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Pentafluorophenyl imidato palladium(II) complexes: catalysts for Suzuki cross-coupling reactions

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Novel N-bonded imidato complexes of general formula [Pd(N–N)(C_6F_5)(imidate)] (imidate = maleimidate, succinimidate or phthalimidate; N–N = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda)), [NBu_4][Pd(C_6F_5)(H_2O)(succinimidate)$_2$] and [NBu_4]-[Pd(C_6F_5)(L)(succinimidate)$_2$] (L = PPh_3 or *t*-BuNC) have been synthesised. These complexes are air-, light- and moisture-stable. The crystal structures of [Pd(tmeda)(C_6F_5)(maleimidate)]·H_2O·0.5$CHCl_3$, [NBu_4][Pd(C_6F_5)-(H_2O)(succinimidate)$_2$]·H_2O and [NBu_4][Pd(C_6F_5)(*t*-BuNC)(succinimidate)$_2$]·2H_2O have been determined by X-ray diffraction. Many of these new complexes are shown to be active phosphine-free palladium catalysts/precatalysts for the Suzuki cross-coupling reactions of aryl bromides and aryl chlorides with phenylboronic acid.

Introduction

Over the last twenty-five years great advances in the development of palladium-catalysed carbon–carbon and carbon–heteroatom bond forming processes have been made.[1–5] Palladium-catalysed cross-coupling utilizing organoboron compounds (the Suzuki reaction) is a powerful tool for the formation of carbon–carbon bonds.[6,7] The practical advantages of this reaction are mainly related to the wide range of functionalized substrates that can be used under mild conditions. The search for appropriate ancillary ligands that facilitate the generation of highly active catalyst precursors is of current interest. Significant progress has been made recently with the employment of ligands such as electron-rich, sterically hindered phosphines[8–12] and N-heterocyclic carbenes.[13–18] The use of cyclometallated Pd(II) complexes as precatalysts, has in part, led the advances seen in the last decade.[19–27] Bedford *et al*.[20,21] have also observed the important role played by the anionic ligand in the overall performance of catalysts. On the other hand, Fairlamb *et al*.[28–33] have recently reported the successful catalytic application of some new imidato palladium complexes of the types [Pd(C^N)-(imidate)(PR_3)], [Pd(imidate)(PPh_3)$_2$(Br)], [Pd(imidate)$_2$(PPh_3)$_2$] and [NBu_4][Pd{C_4(COOMe)$_4$}(imidate)(PR_3)] (imidate = succinimidate, maleimidate or phthalimidate) in Stille, Sonogashira and Suzuki cross-coupling reactions. The conversions appear[28] to be dependent, to some extent, on the type of imidate ligand, suggesting a role for these pseudohalides in the catalytic cycle in these cross-coupling processes. The hemilability of imidate ligands derives from their ability to act as either monodentate or bidentate ligands. Generally four coordination modes to transition metals are considered possible (I–IV, Fig. 1).

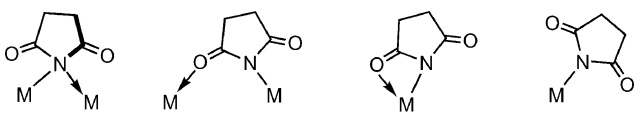

Fig. 1 Possible coordination modes of succinimide ligands to metal centres.

These interesting modes of coordination might offer unique stabilizing properties for key catalytic intermediates.

In view of these catalytic results we report here the preparation of novel pentafluorophenyl imidate complexes of the types [Pd(N–N)(C_6F_5)(imidate)] (imidate = maleimidate, succinimidate or phthalimidate; N–N = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda)), [NBu_4][Pd(C_6F_5)(H_2O)-(succinimidate)$_2$] and [NBu_4][Pd(C_6F_5)(L)(succinimidate)$_2$] (L = PPh_3 or *t*-BuNC). We also report the application of many of these new complexes as catalysts for Suzuki coupling of aryl bromides and aryl chlorides with boronic acid.

Results and discussion

Synthesis and characterisation of complexes 1–9

We have recently described[34,35] the synthesis of monomeric hydroxo palladium(II) complexes of the type [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, Me_2bipy, phen or tmeda) and their reactions with CO or SO_2 in methanol at room temperature to yield the corresponding methoxy carbonyl or alkylsulfito complexes [Pd(N–N)(C_6F_5)(X)] (X = CO_2Me or SO_3Me)]. We have also shown[36] the reactions of the monomeric hydroxo complexes [Pd(N–N)(C_6F_5)(OH)] with some active methyl (CH_3COR or CH_3NO_2) and methylene (CH_2X_2) (X = CO_2Et or CN) to yield the corresponding C-bound enolate palladium complexes.

The reaction of the monomeric hydroxo palladium complex of the type [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, Me_2bipy or tmeda) with maleimide, succinimide or phthalimide in toluene gives the corresponding imidate complex [Pd(N–N)(C_6F_5)(imiditate)] **1–9** (Scheme 1) in 76–95% yield. The acidic proton of the imide is abstracted by the corresponding hydroxo-complex generating the anionic ligand imidate which is subsequently trapped by the organometallic moiety [Pd(N–N)(C_6F_5)]$^+$ to form complexes **1–9** and the concomitant release of water. The structures were assigned on the basis of microanalytical, IR and ^{1}H and ^{19}F NMR data. Complexes **1–9** are all air-stable solids and the thermal analysis shows that they decompose above 181 °C in a dynamic N_2 atmosphere. The IR spectra show the characteristic absorptions of the C_6F_5 group[37] at 1630, 1490, 1450, 1050, 950 and a single band at *ca.* 800 cm^{-1} which is derived from the so-called X-sensitive mode[38] in C_6F_5 halogen molecules, as expected for the presence of only one C_6F_5 group in the coordination sphere of the palladium atom and behaves like a *ν*(M–C) band.[39–41] The IR spectra also show one strong

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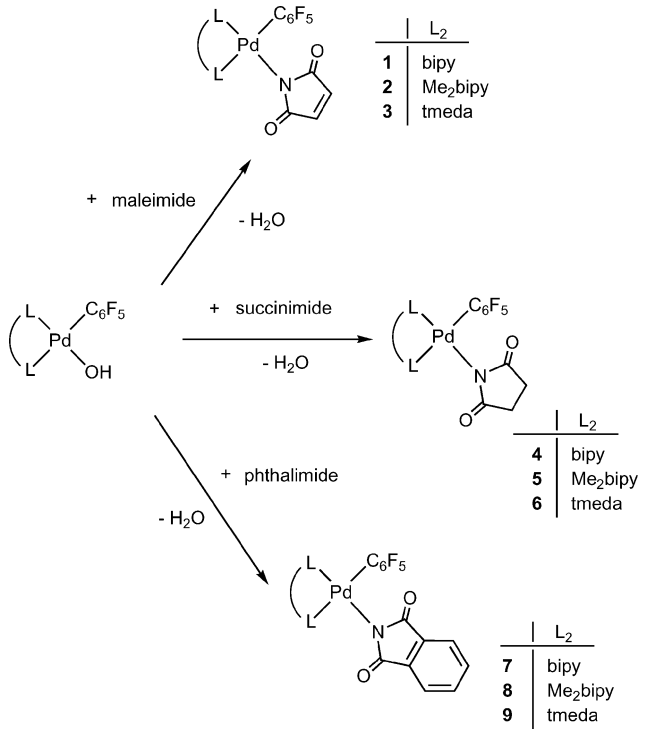


Scheme 1

carbonyl band around 1640 cm^{-1} that is characteristic of the imidate group.[28] The characteristic resonances of the neutral ligands[35,42–44] were observed in the ^1H NMR spectra. The expected resonances of the imidate ligands are also seen.[32] The ^{19}F NMR spectra of complexes **1–9** reveal the presence of a freely rotating pentafluorophenyl ring which gives three resonances (in the ratio 2 : 2 : 1) at *ca.* −118.0, −163.0 and −160.0 for the *o*-, *m*- and *p*-fluorine atoms, respectively.

Fig. 2 shows the X-ray structure of complex **3**·H_2O·0.5$CHCl_3$, with selected bond lengths and angles listed in Table 1. The crystal structure of compound **3**·H_2O·0.5$CHCl_3$ shows two independent molecules in the asymmetric unit with the palladium atom in a slightly distorted square planar geometry. The imidate ligand is approximately perpendicular to the coordination plane, with angles between planes of 85.4(2)° in molecule 1 and 86.9(2)° in molecule 2. The Pd–N maleimidate distance (Pd(1)–N(1) 2.020(5) Å in molecule 1 and Pd(2)–N(4) 2.016(5) Å in molecule 2) is a bit shorter than that observed in [NBu_4][Pd{C_4(COOMe)$_4$}(maleimidate)(P(*p*-$C_6H_4F)_3$)] (2.077(3) Å).[32] The different Pd–N tmeda distances (Pd(1)–N(2) 2.081(5) Å, Pd(1)–N(3) 2.132(5) Å in molecule 1

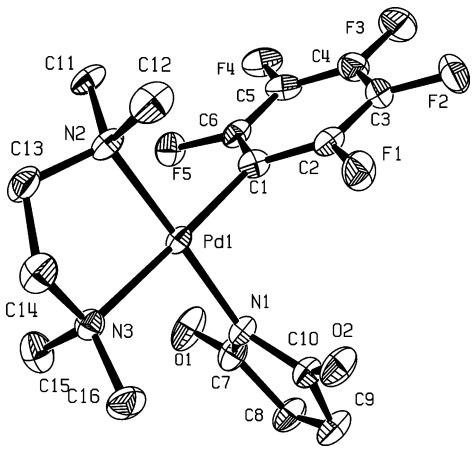


Fig. 2 ORTEP of complex **3**·H_2O·0.5$CHCl_3$ showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for complex **3**·H_2O·0.5$CHCl_3$

Molecule 1			
Pd(1)–C(1)	2.008(6)	Pd(1)–N(2)	2.081(5)
Pd(1)–N(1)	2.020(5)	Pd(1)–N(3)	2.132(5)
C(1)–Pd(1)–N(1)	88.6(2)	C(1)–Pd(1)–N(3)	178.0(2)
C(1)–Pd(1)–N(2)	93.7(2)	N(1)–Pd(1)–N(3)	92.59(19)
N(1)–Pd(1)–N(2)	177.6(2)	N(2)–Pd(1)–N(3)	85.21(19)
Molecule 2			
Pd(2)–C(17)	2.019(6)	Pd(2)–N(5)	2.127(5)
Pd(2)–N(4)	2.016(5)	Pd(2)–N(6)	2.084(5)
C(17)–Pd(2)–N(6)	92.8(2)	C(17)–Pd(2)–N(5)	178.1(2)
C(17)– Pd(2)–N(4)	89.5(2)	N(4)–Pd(2)–N(6)	177.0(2)
N(4)–Pd(2)–N(5)	92.2(2)	N(6)–Pd(2)–N(5)	85.6(2)

Table 2 Hydrogen bonds for complex **3**·H_2O·0.5$CHCl_3$ (Å and °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(5)–H(5A)···O(3)	0.84(6)	2.10(6)	2.942(7)	177(8)
O(5)–H(5B)···O(4)[a]	0.84(6)	2.07(7)	2.870(7)	160(11)
O(6)–H(6A)···O(2)	0.81(6)	2.22(7)	2.960(7)	154(10)
O(6)–H(6B)···O(1)[b]	0.81(6)	2.00(6)	2.772(7)	160(8)

Symmetry transformations used to generate equivalent atoms:[a] $-x+1$, $y-1/2$, $-z+1/2$. [b] $-x$, $y+1/2$, $-z+1/2$.

and Pd(2)–N(6) 2.084(5) Å, Pd(2)–N(5) 2.127(5) Å in molecule 2) are in agreement with the higher *trans* influence of the C_6F_5 group compared to maleimidate. The Pd–C_6F_5 bond length (2.008(6) Å in molecule 1 and 2.019(6) Å in molecule 2) is in the range found in the literature for pentafluorophenyl–palladium complexes.[45] As can be seen in Fig. 3 and Table 2 in the crystal there are OH···O hydrogen bonds (2.772–2.960 Å) involving the maleimidate ligand and the water molecule of crystallization leading to zigzag one-dimensional hydrogen-bonded chains.

Synthesis and characterisation of complexes 10–12

The bisimidate palladium complexes [NBu_4][Pd(C_6F_5)(H_2O)-(succinimidate)$_2$] **10** and [NBu_4][Pd(C_6F_5)(L)(succinimidate)$_2$] **11**, **12** have been prepared by reaction in methanol or dichloromethane of the halo-complexes [NBu_4]$_2$[{Pd(C_6F_5)(Br)-(μ-Br)}$_2$][46] or [{Pd(C_6F_5)(L)(μ-Cl)}$_2$] [L = *t*-BuNC,[47] PPh_3[48]] with [NBu_4]OH and succinimide in the molar ratio 1 : 6 : 6, as shown in Schemes 2 and 3. The preparations of complexes **10–12** have been optimised. When less than 6 equivalents of succinimide were used no pure compounds were obtained. The new complexes **10–12** have been characterized by elemental analysis and spectroscopic data. The IR spectra of complexes **10–12** show one strong carbonyl band around 1620 cm^{-1} that is characteristic of the imidate group.[28] The IR spectrum of complex **11** shows also an absorption assigned to ν(C≡N) of the *t*-BuNC group[49–51] at *ca.* 2220 cm^{-1}. The ^1H NMR spectrum of complex **10** exhibits an unique resonance at δ 2.28 ppm for the succinimidate groups which suggests a *trans* isomer in $CDCl_3$ solution. No isomerization process was observed when a solution of **10** was kept in solution in $CDCl_3$ for a prolonged period. A *trans* structure of **10** was confirmed by X-ray diffraction (*vide infra*). On the other hand, the ^1H NMR spectra of complexes **11** and **12** suggest a *cis* isomer in $CDCl_3$ solution showing two distinct resonances for the protons of the succinimidate groups indicating the presence of two type of imidate ligands, one *trans* to C_6F_5 and the other *trans* to L (L = PPh_3 or *t*-BuNC). A *cis* structure of **11** was revealed by X-ray diffraction (vide infra). The ^1H NMR spectrum of complex

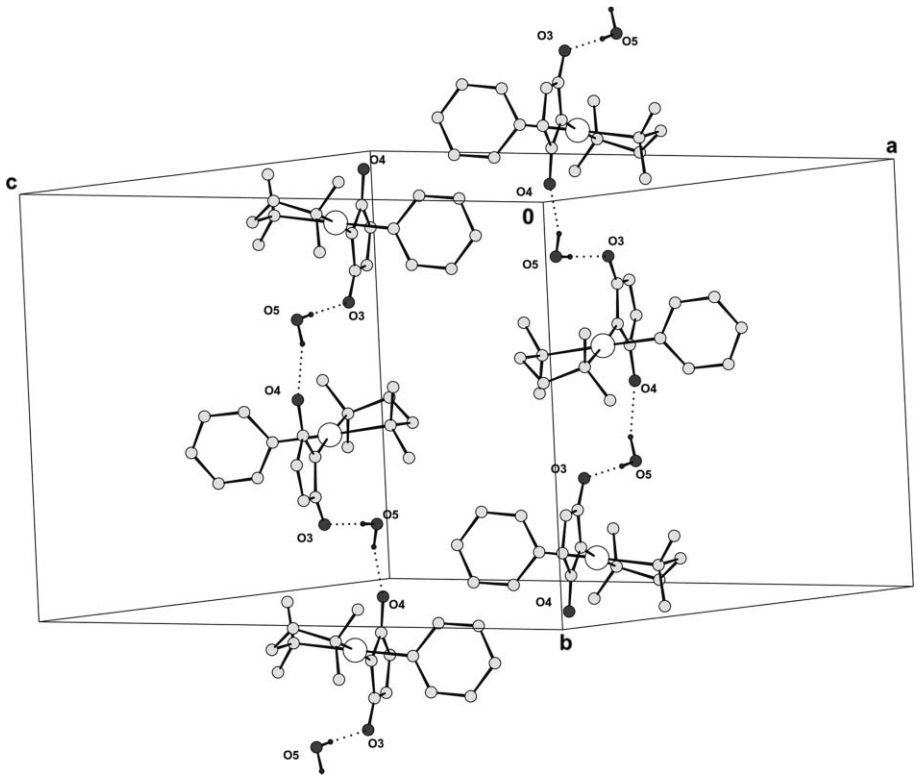
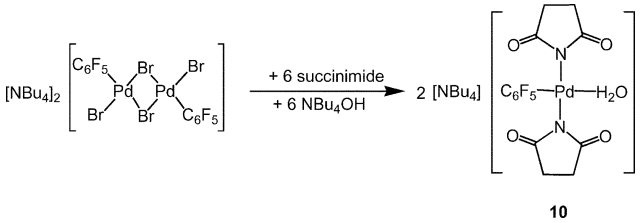
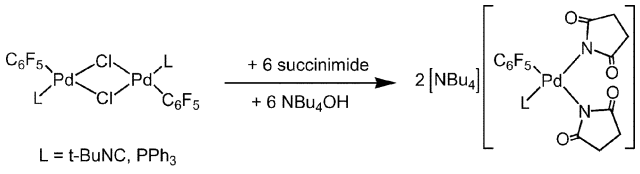


Fig. 3 Schematic showing the zigzag chain formed by hydrogen bonding in complex **3**·H_2O·0.5$CHCl_3$.



10

Scheme 2



L = t-BuNC, PPh_3

	L
11	t-BuNC
12	PPh_3

Scheme 3

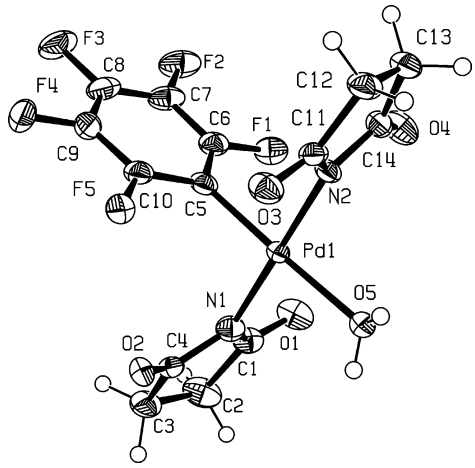


Fig. 4 ORTEP of complex **10**·H_2O showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

11 shows also a singlet resonance for the *t*-BuNC group at δ 1.37 ppm. The ^{31}P MNR spectrum of complex **12** shows a unique resonance for the phosphine ligand at δ 25.5 ppm. The ^{19}F NMR spectra of **10–12** exhibit three resonances with relative intensities of 2 : 1 : 2 ($2F_{ortho}$: $1F_{para}$: $2F_{meta}$) corresponding to only one type of pentafluorophenyl ring.

The crystal structure of compound **10**·H_2O shows three independent molecules in the asymmetric unit. The structure of the first molecule of the unit cell is shown in Fig. 4 and selected bond lengths and angles of the three molecules are in Table 3. A *trans*-geometry around the Pd-centre is observed. For example, in the first molecule of the unit cell the angle N(1)–Pd(1)–N(2) is 179.4(2)°. The crystal structure of the related bisimidato complex *trans*-[$Pd(PPh_3)_2$(succinimidate)$_2$] has been recently reported.[31] The Pd–OH_2 distances are similar to those found in [$Pd(C_6F_5)(AsPh_3)(H_2O)_2$][$CF_3SO_3$].[52] An interesting feature of the crystal structure is the presence of dimeric units of [$Pd(C_6F_5)(H_2O)$(succinimidate)$_2]_2$·$2H_2O$ (Fig. 5). Thus the water molecule coordinated to the Pd1 atom is a hydrogen bond donor to O6 and O9 of the succinimides ligands of molecule 2 (Table 4) and the water molecule coordinated to the Pd2 atom is a hydrogen bond donor to O2 and O3 of molecule 1. The molecules of non-coordinated water are also involved in the formation of the dimeric units. There are also intermolecular π-stacking interactions involving the carbonyl groups,[31] thus relatively short intermolecular contacts O3 · · · C28 (3.091 Å) and O9 · · · C11 (2.985 Å) are observed.

The structure of **11**·$2H_2O$ is shown in Fig. 6 and selected bond lengths and angles in Table 5. The geometry around the palladium atom is approximately square planar. A *cis* structure was revealed with an angle N(1)–Pd–N(2) of 89.25(11)°. The Pd(1)–N(2) bond distance (*trans* to the C_6F_5 group) is longer than the Pd(1)–N(1) bond (*trans* to the *t*-BuNC ligand). Two relatively short intramolecular contacts N2 · · · O1 (2.988 Å) and N1 · · · O4 (3.038 Å) are observed, which suggest a significant extra stabilization of the arrangement due to intramolecular

Table 3 Selected bond lengths (Å) and angles (°) for complex **10**·H_2O

Molecule 1			
Pd(1)–C(5)	1.985(6)	Pd(1)–N(2)	2.016(4)
Pd(1)–N(1)	2.039(5)	Pd(1)–O(5)	2.122(4)
C(5)–Pd(1)–N(2)	89.6(2)	C(5)–Pd(1)–O(5)	177.3(2)
C(5)–Pd(1)–N(1)	89.9(2)	N(2)–Pd(1)–O(5)	87.73(17)
N(2)–Pd(1)–N(1)	179.4(2)	N(1)–Pd(1)–O(5)	92.72(18)
Molecule 2			
Pd(2)–C(19)	1.977(6)	Pd(2)–N(3)	2.015(5)
Pd(2)–N(4)	2.008(5)	Pd(2)–O(10)	2.109(4)
C(19)–Pd(2)–N(4)	90.3(2)	C(19)–Pd(2)–O(10)	176.7(2)
C(19)–Pd(2)–N(3)	89.1(2)	N(4)–Pd(2)–O(10)	88.83(19)
N(4)–Pd(2)–N(3)	177.61(19)	N(3)–Pd(2)–O(10)	91.92(18)
Molecule 3			
Pd(3)–C(33)	1.988(6)	Pd(3)–N(6)	2.018(4)
Pd(3)–N(5)	2.014(4)	Pd(3)–O(15)	2.112(4)
C(33)–Pd(3)–N(5)	89.4(2)	C(33)–Pd(3)–O(15)	177.9(2)
C(33)–Pd(3)–N(6)	89.5(2)	N(5)–Pd(3)–O(15)	90.34(18)
N(5)–Pd(3)–N(6)	178.2(2)	N(6)–Pd(3)–O(15)	90.75(18)

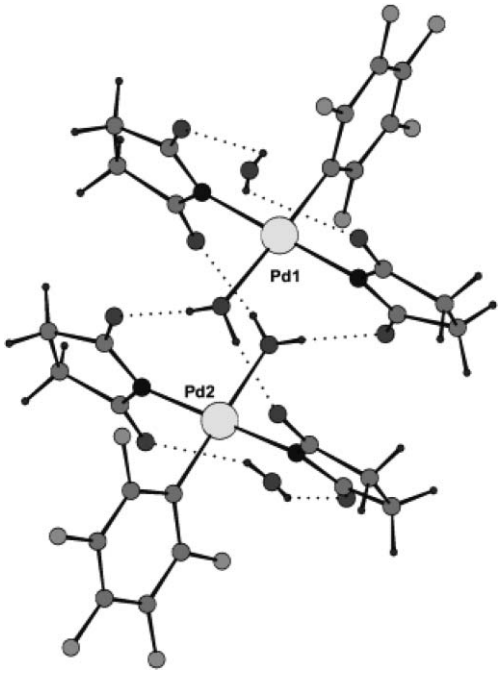


Fig. 5 The dimeric structure of $[Pd(C_6F_5)(H_2O)(succinimidate)_2]_2$·$2H_2O$ showing the hydrogen bonds.

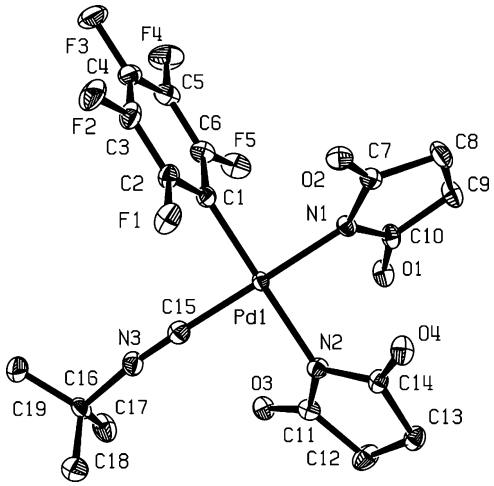


Fig. 6 ORTEP of complex **11**·$2H_2O$ showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 5 Selected bond lengths (Å) and angles (°) for complex **11**·$2H_2O$

Pd(1)–C(15)	1.935(4)	Pd(1)–N(1)	2.041(3)
Pd(1)–C(1)	2.008(3)	Pd(1)–N(2)	2.083(3)
C(15)–Pd(1)–C(1)	89.75(14)	C(15)–Pd(1)–N(2)	90.90(13)
C(15)–Pd(1)–N(1)	173.94(13)	C(1)–Pd(1)–N(2)	179.14(12)
C(1)–Pd(1)–N(1)	90.16(12)	N(1)–Pd(1)–N(2)	89.25(11)

π-stacking interactions involving the carbonyl groups.[31] Another relatively short intramolecular contact O3···C15 (2.993 Å) is also observed. Furthermore, as can be seen in Fig. 7 and Table 6 in the crystal there are OH···O hydrogen bonds (2.782–2.919 Å) involving O4 and O1 of the maleimidate ligands and the water molecules of crystallization leading to the formation of channels along the *b*-axis.

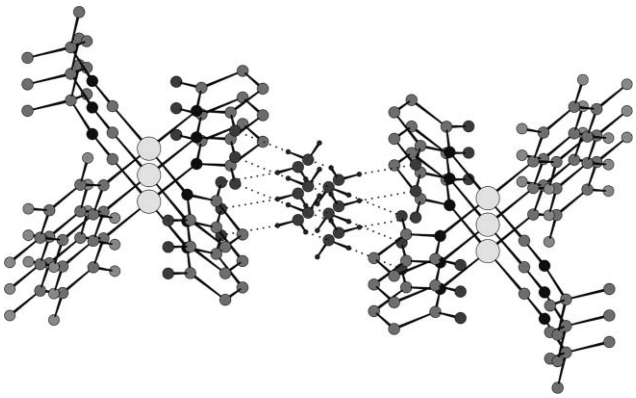


Fig. 7 View of the channels created along the *b*-axis by the hydrogen-bonding interactions in complex **11**·$2H_2O$.

Table 4 Hydrogen bonds for complex **10**·H_2O (Å and °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(*DHA*)
O(5)–H(5A)···O(6)[a]	0.84(7)	1.91(7)	2.729(6)	166(6)
O(5)–H(5B)···O(9)[a]	0.79(7)	1.96(8)	2.750(6)	174(7)
O(10)–H(10A)···O(2)[b]	0.77(7)	1.96(8)	2.727(6)	176(7)
O(10)–H(10B)···O(3)[b]	0.72(8)	2.05(8)	2.760(6)	171(8)
O(15)–H(15A)···O(14)[c]	0.75(8)	1.98(8)	2.713(6)	168(7)
O(15)–H(15B)···O(11)[c]	0.78(9)	1.99(10)	2.759(6)	171(9)
O(16)–H(161)···O(8)	0.67	2.26	2.871(6)	153.4
O(16)–H(162)···O(7)	0.90	1.92	2.819(5)	174.0
O(18)–H(18A)···O(12)	0.67	2.26	2.859(7)	149.4
O(18)–H(18B)···O(13)	0.86	1.98	2.806(6)	161.1

Symmetry transformations used to generate equivalent atoms:[a] $x, y, z+1$. [b] $x, y, z-1$. [c] $-x+2, -y, -z+1$.

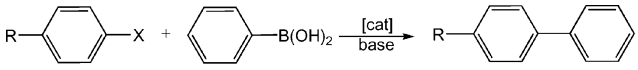
Table 6 Hydrogen bonds for complex **11**·2H_2O (Å and °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(6)–H(61)···O(6)[a]	0.75(2)	2.65(12)	2.919(7)	104(10)
O(6)–H(62)···O(4)[b]	0.748(19)	2.06(2)	2.805(14)	174(5)
O(5)–H(51)···O(6)[c]	0.74(2)	2.16(6)	2.840(5)	153(12)
O(5)–H(52)···O(1)[b]	0.738(19)	2.05(2)	2.782(4)	172(6)

Symmetry transformations used to generate equivalent atoms:[a] $-x, -y, -z$. [b] $-x+1, -y+1, -z+1$. [c] $-x, -y+1, -z$.

Application of the imidato-Pd-complexes as catalysts/precatalysts in Suzuki cross-coupling

The Pd-complexes were screened for catalytic activity in the cross-coupling of aryl bromides or aryl chlorides with phenylboronic acid (Scheme 4).



R = MeC(O), H, MeO; X = Br, Cl

Scheme 4

We first tested the catalytic activity of complexes **3**, **6**, **9–11** and **12** in the Suzuki cross-coupling of aryl bromides with phenylboronic acid, and the results are summarized in Table 7. The reaction conditions were not optimised, but rather toluene was used as solvent and K_2CO_3 as base in order to allow comparison with previous studies in the literature[21,25] (complexes **1**, **2**, **4**, **5**, **7** and **8** could not tested due to their low solubility in toluene).

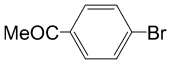
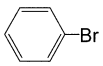
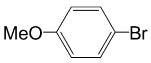
Given that these Pd sources do not possess a phosphine ligand (except complex **12**), the catalytic activity and yields are promising. Thus although it has been recently reported[53] that the $Pd(OAc)_2$/1,4-diazabicyclo[2,2,2]octane system is a highly efficient phosphine-free palladium catalyst for the Suzuki cross-coupling, when the electronically deactivated substrate 4-bromoanisole is used (a good indicator of optimal catalyst performance) only a TON (turnover number) of 420 is achieved after 48 h. In our case, using complex **9** a TON of 55000 with 4-bromoanisole is achieved after 18 h (Table 7, entry 16). It can also be observed that the conversions appear to be dependent on the type of imidate ligand.

We have also tested the catalytic activity of complexes **9**, **10** and **12** in the Suzuki cross-coupling of aryl chloride substrates with phenylboronic acid, and the results are summarized in Table 8. The activity shown is moderate. These yields are, however, improved by the addition of phosphine (Table 9).[54] Presumably the active specie is not the same when PCy_3 is presented.

Conclusion

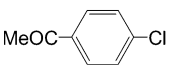
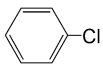
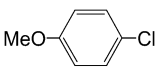
The acid–base reaction between [Pd(N–N)(C_6F_5)(OH)] and imides is a convenient method for the preparation of N-bonded imidato-palladium complexes of the general formula [Pd(N–N)(C_6F_5)(imidate)] which are air-, light- and moisture-stable.

Table 7 Suzuki cross-coupling of aryl bromides with phenylboronic acid[a]

Entry	Aryl bromide	Catalyst	Catalyst loading (mol% Pd)	Conversion (%)	TON (mol product/mol cat)
1		**3**	0.1	83	830
2		**6**	0.01	100	10000
3		**6**	0.001	85	85000
4		**9**	0.01	100	10000
5		**9**	0.001	96	96000
6		**10**	0.01	100	10000
7		**10**	0.001	40	40000
8		**11**	0.01	100	10000
9		**11**	0.001	47	47000
10		**12**	0.001	100	100000
11		**12**	0.0001	19	190000
12		**9**	0.01	100	10000
13		**9**	0.001	69	69000
14		**12**	0.001	84	84000
15		**9**	0.01	100	10000
16		**9**	0.001	55	55000
17		**12**	0.001	10	10000

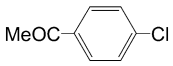
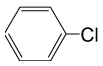
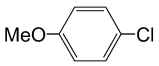
[a] *Conditions*: aryl bromide (2.5 mmol), phenylboronic acid (3.75 mmol), K_2CO_3 (5 mmol), toluene (7.5 mL), 110 °C, 18 h.

Table 8 Suzuki cross-coupling of aryl chlorides with phenylboronic acid by complex **9, 10** or **12**[a]

Entry	Aryl chloride	Catalyst	Catalyst loading (mol% Pd)	Conversion (%)	TON (mol product/mol cat)
1		**9**	1	52	52
2		**10**	1	40	40
3		**12**	1	19	19
4		**9**	1	15	15
5		**9**	1	4	4

[a] *Conditions*: aryl chloride (2.5 mmol), phenylboronic acid (3.75 mmol), K_3PO_4 (5 mmol), toluene (7.5 mL), 110 °C, 18 h.

Table 9 Suzuki cross-coupling of aryl chlorides with phenylboronic acid by mixtures of complex **9**, **10** or **12** and PCy_3[a]

Entry	Aryl chloride	Catalyst	Catalyst loading mol% Pd)	Added PCy_3 (mol%)	Conversion (%)	TON
1		**9**	1	2	100	100
2		**9**	0.5	1	96	192
3		**9**	0.5	0.5	100	200
4		**9**	0.05	0.05	69	1380
5		**10**	1	2	40	40
6		**10**	1	1	50	50
7		**12**	0.5	1	100	200
8		**12**	0.1	0.2	72	720
9		**12**	0.1	0.1	22	220
10		**9**	1	2	68	68
11		**9**	1	1	100	100
12		**9**	0.5	0.5	78	156
13		**12**	0.5	1	34	68
14		**12**	0.5	0.5	3	6
15		**9**	1	2	32	32
16		**9**	1	1	90	90
17		**12**	0.5	1	32	64
18		**12**	0.5	0.5	2	4

[a] *Conditions*: aryl chloride (2.5 mmol), phenylboronic acid (3.75 mmol), K_3PO_4 (5 mmol), toluene (7.5 mL), 110 °C, 18 h.

The bisimidato $[NBu_4][Pd(C_6F_5)(H_2O)(succinimidate)_2]$ and $[NBu_4][Pd(C_6F_5)(L)(succinimidate)_2]$ (L = PPh_3 or *t*-BuNC) have also been synthesised. The crystal structures of $[Pd(tmeda)(C_6F_5)(maleimide)]\cdot H_2O\cdot 0.5CHCl_3$, $[NBu_4][Pd(C_6F_5)(H_2O)(succinimidate)_2]\cdot H_2O$ and $[NBu_4][Pd(C_6F_5)(t\text{-BuNC})(succinimidate)_2]\cdot 2H_2O$ show OH···O hydrogen bonds involving the imidate ligands and the water molecules of crystallization. Many of these new complexes are shown to be active phosphine-free palladium catalysts/precatalysts for the Suzuki cross-coupling reactions of aryl bromides with phenylboronic acid.

Experimental

Instrumental measurements

C, H, N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1} and the solid sample under nitrogen flow (100 mL min^{-1}). The ^1H and ^{19}F NMR spectra were recorded on a Bruker AC 200E, Bruker AC 300E or Bruker AV-400 spectrometer, using $SiMe_4$ or $CFCl_3$ as standards respectively. Infrared spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. GC analyses were performed on a CE instruments GC 8000^{TP} fitted with a 30 m SPB column.

Materials

The starting complexes $[Pd(N–N)(C_6F_5)(OH)]$ [(N–N = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda)],[34] $[NBu_4]_2[\{Pd(C_6F_5)(Br)(\mu\text{-}Br)\}_2]$,[46] and $[\{Pd(C_6F_5)(L)(\mu\text{-}Cl)\}_2]$ (L = *t*-BuNC,[47] PPh_3[48]) were prepared by procedures described elsewhere. The commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification. Solvents were dried by the usual methods.

Preparation of complexes [Pd(N–N)(C_6F_5)(imidate)] (1–9). To a solution or suspension of the corresponding hydroxo complex $[Pd(N–N)(C_6F_5)(OH)]$ (0.24 mmol) in toluene (15 mL) was added the imide (0,24 mmol). The resulting mixture was stirred for 90 min. The solvent was partially evaporated under reduced pressure. On addition of hexane the white complexes **1–9** precipitated and were filtered off and air-dried. **1**: Yield 76% (Found: C, 46.0; H, 2.1; N, 7.8. $C_{20}H_{10}N_3F_5O_2Pd$ requires C, 45.7; H, 1.9; N, 8.0%). Mp 253 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1660, ν(Pd–C_6F_5) 785. ^1H NMR ($CDCl_3$) δ 8.33 (d, 1 H, H_α, $J(H_\alpha H_\beta) = 5.1$ Hz), 8.12 (m, 4 H, $H_\gamma + H_{\gamma'} + H_\delta + H_{\delta'}$), 7.98 (d, 1 H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.1$ Hz), 7.52 (m, 1 H, H_β), 7.40 (m, 1 H, $H_{\beta'}$), 6.58 (s, 2 H, mal). ^{19}F NMR ($CDCl_3$) δ −118.8 (d, $2F_o$, $J(F_oF_m) = 20.9$ Hz), −159.5 (t, 1 F_p, $J(F_mF_p) = 19.9$ Hz), −162.4 (m, 2 F_m). **2**: Yield 89% (Found: C, 47.4; H, 2.6; N, 7.7. $C_{22}H_{14}N_3F_5O_2Pd$ requires C, 47.7; H, 2.6; N, 7.6%). Mp 288 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1658, ν(Pd–C_6F_5) 792. ^1H NMR ($CDCl_3$) δ 8.07 (d, 1 H, H_α, $J(H_\alpha H_\beta) = 5.6$ Hz), 7.79 (s, 2 H, $H_\delta + H_{\delta'}$), 7.72 (d, 1 H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.8$ Hz), 7.21 (d, 1 H, H_β, $J(H_\alpha H_\beta) = 5.6$ Hz), 7.08 (d, 1 H, $H_{\beta'}$, $J(H_{\alpha'}H_{\beta'}) = 5.8$ Hz), 6.49 (s, 2 H, mal), 2.47 (s, 3 H, Me_2bipy), 2.46 (s, 3 H, Me_2bipy). ^{19}F NMR ($CDCl_3$) δ −118.8 (d, $2F_o$, $J(F_oF_m) = 21.2$ Hz), −160.1 (t, 1 F_p, $J(F_mF_p) = 19.8$ Hz), −162.9 (m, 2 F_m). **3**: Yield 92% (Found: C, 39.3; H, 3.6; N, 8.7. $C_{16}H_{18}N_3F_5O_2Pd$ requires C, 39.6; H, 3.7; N, 8.7%). Mp 233 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1652, ν(Pd–C_6F_5) 810. ^1H NMR ($CDCl_3$) δ 6.32 (s, 2 H, mal), 2.67 (m, 4 H, CH_2), 2.59 (s, 6 H, CH_3), 2.55 (s, 6 H, CH_3). ^{19}F NMR ($CDCl_3$) δ −118.9 (d, $2F_o$, $J(F_oF_m) = 21.7$ Hz), −160.3 (t, 1 F_p, $J(F_mF_p) = 19.8$ Hz), −162.9 (m, 2 F_m). **4**: Yield 76% (Found: C, 45.2; H, 2.5; N, 7.8. $C_{20}H_{12}N_3F_5O_2Pd$ requires C, 45.5; H, 2.3; N, 8.0%). Mp: 292 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1630, ν(Pd–C_6F_5) 792. ^1H NMR ($CDCl_3$) δ 8.29 (d, 1 H, H_α, $J(H_\alpha H_\beta) = 5.2$ Hz), 8.11 (m, 4 H, $H_\gamma + H_{\gamma'} + H_\delta + H_{\delta'}$), 7.96 (d, 1 H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.52 (m, 1 H, H_β), 7.39 (m, 1 H, $H_{\beta'}$), 2.66 (s, 4 H, suc). ^{19}F NMR ($CDCl_3$) δ −118.6 (d, $2F_o$, $J(F_oF_m) = 20.5$ Hz), −159.6 (t, 1 F_p, $J(F_mF_p) = 20.3$ Hz), −162.4 (m, 2 F_m). **5**: Yield 88% (Found: C, 47.8; H, 3.2; N, 7.8. $C_{22}H_{16}N_3F_5O_2Pd$ requires C, 47.5; H, 2.9; N, 7.6%). Mp 181 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1625, ν(Pd–C_6F_5) 790. ^1H NMR ($CDCl_3$) δ 8.05 (d, 1 H, H_α, $J(H_\alpha H_\beta) = 5.6$ Hz), 7.78 (s, 2 H, $H_\delta + H_{\delta'}$), 7.71 (d, 1 H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.7$ Hz), 7.23 (d, 1 H, H_β, $J(H_\alpha H_\beta) = 5.6$ Hz), 7.08 (d, 1 H, $H_{\beta'}$, $J(H_{\alpha'}H_{\beta'}) = 5.7$ Hz), 2.70 (s, 6 H, Me_2bipy), 2.47 (s, 4 H, suc). ^{19}F NMR ($CDCl_3$) δ −118.6 (d, $2F_o$, $J(F_oF_m) = 20.9$ Hz), −160.2 (t, 1 F_p, $J(F_mF_p) = 20.6$ Hz), −162.9 (m, 2 F_m). **6**: Yield 87% (Found: C, 39.1; H, 4.1; N, 8.4. $C_{16}H_{20}N_3F_5O_2Pd$ requires C, 39.4; H, 4.1; N, 8.6%). Mp 244 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1644, ν(Pd–C_6F_5) 784. ^1H NMR ($CDCl_3$) δ 2.74 (m, 4 H, CH_2 tmeda), 2.67 (s, 6 H, CH_3), 2.61 (s, 6 H, CH_3), 2.44 (s, 4 H, suc). ^{19}F NMR ($CDCl_3$) δ −118.3 (d, $2F_o$, $J(F_oF_m) = 21.7$ Hz), −160.4 (t, 1 F_p, $J(F_mF_p) = 19.8$ Hz), −162.9 (m, 2 F_m). **7**: Yield 77% (Found: C, 44.9; H, 2.1; N, 6.4. $C_{24}H_{12}N_3F_5O_2Pd$ requires C, 45.2; H, 1.9; N, 6.6%). Mp 295 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1662, ν(Pd–C_6F_5) 794. ^1H NMR ($CDCl_3$) δ 8.32 (d, 1 H,

H_α, $J(H_\alpha H_\beta) = 5.2$ Hz), 8.12 (m, 4 H, $H_\gamma + H_{\gamma'} + H_\delta + H_{\delta'}$), 7.97 (d, 1 H, $H_{\alpha'}$, $J(H_{\alpha'} H_{\beta'}) = 5.3$ Hz), 7.65 (m, 4 H, pht), 7.41 (m, 2 H, $H_\beta + H_{\beta'}$). ^{19}F NMR ($CDCl_3$) δ −118.5 (d, 2F_o, $J(F_o F_m) =$ 21.7 Hz), −159.6 (t, 1 F_p, $J(F_m F_p) = 19.8$ Hz), −162.4 (m, 2 F_m). **8**: Yield 86% (Found: C, 51.5; H, 2.9; N, 6.7. $C_{26}H_{16}N_3F_5O_2Pd$ requires C, 51.7; H, 2.7; N, 7.0%). Mp 269 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1664, ν(Pd–C_6F_5) 792. ^{1}H NMR ($CDCl_3$) δ 8.17 (d, 1 H, H_α, $J(H_\alpha H_\beta) = 5.4$ Hz), 7.89 (s, 2 H, $H_\delta + H_{\delta'}$), 7.82 (d, 1 H, $H_{\alpha'}$, $J(H_{\alpha'} H_{\beta'}) = 5.4$ Hz), 7.65 (m, 4 H, pht), 7.22 (d, 1 H, H_β, $J(H_\alpha H_\beta) = 5.4$ Hz), 7.17 (d, 1 H, $H_{\beta'}$, $J(H_{\alpha'} H_{\beta'}) =$ 5.4 Hz), 2.54 (s, 3 H, Me_2bipy), 2.52 (s, 3 H, Me_2bipy). ^{19}F NMR ($CDCl_3$) δ −118.4 (d, 2F_o, $J(F_o F_m) = 20.6$ Hz), −160.1 (t, 1 F_p, $J(F_m F_p) = 20.9$ Hz), −162.7 (m, 2 F_m). **9**: Yield 95% (Found: C, 44.5; H, 3.8; N, 7.5. $C_{20}H_{20}N_3F_5O_2Pd$ requires C, 44.8; H, 3.8; N, 7.8%). Mp 250 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1660, ν(Pd–C_6F_5) 786. ^{1}H NMR ($CDCl_3$) δ 7.52 (m, 4 H, pht), 2.78 (m, 4 H, CH_2 tmeda), 2.69 (s, 6 H, CH_3), 2.65 (s, 6 H, CH_3). ^{19}F NMR ($CDCl_3$) δ −118.5 (d, 2F_o, $J(F_o F_m) = 25.0$ Hz), −160.4 (t, 1 F_p, $J(F_m F_p) = 21.4$ Hz), −162.8 (m, 2 F_m).

Preparation of complex [NBu_4][Pd(C_6F_5)(succinimidate)$_2$(OH_2)] (10). To a solution of succinimide (66.7 mg, 0.666 mmol) in methanol (5 mL) was added 20% [NBu_4]OH (aq) (873 μL, 0.666 mmol). To the resulting solution was added a solution of [NBu_4]$_2$[{Pd(C_6F_5)(Br)(μ-Br)}$_2$] (150 mg, 0.111 mmol) in methanol (10 mL). The mixture was stirred at room temperature for 12 h and then solvent was partially evaporated under reduced pressure. On addition of water the white complex **10** precipitated and was filtered off and air-dried. **10**: Yield 92% (Found: C, 49.1; H, 6.6; N, 5.6. $C_{30}H_{46}N_3F_5O_5Pd$ requires C, 49.4; H, 6.4; N, 5.8%). Mp: 190 °C (decomp.). IR (Nujol, cm^{-1}) 3450 ν(O–H, H_2O), ν(C=O) 1632, ν(Pd–C_6F_5) 793. ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 8 H, suc). ^{19}F NMR ($CDCl_3$) δ −116.1 (d, 2F_o, $J(F_o F_m) =$ 26.4 Hz), −164.2 (t, 1 F_p, $J(F_m F_p) = 20.7$ Hz), −166.3 (m, 2 F_m).

Preparation of complexes [NBu_4][Pd(C_6F_5)(succinimidate)$_2$(L)] (L = *t*-BuNC 11, PPh_3 12). To a solution of succinimide (78.1 mg, 0.78 mmol) in methanol (5 mL) was added 20% [NBu_4]OH (aq) (1.02 mL, 0.78 mmol). To the resulting solution was added a solution of [{Pd(C_6F_5)(L)(μ-Cl)}$_2$] (L = *t*-BuNC or PPh_3) (0.13 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 12 h and then solvent was removed under reduced pressure and the residue was treated with dichloromethane/hexane. The white solid was filtered off and air-dried. **11**: Yield 78% (Found: C, 52.7; H, 6.6; N, 6.9. $C_{35}H_{53}N_4F_5O_4Pd$ requires C, 52.9; H, 6.7; N, 7.1%). Mp 187 °C (decomp.). IR (Nujol, cm^{-1}) 2214 ν(CN), ν(C=O) 1622, ν(Pd–C_6F_5) 786. ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 4 H, suc), 2.33 (s, 4 H, suc), 1.37 (s, 9H, *t*-Bu). ^{19}F NMR ($CDCl_3$) δ −116.0 (d, 2F_o, $J(F_o F_m) = 23.0$ Hz), −162.2 (t, 1 F_p, $J(F_m F_p) = 23$ Hz), −164.9 (m, 2 F_m). **12**: Yield 83% (Found: C, 58.9; H, 6.3; N, 4.5. $C_{48}H_{59}N_3F_5PO_4Pd$ requires C, 59.2; H, 6.1; N, 4.3%). Mp 213 °C (decomp.). IR (Nujol, cm^{-1}) ν(C=O) 1615, ν(Pd–C_6F_5) 787. ^{1}H NMR ($CDCl_3$) δ 7.63 (m, 6 H, Ph), 7.30 (m, 9 H, Ph), 2.28 (s, 4 H, suc), 1.85 (s, 4 H, suc). ^{19}F NMR ($CDCl_3$) δ −114.2 (d, 2F_o, $J(F_o F_m) = 30.0$ Hz), −163.3 (t, 1 F_p, $J(F_m F_p) = 18.8$ Hz), −164.9 (m, 2 F_m). ^{31}P NMR ($CDCl_3$) δ 25.5 (s).

General method for the Suzuki coupling of aryl halides with phenylboronic acid

All reactions were performed in a Radley's carousel adapted for rigorous inert atmosphere reactions. To a mixture of the appropriate aryl halide (2.5 mmol), aryl boronic acid (471.4 mg, 3.75 mmol), the appropriate base (5 mmol), toluene (7.5 mL) and hexadecane (0.102 mmol, internal standard) was added the Pd catalyst as a toluene solution made up to the correct concentration by multiple volumetric dilutions of a stock solution (for the aryl bromides) or as solid (for the aryl chlorides). In some cases tricyclohexylphosphine (P : Pd ratio 2 : 1 or 1 : 1) was also added. The resultant mixture was then heated at 110 °C for 18 h, cooled in an ice bath, and an aliquot of 0.2 mL was extracted to which HCl(aq) (2 M, 0.5 mL) was added to quench the reaction. The aqueous layer was extracted with toluene (3 × 1 mL). The organic extract was dried over $MgSO_4$. The conversion to product was determined by GC.

X-Ray crystal structure analysis

Suitable crystals of **3**·H_2O·0.5$CHCl_3$, **10**·H_2O and **11**·2H_2O were grown from chloroform–hexane. Data collection for **10**·H_2O and **11**·2H_2O was performed at −173 °C on a Bruker smart CCD diffractometer with a nominal crystal to detector distance of 4.5 cm. Diffraction data were collected based on a ω scan run. A total of 2524 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package[55] and corrected for absorption with SADABS.[56] Data collection for **3**·H_2O·0.5$CHCl_3$ was performed at −100 °C on a Siemens P4 diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms.[57]

Crystallographic data for the compounds are listed in Table 10.

Table 10 Crystal structure determination details

	3·H_2O·0.5$CHCl_3$	**10**·H_2O	**11**·2H_2O
Formula	$C_{32}H_{36}F_{10}N_6O_4Pd_2$·2$H_2O$·$CHCl_3$	$C_{30}H_{46}F_5N_3O_5Pd$·H_2O	$C_{35}H_{53}F_5N_4O_4Pd$·2H_2O
M	1126.87	747.4	831.25
Crystal system	Monoclinic	Monoclinic	Triclinic
a/Å	15.2880(10)	10.3563(5)	10.1604(5)
b/Å	14.3170(10)	41.9620(18)	10.3459(5)
c/Å	20.7880(10)	24.4230(11)	20.5010(10)
α/°	90	90	82.1130(10)
β/°	107.000(10)	97.77(1)	80.4260(10)
γ/°	90	90	69.3144(8)
V/Å^3	4351.2(5)	10516.1(8)	1980.81(17)
T/K	173(2)	100(2)	100(2)
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	12	2
μ/mm^{-1}	1.102	0.599	0.538
Reflections collected	10391	122099	23353
Independent reflections	7639	24434	8933
R_{int}	0.0346	0.0378	0.0412
$R1$ [$I > 2\sigma(I)$][a]	0.0450	0.0853	0.0488
wR_2(all data)[b]	0.1309	0.1796	0.1238

[a] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{0.5}$. [b] $w = 1/[\sigma^2((F_o^2) + (aP)^2 + bP]$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

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See http://www.rsc.org/suppdata/dt/b5/b503101j/ for crystallographic data in CIF or other electronic format.

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