinite-containing catalysts **18**, is still very high. This, coupled with the commercial availability and low cost of the ligand **4a**,[16] makes the use of catalyst **5a** highly attractive.



18: R = *i*Pr, Ph

The size of the orthometallated ligand appears to be important; when the triphenylphosphite-containing catalyst **5d** is used in the coupling of 4-bromoanisole then the maximum TON obtained is significantly reduced (entry 6).

Table 3. The Suzuki coupling of aryl bromides with phenylboronic acid.[a]

	Aryl bromide	Palladium source [mol% Pd]	Added ligand [mol%]	Product	Conv. [%][b]	TON [mol product per mol Pd]
1		**5a** (0.00001)	–		100	100000000
2		**5a** (0.000001)	–		58.5	58500000
3		**5a** (0.0001)	–		63.5	63500
4		**5a** (0.001)	–		100	100000
5		**5a** (0.0001)	–		30	300000
6		**5d** (0.0001)	–		7	70000
7		**5b** (0.0001)	–		43	430000
8		$[Pd(dba)_2]$ (0.0001)	$P(OAr)_3$[c] (0.0001)		24	240000
9		$[Pd(dba)_2]$ (0.0001)	$P(OAr)_3$[c] (0.0002)		26	260000
10		**7a** (0.001)	–		64	64000
11		**7b** (0.001)	–		49	49000
12		**5a** (0.01)			100	10000
13		**5a** (0.0001)			82	820000
14		**5a** (0.01)			85	8500
15		**5a** (0.01)			50	5000
16		**5a** (0.001)			34	34000
17		**12a** (0.001)			97	97000
18		**12a** (0.0001)			22	220000
19		**5a** (0.0001)	PCy_3 (0.0001)		33	330000

[a] Reaction conditions: ArBr (10 mmol), $PhB(OH)_2$ (15 mmol), K_2CO_3 (20 mmol), toluene (30 mL), 110 °C, 18 h. [b] Conversion to Suzuki product, based on aryl bromide, determined by GC (hexadecane standard). [c] $Ar = C_6H_3$-2,4-tBu$_2$.

By contrast when the bulky, cyclic-phosphite-containing complex **5b** is used then the TON is improved (entry 7).

The palladium source also seems to be important to optimal catalyst performance. Thus, while catalysts formed in situ from $[Pd(dba)_2]$ and **4a** show similar TONs to the ortho-metallated catalyst **5a**, the preformed non-orthometallated dichloride complex **7a** shows substantially reduced activity (entries 8–10). The triphenylphosphite-containing complex **7b** is also a poorer catalyst than the orthometallated complex **5d**, but here the discrepancy in performance is nowhere near as pronounced.

The phosphine adducts of complex **5a** show similar activity to the parent dimer in the coupling of 4-bromoanisole with phenylboronic acid, with the preformed triphenylphosphine adduct **12a** showing slightly lower, and the catalyst formed in situ from **5a** and PCy_3 slightly better performance (entries 18 and 19).

It is highly likely that the active catalysts are palladium(0) complexes formed in situ. The palladacyclic catalysts may give such zerovalent species either by reductive elimination of the orthometallated ring with an aryl group introduced by the boronic acid,[17] or possibly by thermal decomposition.[18] It is interesting to note here that Pd–dba precursors show similar activity to both **5a** and the catalyst formed in situ from **4a** and palladium acetate. Dibenzylidene acetone can be a highly tenacious ligand for Pd^0, and competes effectively with incoming substrates.[19] Indeed we previously found $[Pd_2(dba)_3]$ to be a poor precursor for PCy_3-containing catalysts for the Suzuki coupling of aryl chlorides.[20] It is possible that here the triarylphosphite ligand **4a** is sufficiently π acidic to compete effectively with DBA coordination, thus displacing it from the coordination sphere and limiting competitive inhibition.

Plots of conversion against time in the coupling of 4-bromoanisole with phenylboronic acid catalysed by **5a** and the catalyst formed from a mixture **5a** and 1 equivalent of PCy_3 are shown in Figure 3. The complex **5a** shows no

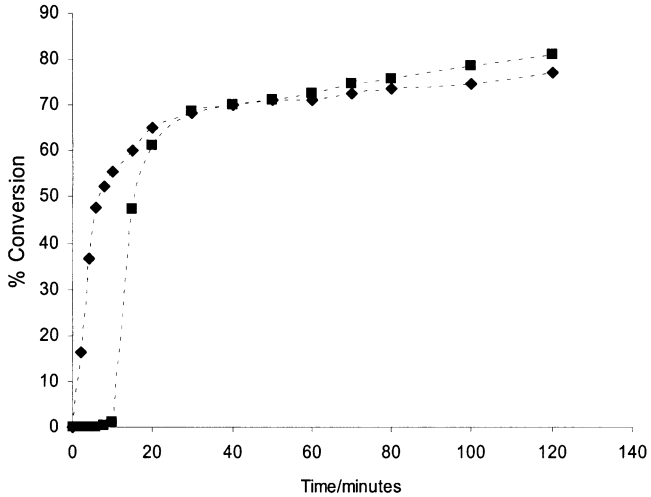


Figure 3. Plots of conversion against time in the Suzuki coupling of 4-bromoanisole with phenylboronic acid catalysed by complex **5a** (◆) or a **5a**/PCy_3 mixture (■). Conditions: 4-BrC_6H_4OMe (10 mmol), $PhB(OH)_2$ (15 mmol), K_2CO_3 (20 mmol), catalyst (0.5 mol% Pd), toluene (30 mL), hexadecane (0.24 mmol, internal standard), 80 °C.

evidence of an induction time whereas one is observed for the catalyst formed from **5a**/PCy_3. The activation of a PCy_3 adduct by a reductive process would be more difficult due to the higher electron density at the palladium centre caused by the presence of the good σ donor phosphine. Conversely the data militate against an oxidative activation process. This supports the proposition that the active catalyst is a zerovalent species and therefore that the catalysis proceeds via a "classical" Pd^0/Pd^{II} pathway rather than a Pd^{II}/Pd^{IV} pathway.[21] After the induction, the rate of the reaction catalysed by **5a**/PCy_3 is very similar to that with just **5a** and the extent of the reaction is also very similar. The data reflect the observations made for these catalyst systems when used under the conditions employed in Table 3.

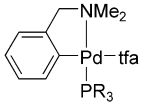
There has recently been increasing interest in the use of alkylboronic acids in coupling reactions.[22] We wondered whether complex **5a** would act as an effective catalyst in such reactions. A solvent/base optimisation study was performed for the coupling of butylboronic acid and 4-bromoanisole by using toluene, DMA, NMP and 1,4-dioxane as solvents and K_2CO_3, Cs_2CO_3, K_3PO_4, KF, K_3PO_4/KF (1:1) and Cy_2NMe as bases. The best results were obtained with K_3PO_4 in 1,4-dioxane, and therefore these conditions were used for the remainder of the study, the results of which are summarised in Table 4.

Catalysts containing the bulky triarylphosphite ligand **4a** do indeed show good activity in the coupling of *n*-butylboronic acid with the deactivated aryl bromide 4-bromoanisole (Table 4, entries 1–5). Similar performances are seen with the preformed catalyst **5a** or those formed in situ from the ligand **4a** and either palladium acetate or $[Pd(dba)_2]$. In order to determine whether the key role played by the ligand is steric or electronic, we examined the use of the bulky, electron-rich ligand tricyclohexylphosphine for comparison (entry 6). As can be seen the PCy_3-containing catalyst shows very similar activity; this implies that it is probably the bulk of the co-ligand that is more important. The much lower cost[16] and greater air-stability of **4a** compared with PCy_3 favour the use of this ligand.

Despite the fact that palladium–phosphite complexes show, at best, limited activity in the coupling of activated (electron-deficient) and nonactivated aryl chlorides,[23] we were surprised to find that catalysts formed in situ from the orthometallated precursor **5a** and one equivalent per palladium centre of tricyclohexylphosphine show extremely high activity in the Suzuki coupling of deactivated aryl chloride substrates.[9] The results from this study are summarised in Table 5.

As can be seen, while excellent results are obtained with the cheaper bases K_3PO_4, KF and K_2CO_3, by far the highest activity is seen with Cs_2CO_3 (compare entries 1–9). The use of the preformed dimer appears to be crucial to maintaining high activity; when a mixture of palladium acetate, tricyclohexylphosphine and ligand **4a** is used, very poor results are obtained (entry 11).

Both PCy_2(*o*-biphenyl) and P*t*Bu_3 have been found to be excellent ligands for catalysts that mediate the Suzuki coupling of aryl chlorides.[15, 24] However catalysts formed in situ from these ligands and complex **5a** did not prove to be as active as **5a**/PCy_3 mixtures. This is in line with our observations that the orthometallated *N*,*N*-dimethylbenzylamine-containing phosphine adducts **19a**,**b** show good activity but not as high as **19c** in the Suzuki coupling of aryl chlorides.[20]



19a: $PR_3 = PCy_2$(*o*-biphenyl)
b: $PR_3 = P$*t*Bu_3
c: $PR_3 = PCy_3$

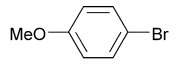
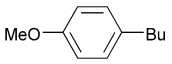
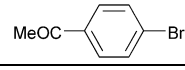
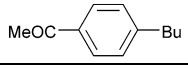
Despite this, the activities obtained with these ligands and **5a** were substantially higher than with palladium acetate under identical conditions, again demonstrating the importance of the palladium source.

The TON observed after 17 hours in the coupling of 4-chloroanisole with phenylboronic acid (34000) is substantially higher than the best previously obtained in this reaction, which vary between 8000 and 12800.[20, 24b] When electronically activated substrates are used (entries 16–22), then TONs of up to an astonishing 1000000 are observed.

While very high activities are seen with **5a**/PCy_3 mixtures, it is important that the ratio of palladium to PCy_3 is maintained at 1:1. Higher loadings of PCy_3 lead to a very rapid diminution in activity (compare entries 8 and 10), until by a ratio of 4:1 no reaction is seen (Figure 4). Presumably this drop-off in activity is due to "over-coordination" of the active catalyst. Such over-coordination has been observed previously with PCy_3 and P*t*Bu_3 complexes in the Suzuki coupling of aryl chlorides.[20]

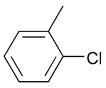
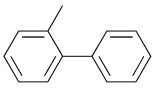
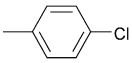
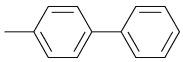
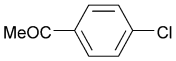
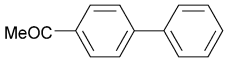
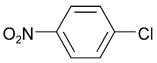
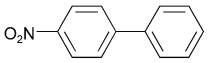
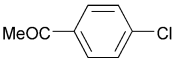
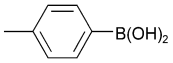
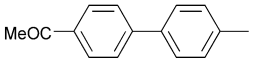
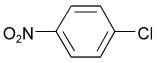
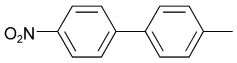
The excellent performance of **5a**/PCy_3 mixtures compared with the orthopalladated dimethylbenzylamine–PCy_3 adduct **19c**, seems not to be dependent on any spectacular increase in the rate of catalysis. Rather it seems that the key factor is

Table 4. The Suzuki coupling of aryl bromides with butylboronic acid.[a]

	R	Palladium source [mol % Pd]	Added ligand [mol %]	Product	Conv. [%][b]	TON [mol product per mol Pd]
1		**5a** (0.5)	–		91	182
2		**5a** (0.1)	–		28	280
3		$[Pd(OAc)_2]$ (0.5)	$P(OAr)_3$[c] (0.5)		87.5	175
4		$[Pd(dba)_2]$ (0.5)	$P(OAr)_3$[c] (0.5)		85	170
5		**5a** (0.5)	$P(OAr)_3$[c] (0.5)		82	164
6		$[Pd(OAc)_2]$ (0.5)	PCy_3 (1.0)		76	152
7		**5a** (0.1)	–		100	1000
8		$[Pd(OAc)_2]$ (0.01)]	$P(OAr)_3$[c] (0.01)		100	10000

[a] Reaction conditions: ArBr (10 mmol), $BuB(OH)_2$ (15 mmol), K_3PO_4 (20 mmol), 1,4-dioxane (30 mL), 100 °C, 18 h. [b] Conversion to Suzuki product, based on aryl bromide, determined by GC (hexadecane standard). [c] $Ar = C_6H_3$-2,4-*t*Bu_2.

Table 5. Suzuki coupling of aryl chloride substrates.[a]

	ArCl	$ArB(OH)_2$	Catalyst [mol %]	Base	Product	Conv. [%][b]	TON [mol prod per mol Pd]
1	MeO–Cl	$B(OH)_2$	**5a** (0.5) + PCy_3 (1.0)	K_3PO_4	MeO–	100	100
2			**5a** (0.005) + PCy_3 (0.01)	K_3PO_4		91	9100
3			**5a** (0.005) + PCy_3 (0.01)	K_2CO_3		82	8200
4			**5a** (0.005) + PCy_3 (0.01)	KF		51	5100
5			**5a** (0.005) + PCy_3 (0.01)	K_3PO_4/KF 1:1		72	7200
6			**5a** (0.005) + PCy_3 (0.01)	Cs_2CO_3		100	10000
7			**5a** (0.0005) + PCy_3 (0.001)	Cs_2CO_3		34	34000
8			**5a** (0.001) + PCy_3 (0.002)	Cs_2CO_3		68	34000
9			**5a** (0.0015) + PCy_3 (0.003)	Cs_2CO_3		99	33000
10			**5a** (0.001) + PCy_3 (0.004)	Cs_2CO_3		37	18500
11			$Pd(OAc)_2$ (0.1) + **4a** (0.1) + PCy_3 (0.1)	Cs_2CO_3		12	120
12			**5a** (0.0005) + PCy_2(*o*-biphenyl) (0.001)	Cs_2CO_3		8	8000
13			**5a** (0.0005) + P*t*Bu_3 (0.001)	Cs_2CO_3		11.5	11500
14			$Pd(OAc)_2$ (0.001) + PCy_2(*o*-biphenyl) (0.002)	Cs_2CO_3		4	4000
15			$Pd(OAc)_2$ (0.001) + P*t*Bu_3 (0.002)	Cs_2CO_3		3	3000
16			**5a** (0.00005) + PCy_3 (0.0001)	Cs_2CO_3		10	100000
17			**5a** (0.0005) + PCy_3 (0.001)	Cs_2CO_3		82	82000
18			**5a** (0.00005) + PCy_3 (0.0001)	Cs_2CO_3		48	480000
19			**5a** (0.00005) + PCy_3 (0.0001)	Cs_2CO_3		88	880000
20			**5a** (0.00005) + PCy_3 (0.0001)	Cs_2CO_3		92	920000
21			**5a** (0.00005) + PCy_3 (0.0001)	Cs_2CO_3		100	1000000
22			**5a** (0.00005) + PCy_3 (0.0001)	Cs_2CO_3		100	1000000

[a] Reaction conditions: ArCl (10 mmol), $ArB(OH)_2$ (15 mmol), base (20 mmol), 1,4-dioxane (30 mL), 100 °C, N_2, 17 h. [b] Conversion to Suzuki product, based on aryl chloride, determined by GC (hexadecane standard).

catalyst longevity. This is illustrated by the plots of conversion against time in the coupling of phenylboronic acid with 4-chloroanisole catalysed by **19c** or **5a**/PCy_3 shown in Figure 5. The increase in catalyst longevity allows for a maximum TON of up to nearly 50000 after 48 hours. The increase in longevity observed for **5a**/PCy_3 compared with **19c** can be explained in terms of stabilisation of the resting state of the active catalyst. If the rate-determining step is oxidative addition, then the resting state will be Pd^0. The π-acidic phosphite ligand would readily coordinate to and stabilise

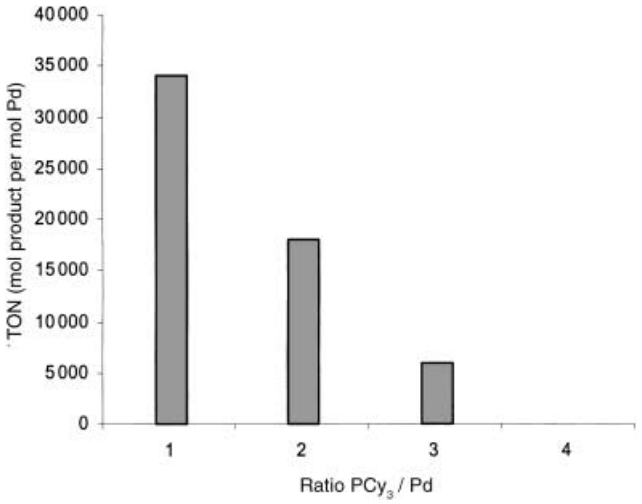


Figure 4. Effect of varying the PCy_3/Pd ratio on the coupling of 4-chloroanisole and phenylboronic acid catalysed by **5a**/PCy_3 mixtures. Conditions are the same as those used in Table 5.

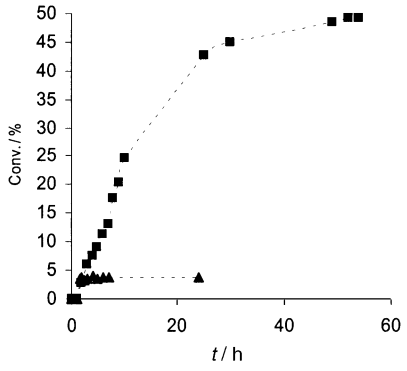


Figure 5. Plots of conversion versus time in the coupling of 4-chloroanisole (10 mmol) with phenylboronic acid (15 mmol) catalysed by **19c** (▲) and 0.5 **5a** + PCy_3 (■) (both at 0.001 mol% Pd). Reaction conditions: Cs_2CO_3 (20 mmol), 1,4-dioxane (27 mL), hexadecane internal standard (0.034 M in 1,4-dioxane, 3.0 mL), 100 °C, N_2. Conversions to product determined by GC.

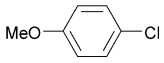
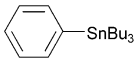
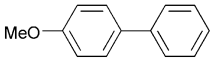
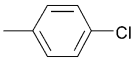
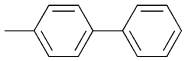
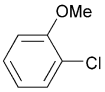
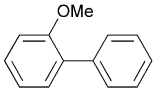
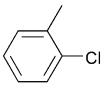
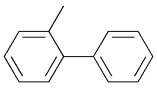
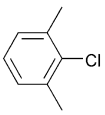
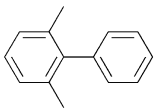
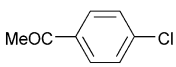
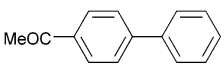
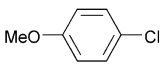
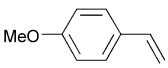
both kinetically and thermodynamically such zerovalent palladium species. Reversible decoordination of the phosphite would generate low-coordinate species able to re-enter the catalytic manifold. This speculation is supported by the observation that increasing the π acidity of the orthometallated co-ligand increases catalyst longevity without unduly affecting rates of catalysis.[25]

b) The Stille coupling of aryl chlorides: Since catalysts formed in situ from complex **5a** and PCy_3 show such excellent activity in the Suzuki coupling of aryl chlorides, we were interested to see if they would be similarly effective in the Stille coupling of aryl chlorides. While many systems show good activity for the Suzuki coupling of aryl chlorides, the Stille coupling of these substrates is comparatively under-investigated. To the best of our knowledge there are in fact only two other catalyst systems that have been reported to couple deactivated aryl chloride substrates. One of these is a Pd–P*t*Bu_3 system developed by Fu and co-workers,[26] while the other is a Pd–imidazolium salt-based system developed by Nolan.[27]

A brief solvent base optimisation was performed for the coupling of 4-chloroanisole with phenyltributyltin, by using 1,4-dioxane or toluene as the solvent and K_2CO_3, K_3PO_4, KF, K_3PO_4/KF (1:1), Cs_2CO_3 or CsF as the base. The best combination was found to be K_3PO_4 in 1,4-dioxane. The results of a range of Stille couplings catalysed by **5a**/PCy_3 or $Pd(OAc)_2$/PCy_3 mixtures are shown in Table 6. As can be seen both catalyst systems show good activity in the coupling of 4-chloroanisole with phenyltributyltin (entries 1–8). The best conversions are seen when the ratio of Pd/PCy_3 is increased from 1:1 to 1:2. This allows quantitative conversion to 4-methoxybiphenyl at 1 mol% Pd within 18 hours. By contrast, the same reaction catalysed by a Pd–P*t*Bu_3 system requires a 3 mol% Pd loading, the use of the far more expensive base CsF and a 48 hour reaction time for comparable conversion.[26] In addition, the PCy_3-containing systems offer the advantages that this ligand is considerably cheaper than P*t*Bu_3 and far easier to handle. The closely related coupling of 4-chloroanisole with $PhSnMe_3$ catalysed by 3 mol% of a Pd–imidazolium salt-based system is reported to give only 35% conversion after 48 hours.[27] Under the optimised conditions a range of electronically activated, nonactivated, deactivated and sterically hindered aryl chlorides can be coupled with phenyltributyltin (entries 8–28). The reaction also works well with vinyltributyltin (entries 29–31).

It is interesting to note that there is very little change in catalyst performance on changing from activated to nonactivated or from small to sterically hindered aryl chloride

Table 6. Stille coupling of aryl chlorides.[a]

	ArCl	$RSnBu_3$	Catalyst	Product	Conversion [%][b]
1			0.5**5a** + PCy_3		56
2					72[c]
3					100[d]
4			0.5**5a** + $2PCy_3$		100
5			$Pd(OAc)_2$ + PCy_3		97
6			$Pd(OAc)_2$ + $2PCy_3$		100
7			0.5**5a** + PCy_3 + **4a**		12.5
8			$Pd(OAc)_2$ + PCy_3 + **4a**		19
9			$Pd(OAc)_2$ + PCy_3		74
10			0.5**5a** + PCy_3		70
11			0.5**5a** + $2PCy_3$		98
12			$Pd(OAc)_2$ + $2PCy_3$		96.5
13			$Pd(OAc)_2$ + PCy_3		72
14			0.5**5a** + PCy_3		65
15			0.5**5a** + $2PCy_3$		91
16			$Pd(OAc)_2$ + $2PCy_3$		94
17			$Pd(OAc)_2$ + PCy_3		71
18			0.5**5a** + PCy_3		74
19			0.5**5a** + $2PCy_3$		97
20			$Pd(OAc)_2$ + $2PCy_3$		93
21			$Pd(OAc)_2$ + PCy_3		78
22			0.5**5a** + PCy_3		76
23			0.5**5a** + $2PCy_3$		95
24			$Pd(OAc)_2$ + $2PCy_3$		92
25			$Pd(OAc)_2$ + PCy_3		76
26			0.5**5a** + PCy_3		71
27			0.5**5a** + $2PCy_3$		100
28			$Pd(OAc)_2$ + $2PCy_3$		100
29			$Pd(OAc)_2$ + PCy_3		56
30			0.5**5a** + PCy_3		32
31			0.5**5a** + $2PCy_3$		70

[a] Conditions: aryl chloride (1.0 mmol), organostannane (1.1 mmol), K_3PO_4 (2.0 mmol), catalyst (1.0 mol% Pd), 1,4-dioxane (5 mL), 100 °C, 18 h. [b] Conversion to Stille-coupled product, based on aryl chloride, determined by GC (hexadecane standard). [c] 24 h. [d] 48 h.

substrates. This strongly suggests that, unlike in the Suzuki reaction, the rate-determining step is not oxidative addition of the aryl chloride substrate, but rather either transmetallation or reductive elimination. It is unlikely that the latter process is rate-limiting as essentially identical intermediates should be involved in this process as in the Suzuki reaction. This would suggest that the rate-determining step is transmetallation. Indeed it has previously been shown that the rate of transmetallation of complexes of the type $[PdCl(Ar)(P_2)]$ with organostannanes is very slow.[28]

In all cases there seems to be no advantage gained from using the orthopalladated precursor **5a** compared with palladium acetate, indeed addition of ligand **4a** to either a mixture of **5a** and PCy_3 or a mixture of palladium acetate and PCy_3 is highly deleterious (entries 7 and 8). This suggests that, unlike in the Suzuki reaction, catalyst longevity and performance are not enhanced by the presence of a π-acidic ligand. This is not surprising if the role of the π-acidic phosphite ligand in the Suzuki reaction is to reversibly coordinate to and stabilise Pd^0 species. Here the rate-determining step appears to be transmetallation, thus the resting state species would be Pd^{II}. π-Acidic phosphite ligands would not be expected to show any particular propensity to stabilise such Pd^{II} resting states.

Conclusion

In summary, the bulky phosphite ligand tris(2,4-di-*tert*-butylphenyl)phosphite readily orthometallates at both palladium and platinum centres to give complexes that offer a rich coordination chemistry. The orthopalladated complex **5a** is an excellent catalyst precursor, not only for the Suzuki coupling of aryl bromides with aryl or alkyl boronic acids, but also, when used in conjunction with PCy_3, for the Suzuki and Stille coupling of aryl chlorides. While in the Stille coupling of aryl chlorides no particular enhancement in catalyst performance is seen compared with palladium acetate, the role played by the phosphite ligand is crucial to the performance in the Suzuki coupling of these substrates. This role appears to be one of enormously increasing the catalyst longevity, rather than increasing the rate of the reaction.

Experimental Section

General: All reactions and manipulations of air-sensitive materials were carried out under nitrogen either in a glove-box or by using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. The complexes **6**,[8] **7b**,[11] **8**[8] and $[Pd(dba)_2]$[29] were prepared according to literature methods. GC analyses were performed on a Varian 3800 GC fitted with a 25 m CP Sil 5CB column, and data were recorded on a Star workstation.

P{(OC$_6$H$_2$-2-*t*Bu-4-Me-6-)$_2$CH$_2$}(OC$_6$H$_3$-2,4-*t*Bu$_2$) (4b): Triethylamine (1.27 mL, 9.16 mmol) was added to a mixture of 2,2′-methylenebis(4-methyl-6-*tert*-butylphenyl)chlorophosphite (2.00 g, 4.58 mmol), 2,4-di-*tert*-butylphenol (0.945 g, 4.58 mmol) in THF (30 mL). The mixture was then heated at reflux for 18 hours, allowed to cool and filtered to remove precipitated triethylamine hydrochloride. Removal of the volatiles in vacuo and recrystallisation from hexane gave **4b** as a white solid (1.95 g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.59$ (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HP} = 2.7$ Hz, 1H; H6), 7.42 (d, $^4J_{HH} = 2.5$ Hz, 1H; H3), 7.16 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2.5$ Hz, 1H; H5), 7.15 (d, $^4J_{HH} = 2.2$ Hz, 2H; H5′), 7.05 (d, $^4J_{HH} = 2.2$ Hz, 2H; H3′), 4.50 (dd, $^2J_{HH} = 12.8$ Hz, $^5J_{HP} = 2.9$ Hz, 1H; CH_2), 3.48 (d, $^2J_{HH} = 12.8$ Hz, 1H; CH_2), 2.32 (s, 6H; CH_3,), 1.53 (s, 9H; *t*Bu), 1.34 (s, 9H; *t*Bu), 1.32 (s, 18H; *t*Bu); $\delta = 132.9$ ppm; elemental analysis calcd (%) for $C_{37}H_{51}O_3P$ (547.8): C 77.3, H 8.9; found: C 76.8, H 9.4.

P{(OC$_6$H$_2$-2-*t*Bu-4-Me-6-)$_2$CH$_2$}(OC$_6$H$_3$-2,4-Me$_2$) (4c): Triethylamine (0.70 mL, 5.00 mmol) was added to a mixture of 2,2′-methylenebis(4-methyl-6-*tert*-butylphenyl)chlorophosphite (2.00 g, 4.58 mmol) and 2,4-dimethylphenol (0.560 g, 4.58 mmol) in toluene (100 mL). The mixture was then heated at reflux for 18 hours, allowed to cool and filtered to remove precipitated triethylamine hydrochloride. Removal of the volatiles in vacuo and recrystallisation from pentane gave **4c** as a white solid (1.75 g, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.49$ (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HP} = 1.1$ Hz, 1H; H6), 7.13 (d, $^4J_{HH} = 2.1$ Hz, 2H; H5′), 7.06 (d, $^4J_{HH} = 2.5$ Hz, 1H; H3), 7.04 (d, $^4J_{HH} = 2.1$ Hz, 2H; H3′), 6.97 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2.5$ Hz, 1H; H5), 4.40 (dd, $^2J_{HH} = 13.6$ Hz, $^5J_{HP} = 2.8$ Hz, 1H; CH_2), 3.50 (d, $^2J_{HH} = 13.6$ Hz, 1H; CH_2), 2.38 (s, 3H; *ortho*-CH_3), 2.31 (s, 9H; *para*-CH_3), 1.34 (s, 18H; *t*Bu); ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): $\delta = 134$ ppm; elemental analysis calcd (%) for $C_{31}H_{39}O_3P$ (490.6): C 75.89, H 8.01; found: C 76.0, H 8.4.

***trans*-[PdCl$_2${P(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_3$}$_2$] (7a)**: A solution of $[PdCl_2(NCMe)_2]$ (1.00 g, 3.85 mmol) and ligand **4a** (4.99 g, 7.70 mmol) in dichloromethane (10 mL) was stirred for 30 min. Methanol (10 mL) was added to precipitate the product, which was collected by filtration and recrystallised from CH_2Cl_2/MeOH to give **7a** as a pale yellow solid (5.20 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60$ (d, $^3J_{HH} = 8.6$ Hz, 6H; H6), 7.36 (d, $^4J_{HH} = 2.4$ Hz, 6H; H3), 6.96 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.5$ Hz, 6H; H5), 1.41 (s, 54H; *t*Bu), 1.28 (s, 54H; *t*Bu) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): $\delta = 84.5$ ppm; IR (KBr): $\tilde{\nu} = 373$ (Pd–Cl) cm^{-1}; elemental analysis calcd (%) for $C_{84}H_{126}Cl_2O_6P_2Pd$ (1471.2): C 68.58, H 8.63; found: C 68.9, H 8.5.

[{Pd(μ-Cl){κ^2-*P*,*C*-P(OC$_6$H$_2$-2,4-*t*Bu$_2$)(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_2$}}$_2$] (5a): A mixture of palladium dichloride (5.00 g, 28.20 mmol) and ligand **4a** (18.24 g, 28.20 mmol) was heated at reflux in 2-methoxyethanol (100 mL) for 2 h. The reaction was allowed to cool and the crude product was collected by filtration and recrystallised from CH_2Cl_2/EtOH to give **5a** as a pale yellow solid (21.21 g, 95.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (*major isomer*) = 7.56 (d, $^3J_{HH} = 8.5$ Hz, 4H; H6 free ring), 7.52 (d, $^4J_{HH} = 2.5$ Hz, 2H; H5, orthometallated ring), 7.37 (d, $^4J_{HH} = 2.4$ Hz, 4H; H3 free ring), 7.08 (br s, 2H; H3, orthometallated ring), 6.94 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2.5$ Hz, 4H; H5 free ring), 1.41 (s, 36H; *t*Bu free ring), 1.35 (s, 18H; *t*Bu orthometallated ring), 1.24 (s, 18H; *t*Bu orthometallated ring), 1.23 (s, 36H; *t*Bu free ring); δ (*minor isomer*) = 7.69 (d, $J = 7$ Hz, 2H; H5, orthometallated ring), 7.40 (br d, $^3J_{HH} = 8.5$ Hz, 4H; H6 free ring), 7.35 (br m, 4H; H3 free ring), 7.12 (br s, 2H; H3, orthometallated ring), 7.04 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2.5$ Hz, 4H; H5 free ring), 1.34 (s, 18H; *t*Bu orthometallated ring), 1.26 (36H; *t*Bu free ring), 1.21 (s, 36H; *t*Bu free ring), 1.17 (s, 18H; *t*Bu orthometallated ring); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): $\delta = 119.2$ (s, major isomer), 118.7 (s, minor isomer); elemental analysis calcd (%) for $C_{84}H_{124}Cl_2O_6P_2Pd_2$ (1575.6): C 64.03, H 7.93; found: C 64.3, H 8.1.

[{Pd(μ-Cl){κ^2-*P*,*C*-P{(OC$_6$H$_2$-2,4-*t*Bu$_2$){(OC$_6$H$_2$-2-*t*Bu-4-Me-6-)$_2$CH$_2$}}}$_2$] (5b): A mixture of $PdCl_2$ (0.150 g, 0.85 mmol) and ligand **4b** (0.500 g, 0.91 mmol) in toluene (15 mL) was heated at reflux for 18 h. The solution was allowed to cool to room temperature, and then the solvent was removed in vacuo. The crude product was dissolved in dichloromethane (25 mL), the solution was filtered through celite, then concentrated under reduced pressure, and methanol was added to precipitate the product as a yellow powder (0.325 g, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.45$ (br m, 1H), 7.05 (br m, 1H), 6.91 (br m, 4H), 4.47 (br m, 1H; CH_2), 3.65 (br m, 1H; CH_2), 2.14 (s, 6H; CH_3), 1.20–0.91 (several signals, br, 36H; *t*Bu); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): $\delta = 119$ (br s, major isomer), 117 (s, minor isomer); elemental analysis calcd (%) for $C_{74}H_{100}Cl_2O_6P_2Pd_2$ (1431.3): C 62.10, H 7.04; found: C 61.9, H 7.1.

[{Pd(μ-Cl){κ^2-*P*,*C*-P{(OC$_6$H$_2$-2,4-Me$_2$){(OC$_6$H$_2$-2-*t*Bu-4-Me-6-)$_2$CH$_2$}}}$_2$] (5c): The same method was used as for the preparation of complex **5b**, by using ligand **4c**, to give the product as a yellow powder (0.232 g, 43%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.25$ (br m, 1H), 7.00 (br m, 4H), 6.74 (br m, 1H), 4.61 (br m, 1H; CH_2), 3.62 (br m, 1H; CH_2), 2.24 (s, 9H; CH_3), 2.16 (s, 3H; *ortho*-CH_3), 1.31 (s, 18H; *t*Bu); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): $\delta = 117.0$ (s, major isomer), 115.0 (s, minor isomer); elemental

analysis calcd (%) for $C_{62}H_{76}Cl_2O_6P_2Pd_2$ (1263.0): C 58.96, H 6.07; found: C 58.6, H 6.1.

[PtCl{κ^2-*P,C*-P(OC$_6$H$_2$-2,4-*t*Bu$_2$)(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_2$}{P(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_3$}] (9): [PtCl$_2${P(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_3$}$_2$] (0.05 g, 0.003 mmol) in 2-methoxyethanol (5 mL) was heated at reflux for 1 hour, the solvent was removed in vacuo, and the colourless residue was recrystallised from dichloromethane/ethanol to give the above compound (0.049 g, 98%). Despite repeated recrystallisations, a microanalytically pure product could not be obtained. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.41$ (br d, 1H; orthometallated ring), 8.02 (br d, 2H; free rings of orthometallated phosphite), 7.28 (br m, 6H; non-orthometallated phosphite), 7.19 (br d, 3H; non-orthometallated phosphite), 7.07 (br d, 1H; orthometallated ring), 6.89 (br d, 2H; free rings of orthometallated phosphite), 6.42 (br d, 2H; free rings of orthometallated phosphite), 1.37 (s, 9H; *t*Bu), 1.33 (s, 18H; *t*Bu), 1.25 (s, 45H; *t*Bu), 1.16 (s, 27H; *t*Bu), 0.92 (s, 9H; *t*Bu) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): $\delta =$ 111.7 (app br s, with sat., non-orthometallated phosphite, $^1J_{PtP} = 3130$ Hz), 100.8 (d, with sat., orthometallated phosphite, $^2J_{PP} = 24$ Hz, $^1J_{PtP} =$ 6330 Hz); IR (CsI): $\tilde{\nu} = 355$ (Pt–Cl) cm^{-1}.

Reaction of complex 7a with HCl: An ethereal solution of anhydrous HCl (1M, 1.0 mL) was added to a solution of complex **7a** (0.080 g, 0.051 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube, and the ^{31}P NMR spectrum was recorded over various time intervals.

General method for the synthesis of the monophosphine and -phosphite adducts: A solution of the appropriate complex (either **5a** or **6**) (0.10–0.13 mmol) and ligand (2.0 equiv) in dichloromethane (5 mL) was stirred at room temperature for 30 minutes. Addition of ethanol (10–15 mL) led to the precipitation of product, which was collected by filtration, washed with ethanol (3×10 mL) and subsequently recrystallised from CH_2Cl_2/EtOH.

Data for complex 12a: Yield: 0.097 g (92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ (minor isomer, P donors *cis*) = 8.48 (ddd, $^4J_{HH} = 2.6$ Hz, $^4J_{HP(cis)} = 2.6$ Hz, $^4J_{HP(trans)} = 6.5$ Hz, 1H; H5, metallated ring), 7.55 (br m, 2H; H3, non-metallated ring), 7.41 (br m, 15H; phenyl), 7.52 (br m, 1H), 7.21 (d, 1H; $J_{HH} = 2.5$ Hz), 7.00 (dd, $^4J_{HH} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, nonmetallated ring), 6.93 (br s, 1H), 1.39 (s, 9H; *t*Bu), 1.31 (s, 18H; *t*Bu), 1.30 (s, 18H; *t*Bu), 0.99 (s, 9H; *t*Bu), (major isomer, P donors *trans*) = 7.7 (m, 2H), 7.35 (m, 15H; phenyl), 7.26 (br dd, $^4J_{HP} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, non-metallated ring), 7.09 (dd, $^4J_{HH} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz 2H; H5, non-orthometallated ring), 6.98 (dd, $^4J_{HP} = 2$ Hz, $^4J_{HH} = 2$ Hz, 2H; H3, non-metallated ring), 1.52 (s, 18H; *t*Bu), 1.33 (s, 18H; *t*Bu), 1.18 (s, 9H; *t*Bu), 0.70 (s, 9H; *t*Bu) ppm (isomer ratio 2.4:1); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 18.7$ (d, $^2J_{PP} = 40.7$ Hz, phosphine, minor isomer), 31.4 (d, $^4J_{PP} = 604$ Hz, phosphine, major isomer); 127.9 (d, $^2J_{PP} = 604$ Hz, phosphite, major isomer) 132.1 (d, $^2J_{PP} = 40.7$ Hz, phosphite, minor isomer) ppm; elemental analysis calcd (%) for $C_{60}H_{77}ClO_3P_2Pd$ (1050.1): C 68.6, H 7.39; found: C 69.1, H 7.41.

Data for complex 12b: Yield: 0.056 g (62%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.32$ (ddd, $^4J_{HH} = 2.2$ Hz, $^4J_{HP(cis)} = 5.6$ Hz, $^4J_{HP(trans)} = 12.7$ Hz, 1H; H5, orthometallated ring), 7.46 (dd, $^4J_{HP} = 2.2$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H6, non-orthometallated ring), 7.41 (dd, $^5J_{HP} = 1.4$ Hz, $^4J_{HH} = 2.3$ Hz, 2H; H3, non-orthometallated ring), 7.13 (app t (dd), $^5J_{HP} = 2.5$ Hz, $^4J_{HH} = 2.2$ Hz, 1H; H3, orthometallated ring), 7.08 (dd, $^4J_{HH} = 2.2$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, non-orthometallated ring), 3.49 (d, 9H; $^3J_{HP} = 12.2$ Hz, OCH_3); 1.51 (s, 18H; *t*Bu), 1.39 (s, 9H; *t*Bu), 1.28 (s, 18H; *t*Bu), 1.08 ppm (s, 9H; *t*Bu); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 128.8$ (d, $J_{PP} = 52.6$ Hz), 130.1 (d, $J_{PP} =$ 52.6 Hz) ppm; elemental analysis calcd (%) for $C_{45}H_{71}ClO_6P_2Pd$ (911.9): C 59.27, H 7.85; found: C 59.8, H 7.5.

Data for complex 12c: Yield: 0.039 g (41%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.32$ (ddd, $^4J_{HH} = 2.3$ Hz, $^4J_{HP(cis)} = 5.5$ Hz, $^4J_{HP(trans)} = 12.6$ Hz, 1H; H5, orthometallated ring), 7.50 (dd, $^4J_{HP} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H6, non-orthometallated ring), 7.38 (dd, $^5J_{HP} = 1.3$ Hz, $^4J_{HH} = 2.5$ Hz, 2H; H3, non-orthometallated ring), 7.09 (app t (dd), $^5J_{HP} = 2.5$ Hz, $^4J_{HH} = 2.3$ Hz, 1H; H3, orthometallated ring), 7.05 (dd, $^4J_{HH} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, non-orthometallated ring), 3.94 (dq, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 8.1$ Hz, 6H; CH_2CH_3); 1.51 (s, 18H; *t*Bu), 1.35 (s, 9H; *t*Bu), 1.24 (s, 18H; *t*Bu), 1.09 (t, 9H; $^3J_{HH} = 7.1$ Hz, CH_2CH_3), 1.01 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 123.4$ (br d, $^2J_{PP} = 50$ Hz); 130.5 (br d, $^2J_{PP} =$ 50 Hz) ppm; elemental analysis calcd (%) for $C_{48}H_{77}ClO_6P_2Pd$ (954.0): C 60.43, H 8.14; found: C 60.3, H 8.1.

Data for complex 12d: Yield: 0.045 g (41%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.13$ (ddd, $^4J_{HH} = 2.2$ Hz, $^5J_{HP(cis)} = 5.5$ Hz, $^5J_{HP(trans)} = 12.6$ Hz, 1H; 7.41 (br s, 2H), 7.18 (m, 2H), 7.10 (br app t (dd), $^5J_{HP} = 2.2$ Hz, $^4J_{HH} = 2.2$ Hz, 2H), 7.06 (m, 9H), 6.98 (m, 6H) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta =$ 109.9 (d, $^2J_{PP} = 51.8$ Hz, $P(OPh)_3$); 129.1 (d, $^2J_{PP} = 51.8$ Hz, orthometallated phosphite) ppm; elemental analysis calcd (%) for $C_{60}H_{77}ClO_6P_2Pd$ (1098.1): C 55.30, H 7.44; found: C 55.0, H 7.4.

Data for complex 13a: Yield: 0.091 g (80%); ^{1}H NMR (300 MHz, $CDCl_3$): two isomers in a 3:1 ratio, some signals obscured; $\delta = 8.47$ (ddd with sat., $^4J_{HH} = 2.0$ Hz, $^4J_{HP(cis)} = 2.0$ Hz, $^4J_{HP(trans)} = 6.3$ Hz, $^3J_{HPt} = 42$ Hz, 1H; H5, metallated ring, minor isomer), 8.16 (dd, $^4J_{HP} = 2.5$ Hz, $^3J_{HH} = 8.6$ Hz, 2H; H6, nonmetallated ring, minor isomer), 7.68 (m, 24H; Ph), 7.63 (dd, $^4J_{HP} =$ 1.7 Hz, $^3J_{HH} = 8.5$ Hz, 3×2H; H6, nonmetallated ring, major isomer), 7.53 (m, 6H), 7.37 (m, 36H; Ph), 7.23 (m, 4H), 7.09 (dd, $^4J_{HH} = 2.5$ Hz, $^3J_{HH} =$ 8.5 Hz, 3×2H; H5, nonmetallated ring, major isomer), 7.00 (dd, $^4J_{HH} =$ 2.5 Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, nonmetallated ring, minor isomer), 6.94 (m, 3H), 6.89 (m, 2H; H3, nonmetallated ring, minor isomer), 1.53 (s, 18H; *t*Bu, major isomer), 1.38 (s, 9H; *t*Bu, minor isomer), 1.31 (s, 18H; *t*Bu, major isomer), 1.29 (s, 18H; *t*Bu, minor isomer), 1.27 (s, 18H; *t*Bu, minor isomer), 1.19 (s, 9H; *t*Bu, major isomer), 0.98 (s, 9H; *t*Bu, minor isomer), 0.68 (s, 9H; *t*Bu, major isomer) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta =$ 23.6 (d with sat., $J_{PtP} = 1807$ Hz, $J_{PP} = 20.4$ Hz, phosphine), 36.1 (d with sat., $J_{PtP} = 2917$ Hz, $J_{PP} = 634.1$ Hz, phosphine), 99.5 (d with sat., $J_{PtP} = 6354$ Hz, $J_{PP} = 20.4$ Hz, phosphite) 118.8 (d with sat., $J_{PtP} = 5041$ Hz, $J_{PP} = 634.1$ Hz, phosphite) ppm; elemental analysis calcd (%) for $C_{60}H_{77}ClO_3P_2Pt$ (1138.7): C 63.3, H 6.82; found: C 62.9, H 7.0.

Data for complex 13b: Yield: 0.070 g (59%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.74$ (dd, $^4J_{HP(cis)} = 7.4$ Hz, $^4J_{HP(trans)} = 17$ Hz, 1H; H5, metallated ring), 7.78 (br dd, $^4J_{HP} = 1.4$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H6, nonmetallated ring), 7.55 (m, 1H), 7.40 (m, 4H), 7.20 (m, 4H), 7.06 (m, 4H), 6.97 (m, 4H), 2.20 (s, 9H; CH_3), 1.55 (s, 18H; *t*Bu), 1.32 (s, 9H; CH_3), 1.28 (s, 18H; *t*Bu), 1.15 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 30.3$ (d with sat., $^1J_{PtP} =$ 2860 Hz, $^2J_{PP} = 619$ Hz, phosphine), 117.0 (d with sat., $^1J_{PtP} = 5240$ Hz, $^2J_{PP} = 619$ Hz, phosphite) ppm; elemental analysis calcd (%)for $C_{63}H_{83}ClO_3P_2Pt$ (1180.8): C 64.08, H 7.08; found: C 63.8, H 7.0.

Synthesis of [PdCl{κ^2-*P,C*-P(OC$_6$H$_2$-2,4-*t*Bu$_2$)(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_2$}(PCy$_3$)] (12e) by using Cy$_3$PCS$_2$: A mixture of complex **12** (0.20 g, 0.13 mmol) and Cy_3PCS_2 (0.09 g, 0.25 mmol) in toluene (60 mL) was heated at reflux for 2 hours, after which time the solution was concentrated under reduced pressure and EtOH was added to induce precipitation of the product, which was collected by filtration and then recrystallised from CH_2Cl_2/EtOH (0.18 g, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): Cy signals partly obscured by *t*Bu; $\delta = 8.56$ (ddd, $^4J_{HH} = 2.1$ Hz, $^4J_{HP(cis)} = 5.4$ Hz, $^4J_{HP(trans)} = 7.5$ Hz, 1H; H5, metallated ring), 7.69 (dd, $^4J_{HP} = 3.0$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H6, nonmetallated ring), 7.36 (dd, $^4J_{HP} = 1.2$ Hz, $^4J_{HH} = 2.5$ Hz, 2H; H3, non-metallated ring), 7.02 (app t (dd), $^5J_{HP} = 2.5$ Hz, $^4J_{HH} = 2.1$ Hz, 1H; H3, metallated ring), 6.99 (dd, $^4J_{HH} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, non-metallated ring), 2.39 (m, 3H; PCH of Cy), 1.85 (br m, 9H; Cy), 1.58 (s, 18H; *t*Bu), 1.39 (s, 9H; *t*Bu), 1.23 (s, 18H; *t*Bu), 0.89 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 26.2$ (d, $^2J_{PP} = 40.7$ Hz, phosphine); 136.0 (d, $^2J_{PP} = 40.7$ Hz, phosphite) ppm; elemental analysis calcd (%) for $C_{60}H_{95}O_3P_2PdCl$ (1068.2): C 67.46, H 8.96; found: C 67.5, H 8.5.

Synthesis of [PtCl{κ^2-*P,C*-P(OC$_6$H$_2$-2,4-*t*Bu$_2$)(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_2$}(PCy$_3$)] (13c) by using Cy$_3$PCS$_2$: A mixture of complex **6** (0.20 g, 0.11 mmol) and Cy_3PCS_2 (0.08 g, 0.23 mmol) in CH_2Cl_2 (6 mL) was stirred for 30 minutes after which time EtOH (10 mL) was added to precipitate the product. This was collected by filtration, washed with ethanol (3×10 mL) and recrystallised from CH_2Cl_2/EtOH (0.13 g, 48% yield). ^{1}H NMR (300 MHz, $CDCl_3$): two isomers in a 2:1 ratio, some signals obscured; $\delta = 8.56$ (ddd with sat., $^4J_{HH} = 2.1$ Hz, $^4J_{HP(cis)} = 2.0$ Hz, $^4J_{HP(trans)} = 5.8$ Hz, $^3J_{HPt} = 40$ Hz, 1H; H5, metallated ring, major isomer), 7.78 (dd, $^4J_{HP} = 2.3$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H6, nonmetallated ring, major isomer), 7.44 (dd, $^4J_{HP} = 1.7$ Hz, $^3J_{HH} =$ 8.5 Hz, 2H; H6, nonmetallated ring, minor isomer), 7.33 (m, 2H+1H; H3, nonmetallated rings), 7.07 (m, 1H; H3, metallated ring, minor isomer), 7.00 (app t (dd), $^4J_{HH} = 2.2$ Hz, $^5J_{HP} = 2.1$ Hz, 1H; H3, metallated ring, major isomer), 6.98 (dd, $^4J_{HH} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, nonmetallated ring, major isomer), 6.97 (dd, $^4J_{HH} = 2.5$ Hz, $^3J_{HH} = 8.5$ Hz, 2H; H5, nonmetallated ring, minor isomer), 2.41 (m, 3H; PCH of Cy), 1.88 (m, 9H; Cy), 1.69 (m, 3H; Cy), 1.57 (s, 18H; *t*Bu, major isomer), 1.49 (s, 18H; *t*Bu, minor isomer), 1.40 (s, 18H; *t*Bu, major isomer), 1.36 (s, 18H; *t*Bu, minor isomer), 1.28 (s, 9H; *t*Bu, minor isomer), 1.24 (s, 9H; *t*Bu, major isomer), 1.20 (s, 9H; *t*Bu, minor isomer), 0.91 (s, 9H; *t*Bu, major isomer) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 26.9$ (d with sat., $J_{PtP} = 2788$ Hz, $J_{PP trans} =$

597 Hz), 27.5 (d with sat., $J_{PtP}=1804$ Hz, $J_{PP cis}=20$ Hz), 103.1 (d with sat., $J_{PtP}=6700$ Hz, $J_{PP cis}=22$ Hz), 117.6 (d with sat., $J_{PtP}=4874$ Hz, $J_{PP trans}=597$ Hz) ppm; elemental analysis calcd (%) for $C_{60}H_{95}ClO_3P_2Pt$ (1156.9): C 62.29, H 8.28; found: C 61.75, H 7.95.

General method for the synthesis of the chelating bisphosphine adducts: A solution of the appropriate complex (either **5a** or **6**) (0.10–0.13 mmol) and ligand (2.0 equiv) in dichloromethane (5 mL) was stirred at room temperature for 30 minutes. Addition of ethanol (10–15 mL) led to the precipitation of product which was collected by filtration, washed with ethanol (3×10 mL) and subsequently recrystallised from CH_2Cl_2/EtOH.

Data for complex 14a: Yield: 0.114 g (96%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.96$ (m, 4H) 7.61 (m, 6H), 7.37 (brs, 2H), 7.20 (m, 6H), 7.07 (m, 8H), 6.89 (dd, $^4J_{HH}=2.5$ Hz, $^3J_{HH}=8.5$ Hz, 2H; H5, nonmetallated ring), 2.77 (brm, 4H; CH_2), 1.32 (s, 18H; *t*Bu), 1.23 (s, 18H; *t*Bu), 1.04 (s, 9H; *t*Bu), 0.76 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=45.1$ (dd, $^2J_{PP}=31$ Hz, $^2J_{PP}=32$ Hz), 59.2 (dd, $^2J_{PP}=31$ Hz, $^2J_{PP}=501$ Hz), 140.6 (dd, $^2J_{PP}=33$ Hz, $^2J_{PP}=502$ Hz) ppm; elemental analysis calcd (%) for $C_{68}H_{86}ClO_3P_3Pd$ (1186.2): C 70.97, H 7.53; found: C 70.5; H 7.6.

Data for complex 15a: Yield: 0.117 g (92%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.05$ (m, 4H) 7.60(m, 6H); 7.42 (ddd with sat., $^4J_{HH}=2.0$ Hz, $^4J_{HP}=2.5$ Hz, $^4J_{HP}=6.6$ Hz, $^3J_{HPt}=42$ Hz, 1H; H5, metallated ring) 7.36 (dd, $^4J_{HH}=2.4$ Hz, $^4J_{HP}=1.5$ Hz, 2H; H3, nonmetallated ring); 7.22 (m, 8H), 7.14 (dd, $^4J_{HH}=2.0$ Hz, $^5J_{HP}=2.0$ Hz, 2H; metallated ring), 7.04 (m, 4H); 6.95 (dd, $^4J_{HH}=2.5$ Hz, $^3J_{HH}=8.5$ Hz, 2H; H5, nonmetallated ring), 2.51 (m, 4H; CH_2), 1.33 (s, 18H; *t*Bu); 1.21 (brs, 18H), 1.00 (s, 9H; *t*Bu), 0.74 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=45.4$ (dd with sat., $J_{PtP}=1756$ Hz, $J_{PP}=22$ Hz, $J_{PP}=8.6$ Hz), 57.2 (dd with sat., $^1J_{PtP}=1030$ Hz, $^2J_{PP}=8.5$ Hz, $^2J_{PP}=515$ Hz), 132 (dd with sat., $^1J_{PtP}=4360$ Hz, $^2J_{PP}=22$ Hz, $^2J_{PP}=514$ Hz) ppm; elemental analysis calcd (%) for $C_{68}H_{86}ClO_3P_3Pt$ (1274.9): C 64.06, H 6.80; found: C 63.7, H 7.05.

Data for complex 15b: (0.092 g, 64%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.16$ (dd, $^4J_{HP}=2.5$ Hz, $^3J_{HH}=8.5$ Hz, 2H; H6, nonmetallated ring), 8.00 (m, 4H), 7.64 (m, 2H), 7.58 (m, 2H), 7.41 (m, 9H), 7.15 (m, 8H), 6.90 (brs, 1H), 4.65 (brs, 4H; Cp), 4.36 (brs, 2H; Cp), 3.25 (brs, 2H; Cp), 1.28 (brs, 18H; *t*Bu), 1.25 (brs, 18H; *t*Bu), 0.80 (s, 9H; *t*Bu), 0.56 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=15.6$ (dd with sat., $J_{PtP}=1892$ Hz, $J_{PP}=27$ Hz, $J_{PP}=65$ Hz); 27.1 (dd with sat., $J_{PP}=3040$ Hz, $J_{PP}=510$ Hz, $J_{PP}=67$ Hz); 117.1 (dd with sat., $J_{PtP}=4712$ Hz, $J_{PP}=30$ Hz, $J_{PP}=544$ Hz) ppm; elemental analysis calcd (%) for $C_{76}H_{90}ClFeO_3P_3Pt$ (1430.8): C 65.56, H 6.30; found: C 66.1, H 6.0.

[Pd{κ^2-*P,C*-P(OC$_6$H$_2$-2,4-*t*Bu$_2$)(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_2$}(κ^2-dppf)][OTf] (14b): A mixture of complex **5a** (0.50 g, 0.32 mmol) and silver triflate (0.16 g, 0.64 mmol) in acetonitrile (30 mL) was stirred for 5 minutes. Then DPPF (0.35 g, 0.32 mmol) was added, and the mixture was stirred for 1 hour, after which time the AgCl generated in the reaction was removed by filtration. The filtrate was evaporated to dryness, and the solid was recrystallised from dichloromethane/pentane (0.55 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.79$–7.94 (m, 8H), 7.60–7.75 (m, 4H), 7.46–7.55 (m, 8H), 7.37 (brm, 4H), 7.13 (brd, $^2J_{HH}=2.5$ Hz, 2H; H3, nonmetallated ring), 6.90 (brd, $^3J_{HH}=8.25$ Hz, 2H; H5, nonmetallated ring), 4.63 (s, 2H; Cp), 4.40 (s, 2H; Cp), 3.70 (s, 2H; Cp), 3.60 (s, 2H; Cp), 1.34 (s, 18H; *t*Bu), 1.28 (s, 18H; *t*Bu), 0.89 (s, 9H; *t*Bu), 0.57 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=17.0$ (dd, $^2J_{PP}=50$ Hz, $^2J_{PP}=41$ Hz); 32.7 (dd, $^2J_{PP}=41$ Hz, $^2J_{PP}=540$ Hz); 130 (dd, $^2J_{PP}=52$ Hz, $^2J_{PP}=540$ Hz) ppm.

[Pd{κ^2-*P,C*-P(OC$_6$H$_2$-2,4-*t*Bu$_2$)(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_2$}(κ^2-S$_2$CNMe$_2$)] (16): A solution of complex **5a** (0.30 g, 0.20 mmol) and $Na[S_2CNEt_2]\cdot3H_2O$ (0.09 g, 0.39 mmol) in a mixture of CH_2Cl_2 (10 mL), ethanol (10 mL) and water (1 mL) was stirred for 5 mins. Concentration under reduced pressure led to precipitation of the product, which was then recrystallised from CH_2Cl_2/EtOH to give colourless crystals (0.22 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.44$ (dd, $^4J_{HP}=1.9$ Hz, $^3J_{HH}=8.5$ Hz, 2H; H6, nonmetallated ring), 7.35 (dd, $^5JHP=1.0$ Hz, $^4J_{HH}=2.5$ Hz, 2H; H3, nonmetallated ring), 7.15 (appt (dd), $^4J_{HH}=2.2$ Hz, $^5J_{HP}=2.2$ Hz, 1H; H3, metallated ring), 7.10 (appt (dd), $^4J_{HH}=2.2$ Hz, $^4J_{HP}=2.2$ Hz, 1H; H5, metallated ring), 7.08 (dd, $^4J_{HH}=2.5$ Hz, $^3J_{HH}=8.5$ Hz, 2H; H5, nonmetallated ring), 3.85 (q, $^3J_{HH}=7.2$ Hz, 2H; CH_2CH$_3$), 3.78 (q, $^3J_{HH}=7.2$ Hz, 2H; CH_2CH$_3$), 1.41 (s, 18H; *t*Bu), 1.33 (s, 9H; *t*Bu), 1.31 (t, $^3J_{HH}=7.2$ Hz, 3H; CH$_2$CH_3), 1.27 (s, 18H; *t*Bu), 12.4 (s, 9H; *t*Bu), 1.23 (t, $^3J_{HH}=7.2$ Hz, 3H; CH$_2$CH_3) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=137.6$ ppm; elemental analysis calcd (%) for $C_{47}H_{72}NO_3PPdS_2$ (900.6): C 62.61, H 8.16; found: C 62.3, H 8.4.

[Pt{κ^2-*P,C*-P(OC$_6$H$_2$-2,4-*t*Bu$_2$)(OC$_6$H$_3$-2,4-*t*Bu$_2$)$_2$}(κ^2-S$_2$CNMe$_2$)] (17): A mixture of complex **6** (0.20 g, 0.11 mmol) and $Na[S_2CNEt_2]\cdot3H_2O$ (0.05 g, 0.23 mmol) in CH_2Cl_2 (6 mL) was stirred for 30 minutes, after which time EtOH (10 mL) was added, and the product precipitated. The supernatant liquid was removed, and the product washed with EtOH (3×10 cm^3) and recrystallised from CH_2Cl_2/EtOH to give **17** as a colourless solid (0.12 g, 43% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.49$ (dd, $^4J_{HP}=1.7$ Hz, $^3J_{HH}=8.5$ Hz, 2H; H6, nonmetallated ring), 7.36 (dd, $^5J_{HP}=1.7$ Hz, $^4J_{HH}=2.4$ Hz, 2H; H3, nonmetallated ring), 7.19 (d, $^4J_{HH}=2.2$ Hz, 1H; H3, metallated ring), 7.10 (appt (dd), $^4J_{HH}=2.2$ Hz, $^4J_{HP}=2.2$ Hz, 1H; H5, metallated ring), 7.08 (dd, $^4J_{HH}=2.5$ Hz, $^3J_{HH}=8.5$ Hz, 2H; H5, nonmetallated ring), 3.75 (q, $^3J_{HH}=7.1$ Hz, 2H; CH_2CH$_3$), 3.71 (q, $^3J_{HH}=7.1$ Hz, 2H; CH_2CH$_3$), 1.43 (s, 18H; *t*Bu), 1.36 (t, 3H; $^3J_{HH}=7.1$ Hz, CH$_2$CH_3), 1.38 (s, 9H; *t*Bu), 1.28 (t, 3H; CH$_2$CH_3), 1.28 (s, 18H; *t*Bu), 1.25 (s, 9H; *t*Bu) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=109.35$ (s with sat., $J_{PtP}=6220$ Hz) ppm; elemental analysis calcd (%) for $C_{47}H_{72}NO_3PPtS_2$ (989.3): C 57.00, H 7.43; found: C 56.7, H 7.6.

Catalysis

Suzuki coupling of aryl bromides with phenylboronic acid: (Table 3) The appropriate aryl bromide (10.0 mmol), phenyl boronic acid (1.83 g, 15.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol) and toluene (30 mL total, including catalyst/added ligand solution) were placed in a three-necked flask under an atmosphere of nitrogen. The correct amount of catalyst/added ligand was added as a solution in toluene (1.00 mL) made up by multiple volumetric dilutions of a stock solution. The mixture was then heated at reflux for 18 h, cooled in an ice bath, quenched with aqueous HCl (2 M, 100 mL), extracted with dichloromethane (3×100 mL), dried ($MgSO_4$) and evaporated to dryness. Hexadecane (0.068 M in CH_2Cl_2, 3.00 mL) and dichloromethane (5–7 mL, to ensure complete dissolution) were added. The conversion to coupled product was then determined by GC analysis.

Suzuki coupling of aryl bromides with n*-butylboronic acid*: (Table 4) The appropriate aryl bromide (10.0 mmol), butylboronic acid (1.56 g, 15.0 mmol), K_3PO_4 (4.24 g, 20.0 mmol) and 1,4-dioxane (30 mL total, including catalyst/added ligand solution) were placed in a three-necked flask under an atmosphere of nitrogen. The catalyst was added as a solution in dioxane (1.00 mL) made up by multiple volumetric dilution of a stock solution. The mixture was heated at reflux for 18 h, cooled in an ice bath, quenched with aqueous HCl (2 M, 100 mL) and extracted with DCM (3×100 mL). The combined extracts were dried ($MgSO_4$), and then the solvent was removed on a rotary evaporator. Hexadecane (0.068 M in CH_2Cl_2, 3.00 mL) and dichloromethane (5–7 mL, to ensure complete dissolution) were added. The conversion to coupled product was then determined by GC analysis.

Suzuki coupling of aryl bromides with arylboronic acids: (Table 5) As for the coupling of aryl bromides with phenylboronic acid but with aryl chloride (10.0 mmol) arylboronic acid (15.0 mmol), base (20.0 mmol) and 1,4-dioxane (30 mL) and a total heating time of 17 hours.

Time-dependant study on the coupling of phenylboronic acid with 4-bromoanisole: (Figure 4) 4-Bromoanisole (1.87 g, 10 mmol), phenylboronic acid (1.83 g, 15 mmol), K_2CO_3 (2.76 g, 20.0 mmol), hexadecane (0.204 mmol, internal standard) and toluene (29 mL) were placed in a two-necked flask under an atmosphere of nitrogen. The mixture was then heated to 80 °C, and the catalyst (either complex **5a** (0.5 mol% Pd) or a mixture of complex **5a** (0.5 mol% Pd) and PCy_3 (0.5 mol%)) was added as a volumetric solution in toluene (1.00 mL). The temperature was maintained at 80 °C for 120 mins, and 0.2 mL aliquots were taken at regular intervals. These samples were quenched in aqueous HCl (2 M, 0.5 mL), the mixture was extracted with toluene (3×1 mL), the combined organic extracts were dried over $MgSO_4$ and then the conversion to coupled product was determined by GC.

Time-dependant study on the coupling of phenylboronic acid with 4-chloroanisole: (Figure 5) As above with 4-chloroanisole (1.42 g, 10 mmol), phenylboronic acid (1.83 g, 15 mmol), Cs_2CO_3 (6.56 g, 20.0 mmol) and 1,4-dioxane (30 mL total, including catalyst solutions). The appropriate catalyst mixture was added as a solution in dioxane (1.00 mL) made up by multiple volumetric dilution of a stock solution. The reaction temperature used was 100 °C.

Stille coupling of aryl chlorides: (Table 6) These reactions were performed on a Radleys Carousel Reactor™, which consists of twelve approximately 45 mL tubes that are fitted with screw-on Teflon caps equipped with valves for the introduction of inert gas and septa for the introduction of reagents. The twelve reaction tubes sit in two stacked aluminium blocks, the lower one fits onto a heater–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 and allows reactions to be performed at reflux temperature. Aryl chloride (1.0 mmol), the appropriate organostannane (1.1 mmol), K_3PO_4 (2.0 mmol) and 1,4-dioxane (5 mL) were placed in a carousel reaction tube under an atmosphere of nitrogen. The appropriate catalyst (1.0 mol%) was added as a solution in 1,4-dioxane (1.00 mL). The reaction was heated at reflux for 18 h, then cooled in an ice bath, diethyl ether was added, and the mixture was filtered through a pad of silica. The pad of silica was washed with portions of diethyl ether, and then the combined filtrate and washings evaporated to dryness. Hexadecane (0.068 M in dichloromethane, 1.00 mL) and dichloromethane (2–5 mL, to ensure complete dissolution) were added and the conversion to coupled product was determined by GC.

X-ray structure determinations

Complex 5c: All data were collected on an Enraf–Nonius CAD-4 diffractometer at 293 K by using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares with the SHELXL-97[30] suite of programs. Triclinic ($P\bar{1}$), $a = 10.4907(9)$, $b = 11.504(2)$, $c = 13.345(2)^\circ$, $\beta = 69.9550(10)$ Å, $Z = 2$. 5432 reflections collected (5125 observed ($I > 2\sigma I$) with $R_{int} = 0.0229$) for a crystal with dimensions $0.3 \times 0.1 \times 0.05$ mm. The final R indices are $R1 = 0.0610$ and $wR2 = 0.0876$ for all data. Non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were refined isotropically in geometric positions using the riding model.

Complex 17: All data were collected on a Bruker–Nonius KappaCCD area detector diffractometer at 150 K with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) produced by a Bruker–Nonius FR591 rotating-anode generator. The structures were solved by direct methods and refined by full-matrix least-squares by using the SHELX-97[30] suite of programs. Monoclinic ($P2_1/c$), $a = 14.644(3)$, $b = 11.148(2)$, $c = 30.713(6)^\circ$, $\beta = 92.21(3)$ Å, $Z = 4$, 25568 reflections collected (6812 observed ($I > 2\sigma I$) with $R_{int} = 0.0556$) for a crystal of dimensions $0.3 \times 0.25 \times 0.25$ mm. The final R indices are $R1 = 0.0699$ and $wR_2 = 0.2129$ for all data. Non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were refined isotropically in geometric positions by using the riding model. Data were corrected for absorption by comparison of equivalent reflections by using the program SORTAV.[31] The Figure was prepared with the program PLATON.[32] CCDC-206867 (**5c**) and 205978 (**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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