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PAPER

Cyclopropenylidene carbene ligands in palladium catalysed coupling reactions: carbene ligand rotation and application to the Stille reaction†

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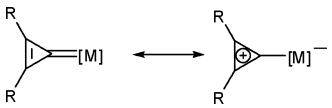
Reaction of $[Pd(PPh_3)_4]$ with 1,1-dichloro-2,3-diarylcyclopropenes gives complexes of the type *cis*-$[PdCl_2(PPh_3)(C_3(Ar)_2)]$ (Ar = Ph **5**, Mes **6**). Reaction of $[Pd(dba)_2]$ with 1,1-dichloro-2,3-diarylcyclopropenes in benzene gave the corresponding binuclear palladium complexes *trans*-$[PdCl_2(C_3(Ar)_2)]_2$ (Ar = Ph **7**, *p*-$(OMe)C_6H_4$ **8**, *p*-$(F)C_6H_4$ **9**). Alternatively, when the reactions were performed in acetonitrile, the complexes *trans*-$[PdCl_2(NCMe)(C_3(Ar)_2)]$ (Ar = Ph **10**, *p*-$(OMe)C_6H_4$ **11** and *p*-$(F)C_6H_4$) **12**) were isolated. Addition of phosphine ligands to the binuclear palladium complex **7** or acetonitrile adducts **11** and **12** gave complexes of the type *cis*-$[PdCl_2(PR_3)(C_3(Ar)_2)]$ (Ar = Ph, R = Cy **13**, Ar = *p*-$(OMe)C_6H_4$, R = Ph **14**, Ar = *p*-$(F)C_6H_4$, R = Ph **15**). Crystal structures of complexes **6**·3.25$CHCl_3$, **10**, **11**·H_2O and **12–15** are reported. DFT calculations of complexes **10–12** indicate the barrier to rotation about the carbene-palladium bond is very low, suggesting limited double bond character in these species. Complexes **5–9** were tested for catalytic activity in C–C coupling (Mizoroki–Heck, Suzuki–Miyaura and, for the first time, Stille reactions) and C–N coupling (Buchwald–Hartwig amination) showing excellent conversion with moderate to high selectivity.

Introduction

N-heterocyclic carbenes are versatile supporting ligands for homogeneous catalysis,[1] their strong σ-donor capabilities resulting in advantages over many other ligand types in a range of reactions, including C–C and C–N coupling.[2] Numerous variations to the structure of *N*-heterocyclic carbene ligands have been investigated, often giving marked improvements in performance.[3] It is perhaps surprising that other types of carbene ligand are much less studied as supporting ligands in catalysis; for example, carbocyclic carbene ligands, *i.e.*, with no heteroatom, are much rarer.[4] This lack of utility in catalysis is despite a wide range of such ligands being reported in the synthetic organometallic literature. As early as 1968, Öfele reported the stable carbocyclic carbene complex $[Cr(CO)_5$(2,3-diphenylcyclopropenylidene)].[5] We were attracted to this result, particularly the reported CO stretching frequencies of the complex which suggest that the 3-membered ring carbene ligand to be an exceptionally strong σ-donor. Kawada and Jones supported this thesis and also indicated such ligands are very robust to thermal and chemical decomposition.[6] The reason for these attributes lies in the possibility of a contribution from a resonance form in which a 2π aromatic cationic cyclopropenium moiety is formed (Scheme 1).



Scheme 1 Cyclopropenylidene ligands.

Certain palladium complexes of related ligands have been reported.[7,8] There has also been recent interest in free carbenes of this type (when R = dialkylamino),[9] extending also to chiral derivatives.[10] However, the potential of cyclopropenylidene carbene complexes in catalysis remained unrealised until our report of the use of such complexes as highly active and efficient catalysts for C–C coupling reactions.[11] In the same year these results were independently confirmed by Herrmann and co-workers.[12] Following these promising results we, and Herrmann *et al.*, extended the utility of cyclopropenylidene carbene complexes to C–N coupling processes.[13] In this full paper, we build on our preliminary communications and report the synthesis of new palladium complexes of cyclopropenylidene ligands which show broad applicability in catalytic C–C and C–N bond forming reactions.

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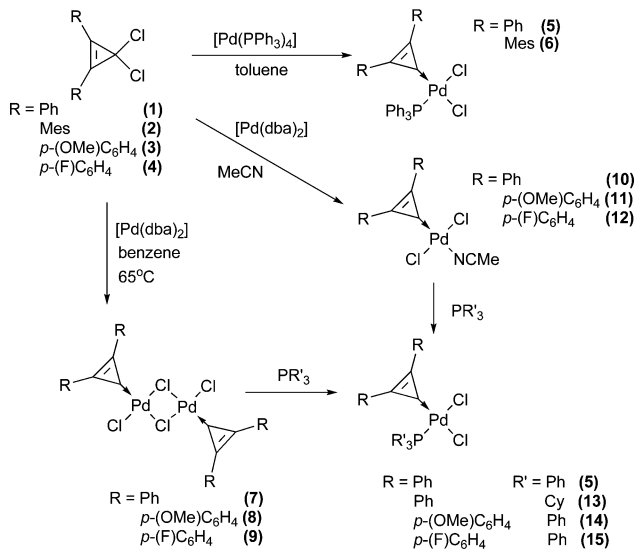
† Electronic supplementary information (ESI) available: Relative energy values for rotation of cyclopropenylidene ligands about the Pd–C1 bond in complexes **10**, **11** and **12**. Catalysis data and experimental details for selected Mizoroki–Heck, Suzuki–Miyaura and Buchwald–Hartwig reactions. Crystal structures of complexes **13**, **14** and **15**. Cif files for all structures are available. CCDC reference numbers 809246–809254. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10109a

Results and discussion

1. Synthesis of ligands and palladium complexes

The carbene precursors 1,1-dichloro-2,3-diphenylcyclopropene (**1**) and 1,1-dichloro-2,3-dimesitylcyclopropene (**2**) can be conveniently prepared from commercially available diphenylcyclopropenone and dimesitylcyclopropenone, respectively. The aryl functionalised 1,1-dichloro-2,3-diarylcyclopropenes **3** and **4** (aryl = *p*-(OMe)C_6H_4 **3** and *p*-(F)C_6H_4 **4**) are synthesised by first preparing tetrachlorocyclopropene using a modification of Tobey and West's method[14] and then a Friedel–Crafts alkylation of the appropriate aromatic compounds to produce the diarylcyclopropenone precursors.[15] Reactions with thionyl chloride or oxalyl chloride give **3** and **4** in moderate to good yields.

The oxidative addition of 1,1-dichloro-2,3-diarylcyclopropenes (**1–4**) to well-defined soluble Pd(0) sources enables the synthesis of a range of palladium(II) cyclopropenylidene complexes (Scheme 2). Herrmann and co-workers report a complementary synthesis of similar compounds *via* direct addition to metallic palladium;[12] our method certainly suffers from lower atom efficiency in comparison but has the advantage of being reproducible and proceeding smoothly at lower temperatures and shorter reaction times. We have previously reported the synthesis of complexes **5** and **7** and indeed the conversion of **7** to **5** *via* a bridge splitting reaction with triphenylphosphine.[11,13] The reaction of 1,1-dichloro-2,3-diarylcyclopropenes **3** and **4** with [Pd(dba)$_2$] (dba = dibenzylideneacetone) in benzene at 65 °C yields the binuclear palladium complexes **8** and **9** respectively. When the oxidative addition of **1**, **3** and **4** to [Pd(dba)$_2$] is performed using acetonitrile as the solvent mononuclear palladium(II) complexes **10–12** are formed, in which an acetonitrile ligand is bound *trans* to the carbene. Crystals of complexes **10–12** were obtained and studied by X-ray crystallography. The molecular structures are shown in Figures 1–3 with bond distances and angles in Table 1.



Scheme 2 Routes to cyclopropenylidene palladium(II) complexes.

Complexes **10**, **11**·H_2O and **12** crystallise in space groups *C*2/*c*, *Pbcn* and $P2_1/c$, respectively. Complexes **10** and **11**·H_2O have exact C_2 symmetry with one half of the molecule present in the asymmetric unit ($Z' = \frac{1}{2}$). The palladium(II) centres of each complex have a square planar geometry, and are coordinated by the cyclopropenylidene ligand which lies *trans* to an acetronitrile

Table 1 Selected bond distances (Å) and angles (°) for **10**, **11**·H_2O and **12**

	10	**11**·H_2O	**12**
Pd1–C1	1.922(5)	1.929(6)	1.920(8)
Pd1–N1	2.074(5)	2.079(6)	2.087(7)
Pd1–Cl1	2.3030(9)	2.315(4)	2.302(2)
Pd1–Cl2	—	—	2.297(2)
C1–C2	1.374(6)	1.374(7)	1.393(11)
C1–C3	—	—	1.368(11)
C2–C3/C2A	1.354(8)	1.365 (9)	1.387(12)
C1–Pd1–Cl1	88.59(3)	89.82(12)	88.0(3); 88.3(3)
Cl1–Pd1–Cl2	177.19(6)	179.6 (3)	175.49(9)
C2–C1–Pd1	150.49(19)	150.2(2)	148.1(7); 151.6(7)
Pd1–N1–C	180.00(1)	180.0	170.6(8)
C3–C1–C2	59.0(4)	59.6(5)	60.3(6)
Cl1–Pd1–C1–C2	−78.9(3)	−66.3(5)	−39.9(12)
C1–C2–C–C (Ph tilt)	9.4(8)	1.4(11)	−6(2); 2(2)

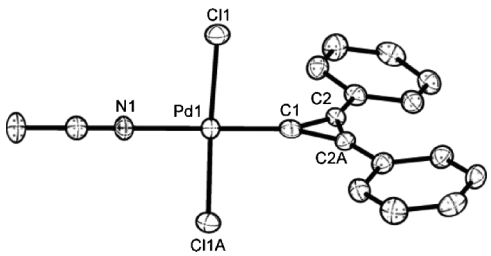


Fig. 1 Thermal ellipsoid plot of **10**, [$PdCl_2$(MeCN)(*cyclo*-$C_3(C_6H_5)_2$)], generated by molecular C_2-symmetry. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

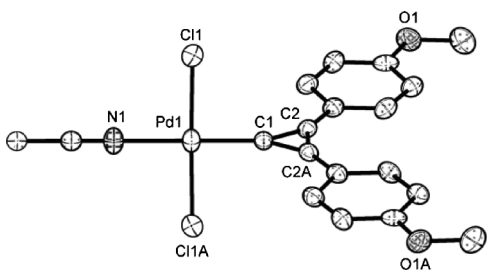


Fig. 2 Thermal ellipsoid plot of **11**·H_2O, [$PdCl_2$(MeCN)(*cyclo*-C_3(*p*-(OMe)$C_6H_4)_2$)], generated by molecular C_2-symmetry. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

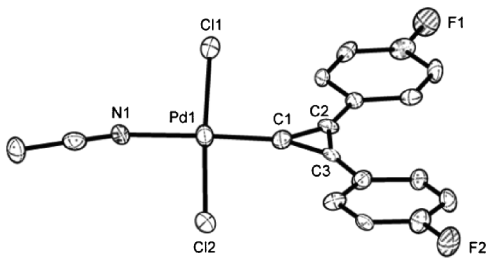


Fig. 3 Thermal ellipsoid plot of **12**, [$PdCl_2$(MeCN)(*cyclo*-C_3(*p*-(F)$C_6H_4)_2$)]. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

ligand and *cis* to two chloride ligands. In each case, the similarity in bond lengths C1–C2 and C2–C3/C2A suggests the carbocyclic ligand is best described by a cyclopropenium resonance form. There is significant variation in the plane of the cyclopropenylidene ligands to the square plane of the complex. In **10** this is approximately perpendicular to the chloride ligand axis, being offset by *ca* 11° (torsion angle Cl1–Pd1–C1–C2 = −78.9°). Whereas cyclopropenylidene planes of complexes **11**·H_2O and **12** are offset from perpendicular to the chloride axis, by *ca* 23° and 50°, respectively (torsion angles and bond lengths are shown in Table 1).

Initially we speculated that variation in the cyclopropenylidene plane may be due to differing π-bonding characteristics for the various ligands; a more co-planar orientation of the carbocyclic ring with the square plane of the complex would maximise possible overlap between the cyclopropenylidene π-system and the palladium d_{yz} or d_{xz} orbitals. Orienting the cyclopropenylidene perpendicular to the square plane would maximise overlap with the d_{xy} orbital. In order to test this hypothesis the geometries in the crystal structures were optimised computationally using DFT, and then the cyclopropenylidene ligand was rotated about the Pd–C1 bond in 15° intervals. The energy profiles for **10**, **11**·H_2O and **12** are very shallow (Figure 4), with a barrier height between 2.5–3 kcal mol^{-1} with a maximum when Cl1–Pd1–C1–C2 = 90° and a minimum close to 40°. There is little distinction between the different ligands, implying the observed structural differences are in fact a manifestation of packing effects. Certainly, in the case of **11**·H_2O and **12**, intermolecular distances between phenyl rings of the cyclopropenylidene ligand are less than 3.6 Å, suggesting π–π stacking may have an influence.

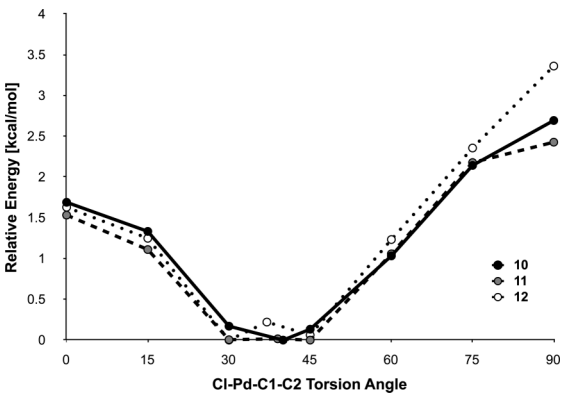


Fig. 4 B3LYP/6-31G*&LACV3P calculated energy barrier for rotation about the Pd–C1 bond in complexes **10**, **11** and **12**.

The oxidative addition of 1,1-dichloro-2,3-diarylcyclopropenes **1** and **2** to [$Pd(PPh_3)_4$] gives cyclopropenylidene phosphine complexes **5** (previously published and structurally characterised[11]) and **6** (Scheme 2). Crystals of **6**·3.25$CHCl_3$ were obtained from a saturated chloroform and hexane solution and crystallised in space group $P\bar{1}$ (see Figure 5 and Table 2 for bond distances and angles). The structure includes three molecules of chloroform, and a fourth chloroform was located in the asymmetric unit with 25% occupancy, disordered over two positions. The palladium(II) centre has square planar geometry, and is coordinated by the cyclopropenylidene ligand *cis* to PPh_3, both of which are *trans* to a chloride ligand.

Table 2 Selected bond distances (Å) and angles (°) for **6**·3.25$CHCl_3$

	6·3.25$CHCl_3$
Pd1–C1	1.941(4)
Pd1–P1	2.2552(11)
Pd1–Cl1 (*trans* P1)	2.3668(10)
Pd1–Cl2 (*trans* C1)	2.3451(10)
C1–C2	1.392(6)
C1–C3	1.380(6)
C2–C3	1.372(5)
C1–Pd1–Cl1	82.65(13)
C1–Pd1–P1	94.83(13)
Cl1–Pd1–Cl2	91.79(4)
C2–C1–Pd1	145.5(3)
C3–C1–C2	59.3(3)
Cl1–Pd1–C1–C2	– 78.4(7)
Cl1–Pd1–C1–C3	65.9(6)
C1–C2–C4/C13–C5/C18 (Ph tilt)	25.4(10), 54.3(9)

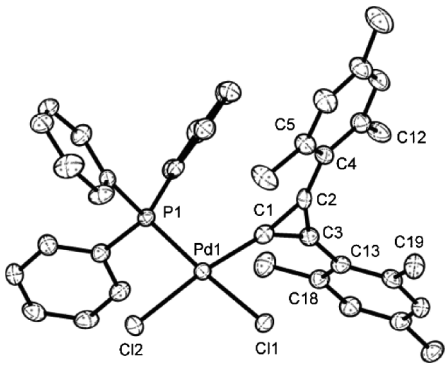


Fig. 5 Thermal ellipsoid plot of complex **6**·3.25$CHCl_3$, [$PdCl_2$(*cyclo*-$C_3(Mes)_2$)(PPh_3)]. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms and solvent molecules have been omitted for clarity.

The plane of the cyclopropenylidene ring is approximately perpendicular to the coordination plane (torsion angle Cl1–Pd1–C1–C2 = −78.4°). The mesityl substituents do not lie in the same plane as the cyclopropenyl ring (torsion angles C1–C2–C4–C5 = 25.4° and C1–C3–C13–C18 = 54.3 °), but are tilted to reduce the steric clash between carbon atoms at the internal *ortho* positions (C12 and C19). The palladium–chlorine bond length *trans* to the carbene (Pd1–Cl2) is slightly shorter than that *trans* to the phosphine (Pd1–Cl1) by 0.021 Å. This is in agreement with the previously reported structure of complex **5**, and suggests that the *trans* influence of the phosphine ligand is stronger than that of the cyclopropenylidene. In 1979, Ibers and co-workers reported the same *trans* influence effect in their complex, [$PdCl_2$(2,3-bis(dimethylamino)cyclopropenylidene)(P^nBu_3)].[8] Pd–Cl bond lengths *trans* to the carbene and the phosphine are 2.361(1) Å and 2.385(1) Å, respectively. The Pd-carbene bond length in **6**·3.25$CHCl_3$ (Pd1–C1 1.941(4) Å) is slightly shorter than the equivalent bond length in Ibers' complex (1.961(3) Å) and in both Herrmann's cycloheptatrienylidene[16] and cyclopropenylidene[12] complexes (1.968(2) Å and 1.945(2) Å, respectively), but slightly longer than our 2,3-diphenylcyclopropenylidene complex (1.939(3) Å).[11] This suggests that there is little influence of electron donation from the mesityl groups on the cyclopropenylidene ring compared to phenyl groups.

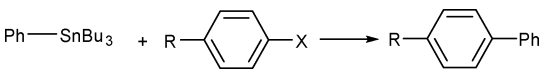
Complexes of this type, containing mutually *cis* phosphine and carbene ligands, can also be prepared by bridge splitting reactions of **7–9** with suitable phosphine ligands (*e.g.*, **5** and **13** were prepared by reaction of **7** with triphenylphosphine and tricyclohexylphosphine respectively) or by reaction of a phosphine with complexes **10–12** (*e.g.* **14** and **15** were prepared by reaction of triphenylphosphine with **11** and **12** respectively) (Scheme 2). Complexes **13**, **14** and **15** were also structurally characterised. The molecular structures are as expected and are included in the supplementary information.

2. Catalytic results

A selection of cyclopropenylidene complexes were tested in four well-known catalytic coupling reactions; Stille, Mizoroki–Heck and Suzuki–Miyaura C–C cross coupling and Buchwald–Hartwig C–N coupling reactions. We have published preliminary data for all except the first of these reactions previously, and the new palladium complexes described in this paper exhibit very similar performance; the relevant catalysis data, including conversion and yields, is presented in the supplementary information.†

We have not previously communicated the use of cyclopropenylidene catalysts in Stille cross coupling reactions, and a range of substrates was investigated, as shown in Table 3. Some interesting trends emerge. Complex **7** has good performance across a range of substrates with both high conversion and selectivity; complexes **5**, **6**, **8** and **9** give rise to good conversion but are less selective. Chloroarene substrates prove more challenging although good conversions are observed when basic phosphines are added as co-ligands; selectivity with these substrates is capricious but modestly high selectivity is observed in selected examples.

Table 3 Catalytic activity of cyclopropenylidene palladium(II) complexes in Stille coupling reactions



[a]Entry	X	Cat.	R	[b]phosphine	mol % Pd	[c]conversion (yield)/%	TON
1	Br	**7**	OMe	PPh_3	2	52(52)	26
2	Br	**7**	OMe	P^tBu_3	2	66(66)	33
3	Br	**7**	C(O)Me	PPh_3	2	98(98)	49
4	Br	**7**	C(O)Me	P^tBu_3	2	98(98)	49
5	Br	7	CH_3	PPh_3	2	36(36)	18
6	Br	**7**	CH_3	P^tBu_3	2	54(54)	27
7	Br	**8**	OMe	PPh_3	2	100(48)	24
8	Br	**8**	OMe	P^tBu_3	2	100(50)	25
9	Br	**8**	C(O)Me	PPh_3	2	100(47)	24
10	Br	**8**	C(O)Me	P^tBu_3	2	100(51)	26
11	Br	**9**	C(O)Me	PPh_3	2	99(50)	25
12	Br	**9**	C(O)Me	P^tBu_3	2	100(42)	21
13	Br	**5**	OMe	none	2	96(11)	6
14	Br	**5**	C(O)Me	none	2	94(19)	10
15	Br	**6**	OMe	none	2	100(20)	10
16	Br	**6**	C(O)Me	none	2	94(15)	8
17	Cl	**7**	OMe	PPh_3	2	0(0)	0
18	Cl	**7**	OMe	P^tBu_3	2	84(84)	42
19	Cl	**7**	C(O)Me	PPh_3	2	0(0)	0
20	Cl	**7**	C(O)Me	P^tBu_3	2	98(98)	49
21	Cl	**7**	CH_3	PPh_3	2	0(0)	0
22	Cl	**7**	CH_3	P^tBu_3	2	76(76)	38
23	Cl	**8**	C(O)Me	PPh_3	2	96(40)	20
24	Cl	**8**	C(O)Me	P^tBu_3	2	100(27)	14
25	Cl	**8**	OMe	P^tBu_3	2	92(28)	14
26	Cl	**9**	C(O)Me	PPh_3	2	95(6)	3
27	Cl	**9**	C(O)Me	P^tBu_3	2	100(38)	19

[a] Conditions: 1.0 mmol aryl halide, 1.1 mmol Bu_3SnPh, 2 mL dioxane diluent, 1.1 mmol CsF base, 90 °C, 18 h. [b] 1 mol equiv. of phosphine with respect to amount of palladium used. [c] Conversion and yield were determined by GC relative to the internal standard hexadecane. Products were checked by NMR spectroscopy against authentic samples.[17]

We have previously reported 'standard blank' experiments using palladium phosphine complexes in the absence of cyclopropenylidene moieties.[13] We have also reported how plots of conversion with time reveal no catalyst initiation period in both Heck[11] and Buchwald–Hartwig[13] coupling. These results confirm that the cyclopropenylidene ligand is influencing catalytic performance but, given that so many 'homogeneous' palladium coupling catalysts are in fact likely to be colloidal palladium metal,[18] it is prudent to avoid bold claims in this regard. To date, we have been unable to detect bound cyclopropenylidene species during ongoing catalytic runs using ^1H or ^{13}C NMR spectroscopy (although detection of such species is hampered by the high concentration of other species including substrates and products). Although it is tempting to attribute the superior performance of these catalysts to cyclopropenylidene complexes during the catalytic cycle, until such species are detected, we cannot rule out a role for such ligands in facilitating the initiation of the palladium(II) procatalysts to ligand-free palladium(0) active species.

Conclusions

Palladium complexes supported by cyclopropenylidene ligands may be conveniently synthesised by the addition of 1,1-dichloro-2,3-diarylcyclopropenes to palladium(0) sources. Structural characterisation of a number of these compounds reveals the coordinated cyclopropenylidene ligand is best described as a cyclopropenium moiety. DFT calculations suggest that variations to the torsion angle of these ligands with respect to the square plane of the complex are not significant in terms of ligand bonding effects. Such palladium complexes are effective in a wide range of Pd-catalysed coupling reactions.

Experimental

General procedures

All procedures were carried out under an inert (N_2) atmosphere using standard Schlenk line techniques or in an inert atmosphere (Ar) glovebox. Chemicals were obtained from Sigma–Aldrich, Fisher Scientific, Acros Organics, Fluka, or Alfa Aesar and used without further purification unless otherwise stated. Tetrachlorocyclopropene was synthesised by the literature method.[19] All solvents were purified using an Anhydrous Engineering Grubbs-type solvent system.[20] NMR spectra were recorded on Jeol ECP 300, Jeol Lambda 300, Jeol ECP 400 or Varian 400-MR spectrometers. ^1H NMR chemical shifts were referenced relative to the residual solvent resonances in the deuterated solvent. $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were referenced relative to TMS, $CFCl_3$ and H_3PO_4 respectively at 23 °C. Mass spectra were recorded on a VG Analytical Quattro (ESI) or a VG Autospec (EI) spectrometer. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at

Table 4 Crystallographic data for structures **6**·3.25$CHCl_3$, **10**, **11**·H_2O and **12**

Compounds	**6**·3.25$CHCl_3$	**10**	**11**·H_2O	**12**
Colour, habit	Colourless block	Yellow plate	Yellow lath	Yellow rod
Size/mm	0.15 × 0.11 × 0.06	0.07 × 0.05 × 0.02	0.12 × 0.08 × 0.02	0.078 × 0.023 × 0.02
Empirical formula	$C_{42.25}H_{40.25}Cl_{11.75}PPd$	$C_{17}H_{13}Cl_2NPd$	$C_{19}H_{18}Cl_2NO_{2.5}Pd$	$C_{17}H_{11}Cl_2F_2NPd$
M	1101.90	408.58	477.64	444.57
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$Pbcn$	$P2_1/c$
a/Å	11.4288(6)	10.4687(4)	15.7371(8)	13.0238(8)
b/Å	13.7141(8)	18.5853(7)	16.6448(9)	7.3625(4)
c/Å	17.3825(10)	8.5376(4)	7.4293(4)	17.0969(9)
α/°	94.734(4)	90.00	90.00	90.00
β/°	106.928(3)	110.274(2)	90.00	92.697(3)
γ/°	108.301(3)	90.00	90.00	90.00
V/A^3	2428.8(2)	1558.2(11)	1946.04(18)	1637.6(16)
Z	2	4	4	4
μ/mm^{-1}	1.091	1.525	1.243	1.476
T/K	100 (2)	120(2)	120(2)	120(2)
Reflections: total/independent	57 119/11 894	8623/1776	9707/2227	15 754/3755
R_{int}	0.0827	0.0545	0.0564	0.1310
Final R1 (observed data)	0.0533	0.0418	0.0547	0.0891
Largest peak, hole/eA^{-3}	2.44, –1.93	0.58, –0.54	0.63, –0.73	0.98, –0.89
ρ_{calc}/g cm^{-3}	1.507	1.74	1.63	1.80

the University of Bristol. All catalytic samples were analysed by GC-FID, using a Varian L3800 gas chromatograph, fitted with a Varian WC07 fused silica capillary column, 25 m × 0.25 mm, ID coating CP-Sil 5CB, DF = 0.25. Method: hold at 50 °C for 4 min, heat to 58 °C at 1 °C min^{-1}, heat to 200 °C at 40 °C min^{-1}, hold at 200 °C for 5 min, heat to 250 °C at 50 °C min^{-1}, hold at 250 °C for 5 min.

Crystal structure determination

X-ray diffraction experiments for **10**, **11**·H_2O and **12** were carried out at 120 K on a Bruker–Nonius Kappa CCD diffractometer, using Mo-Kα radiation (λ = 0.71073 Å) generated by a Bruker–Nonius FR591 rotating anode. All data collections were performed using a single crystal coated in paraffin oil and mounted on a glass fibre. Intensities were integrated[21] from several series of exposures in φ and ω calculated by the COLLECT[22] and DENZO programs after unit cell determination by the DirAx program. X-ray diffraction on **6**·3.25$CHCl_3$ was carried out at 100 K on a Bruker Kappa Apex II CCD diffractometer. Intensities were integrated[23] from several series of exposures in φ and ω calculated by the Apex II[24] program after unit cell determination. Absorption corrections were based on equivalent reflections using SADABS, and structures were refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL. The high R_{int} and $R1$ values for **12** reflect the fact that all crystals of **12** diffracted only weakly at high angle, despite data being collected for an extended period. Crystal structure and refinement data are given in Table 4.

Computation

All geometries were optimised in the gas phase using the Jaguar package[25] and the standard Becke–Lee–Yang–Parr (B3LYP)[26] hybrid density function. The Jaguar triple-ζ form of the standard Los Alamos ECP basis set (LACV3P) was used to describe the palladium atom, employing the 6-31G* basis for all other atoms. The geometries for computation were taken from crystal structures **10**, **11**·H_2O and **12**, and were individually optimized before torsion angle restraints were applied, to build up the energy profile of rotating the cyclopropenylidene ligand about the Pd–C1 bond.

Synthesis of diarylcyclopropenone precursors

Diarylcyclopropenone precursors were synthesised using a modification of Poloukhtine and Popik's method.[15]

2,3-di(*p*-methoxyphenyl)cyclopropenone. A solution of methoxybenzene (1.90 mL, 17.40 mmol) in 5 mL of dichloromethane was added to a suspension of aluminium trichloride (1.40 g, 10.50 mmol) in tetrachlorocyclopropene (1.00 mL, 8.70 mmol) at –78 °C. The reaction mixture was stirred for 2 h at low temperature. The reaction mixture was allowed to warm to room temperature and stirred for 30 min before ice was added. The product was extracted into dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude solid was purified by precipitation from a 1 : 10 dichloromethane/hexane solution to give a colourless powder (980 mg, 42%) (Found: C, 77.3; H, 5.4, Calc. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3%); δ_H(300 MHz; $CDCl_3$) 7.92 (4 H, d, $^3J_{HH}$ 8.9 Hz, Ar*H*), 7.06 (4 H, d, $^3J_{HH}$ 8.6 Hz, Ar*H*), 3.91 (6 H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 162.6 (Ar*C*), 155.2 (*C*$_3$ ring), 144.0 (*C*O), 133.4 (Ar*C*), 117.0 (Ar*C*), 114.6 (Ar*C*), 55.5 (*C*H_3); *m*/*z* (ESI): 267 (M^+ + H).

2,3-di(*p*-fluorophenyl)cyclopropenone. Essentially the same procedure was followed, only using fluorobenzene (6.50 mL, 69.00 mmol), aluminium trichloride (2.28 g, 17.10 mmol) and tetrachlorocyclopropene (2.00 mL, 16.30 mmol). The reaction mixture was stirred at 0 °C for 10 min and then increased to 50 °C for 2 h. The crude solid was purified by recrystallisation from a methanol/diethyl ether solution to give colourless crystals (1.90 g, 45%) (Found: C, 74.1; H 3.8, Calc. for $C_{15}H_8F_2O$: C, 74.4; H, 3.3%); δ_H(300 MHz, $CDCl_3$) 7.98 (4 H, dd, $^3J_{HH}$ 5.3 Hz, Ar*H*), 7.28 (4 H, t, $^3J_{HH}$ 8.6 Hz, Ar*H*); δ_C(75 MHz, $CDCl_3$) 165.0 (d, $^1J_{CF}$

257 Hz *C*F), 154.7 (*C*$_3$ ring), 146.2 (*C*O), 133.7 (d, $^3J_{CF}$ 9 Hz, Ar*C*) 120.4 (d, $^4J_{CF}$ 4 Hz, Ar*C*), 116.8 (d, $^2J_{CF}$ 22 Hz, Ar*C*); δ_F(283 MHz, $CDCl_3$) −103.2 (s); *m*/*z* (ESI): 243 (M^+ + H).

Synthesis of 1,1-dichloro-2,3-diarylcyclopropenes

1,1-dichloro-2,3-diarylcyclopropenes **1–3** are synthesised using a modification of Tobey and West's method.[14] **4** was synthesised following a modification of Herrmann's method.[12]

1,1-dichloro-2,3-diphenylcyclopropene (1). Diphenylcyclopropenone (500 mg, 2.40 mmol) was heated at 40 °C in excess thionyl chloride (2 mL). The resulting solution was stirred and the evolution of SO_2 was observed. The reaction mixture was stirred for approximately 2 h until gas evolution ceased. The volatiles were removed *in vacuo* to give a beige powder. The solid was dissolved in cyclohexane (6 mL) with heating and placed in a freezer overnight to give **1** as pale yellow crystals (550 mg, 88%) (Found: C, 69.0; H, 4.25, Calc. for $C_{15}H_{10}Cl_2$: C, 69.0; H, 3.9%); δ_H(300 MHz, $CDCl_3$) 7.56 (10 H, m, Ar*H*); δ_C(75 MHz, $CDCl_3$) 131.4, 130.4, 129.5 (Ar*C*), 128.4 (Ar*C*), 125.9 (Ar*C*), 92.7 (*C*Cl_2); *m*/*z* (EI): 225 (M^+ − Cl, 100%), 189.1 (M^+ − 2Cl, 50).

1,1-dichloro-2,3-dimesitylcyclopropene (2). An analogous procedure was followed, using mesitylcyclopropenone (523 mg, 1.80 mmol) to give **2** as a white powder (570 mg, 91%) (Found: C, 72.8; H, 6.45, Calc. for $C_{21}H_{22}Cl_2$: C, 73.0; H, 6.4%); δ_H(400 MHz, $CDCl_3$) 6.99 (4 H, s, Ar*H*), 2.38 (12 H, s, *o*-C*H*$_3$), 2.35 (6 H, s, *p*-C*H*$_3$); δ_C(100 MHz, $CDCl_3$) 151.2 (Ar*C*), 140.6 (Ar*C*), 139.7 (*C*$_3$ ring), 130.1(Ar*C*), 128.9 (Ar*C*), 95.7 (*C*Cl_2), 21.5 (*p*-*C*H$_3$), 20.7 (*o*-*C*H$_3$); *m*/*z* (EI): 309 (M^+ − Cl, 60%), 274 (M^+ − 2Cl, 10).

1,1-dichloro-2,3-di(*p*-methoxyphenyl)cyclopropene (3). An analogous procedure was followed, using 2,3-di(*p*-methoxyphenyl)cyclopropenone (320 mg, 1.20 mmol) to give **3** as a yellow solid (330 mg, 85%) (Found: C, 62.95; H, 4.7; Cl, 21.6, Calc. for $C_{17}H_{14}Cl_2O_2$: C, 63.6; H, 4.4; Cl, 22.1%); δ_H(300 MHz, $CDCl_3$) 7.80 (4 H, d, $^3J_{HH}$ 8.8 Hz, Ar*H*), 7.08 (4 H, d, $^3J_{HH}$ 8.8 Hz, Ar*H*), 3.88 (6 H, s, C*H*$_3$); δ_C(75 MHz, $CDCl_3$) 161.9 (*C*O*C*H$_3$), 132.9 (*C*$_3$ ring), 131.8 (Ar*C*), 123.3 (Ar*C*), 116.8 (Ar*C*), 105.4 (*C*Cl_2), 55.6 (O*C*H$_3$); *m*/*z* (EI): 320 (M^+, 30%), 285 (M^+ − Cl, 100), 250 (M^+ − 2Cl, 5).

1,1-dichloro-2,3-di(*p*-fluorophenyl)cyclopropene (4). An excess of oxalyl chloride (171 μL, 2.00 mmol) was added dropwise to a stirred solution of the 2,3-di(*p*-fluorophenyl)cyclopropenone (194 mg, 0.80 mmol) in 5 mL of dichloromethane at −78 °C. The reaction mixture was allowed to warm to room temperature and the evolution of CO_2 was observed. The reaction was stirred for approximately 4 h until gas evolution ceased. The volatiles were removed *in vacuo* to give **4** as a white solid (220 mg, 92%) (Found: C, 60.7; H, 2.8, Calc. For $C_{15}H_8Cl_2F_2$: C, 60.6; H, 2.7%); δ_H(300 MHz, $CDCl_3$) 7.85 (4 H, dd, $^3J_{HH}$ = 9.7 Hz, $^3J_{FH}$ = 3.6 Hz, Ar*H*), 7.28 (4 H, t, $^3J_{HH}$ = 8.8 Hz, Ar*H*); δ_C(75 MHz, $CDCl_3$) 164.9 (Ar*C*), 154.3 (Ar*C*), 144.5 (*C*$_3$ ring), 132.5 (Ar*C*), 128.4 (Ar*C*), 117.1 (*C*Cl_2); δ_F(283 MHz, $CDCl_3$) − 106.0 (s); *m*/*z* (EI): 298 (M^+, 10%), 263 (M^+ − Cl, 65).

Synthesis of palladium(II) complexes

[$PdCl_2$(*cyclo*-C_3(Ph)$_2$)(PPh_3)] (5). 1,1-dichloro-2,3-diphenylcyclopropene (**1**) (94.0 mg, 0.36 mmol) was dissolved in 5 mL of toluene and added dropwise to a solution of tetrakis(triphenylphosphine)palladium(0) (416 mg, 0.36 mmol) in 15 mL of toluene. A colourless solid precipitated immediately and the mixture was stirred for 5 h. The precipitate was collected by filtration and dried *in vacuo* to give **5** as a white solid (200 mg, 87%). **5** can be recrystallised from $CHCl_3$ (Found: C, 62.8; H, 4.15. Calc. for $C_{33}H_{26}Cl_2PPd$: C, 63.0; H, 4.25%); δ_H(400 MHz, $CDCl_3$) 8.03 (4 H, m, Ar*H*), 7.64 (8 H, m, Ar*H*), 7.53 (4 H, m, Ar*H*), 7.25 (3 H, m, Ar*H*), 7.15 (6 H, m, Ar*H*); δ_P(121 MHz, $CDCl_3$) 27.6 (s, *P*Ph_3); *m*/*z* (ESI): 653 (M^- + Na^+), 595 (M^+ − Cl).

[$PdCl_2$(*cyclo*-C_3(Mes)$_2$)(PPh_3)] (6). 1,1-dichloro-2,3-dimesitylcyclopropene (**2**) (173 mg, 0.50 mmol) and tetrakis-(triphenylphosphine)palladium(0) (578 mg, 0.50 mmol) were weighed into a Schlenk flask. Toluene (10 mL) was added to give a yellow solution and a precipitate immediately. The mixture was stirred at 80 °C for 3 h. The precipitate was collected by filtration and dried *in vacuo* to give **6** as a yellow solid. **6** can be recrystallised from $CHCl_3$ and hexane to give white crystals (130 mg, 35%) (Found: C, 63.9; H, 4.7, Calc. for $C_{39}H_{37}Cl_2PPd$·0.25$CHCl_3$: C, 63.4; H, 5.1%, chloroform present in the crystal structure); δ_H(300 MHz, $CDCl_3$) 7.76–7.69 (15 H, m, P(C$_6$*H*$_5$)$_3$), 6.95 (4 H, s, Ar*H*), 2.31 (12 H, s, *o*-C*H*$_3$), 2.18 (6 H, s, *p*-C*H*$_3$); δ_P(121 MHz, $CDCl_3$) 27.6 (s, *P*Ph_3); *m*/*z* (ESI): 678.5 (M^+ − Cl).

[$PdCl_2$(*cyclo*-C_3(Ar)$_2$)]$_2$ complexes (7–9)

General procedure: The complexes were synthesised following a modification of the literature method.[13] A solution of 1,1-dichloro-2,3-diarylcyclopropene (**1**, **3** or **4**) in benzene (1 mL) was added dropwise to a stirred suspension of palladium dibenzylideneacetone, [Pd(dba)$_2$], in 15 mL of benzene at 65 °C. The reaction mixture was refluxed overnight. The solid precipitate was collected on a d4 glass filter. The product, [$PdCl_2$(*cyclo*-C_3(Ar)$_2$)]$_2$ (**7–9**), was washed with diethyl ether and dried in air.

[$PdCl_2$(*cyclo*-C_3(C_6H_5)$_2$)]$_2$ (7). Reaction of 1,1-dichloro-2,3-diphenylcyclopropene (**1**) (210 mg, 0.80 mmol) with [Pd(dba)$_2$] (440 mg, 0.80 mmol) gave **7** as a fine brown solid. (190 mg, 65%); *m*/*z* (ESI): 758 (M^+ + Na^+); HRMS (ESI): Calc. for [$C_{30}H_{20}Cl_4Pd_2$]Na^+: 754.8281, found 754.8305.

[$PdCl_2$(*cyclo*-C_3(*p*-(OMe)C_6H_4)$_2$)]$_2$ (8). Reaction of 1,1-dichloro-2,3-di(*p*-methoxyphenyl) cyclopropene (**3**) (266 mg, 0.83 mmol) with [Pd(dba)$_2$] (288 mg, 0.50 mmol) gave **8** as a brownish solid (200 mg, 55%); *m*/*z* (ESI): 878 (M^+ + Na^+); HRMS (ESI); Calc. for [$C_{34}H_{28}Cl_4O_4Pd_2$]Na^+: 874.8704, found 874.8734.

[$PdCl_2$(*cyclo*-C_3(*p*-(F)C_6H_4)$_2$)]$_2$ (9). Reaction of 1,1-dichloro-2,3-di(*p*-fluorophenyl)cyclopropene (**4**) (277 mg, 0.93 mmol) with [Pd(dba)$_2$] (536 mg, 0.93 mmol) gave **9** as a black solid (220 mg, 59%); *m*/*z* (ESI): 831 (M^+ + Na^+); HRMS (ESI); Calc. for [$C_{30}H_{16}Cl_4F_4Pd_2$]Na^+: 826.7904, found: 826.7923.

NMR spectroscopic data was not obtained due to the insolubility of bimetallic complexes **7–9** in non-coordinating organic solvents. The complexes were soluble in acetonitrile to give [$PdCl_2$(MeCN)(*cyclo*-C_3(Ar)$_2$)] complexes (**10–12**) *via* a bridge splitting reaction. Alternatively complexes **10–12** can be synthesised directly using the general procedure below.

General procedure: Acetonitrile (4 mL) was added to a mixture of 1,1-dichloro-2,3-diarylcyclopropene (**1**, **3** or **4**) and [Pd(dba)$_2$]

at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, then at room temperature for 72 h. The reaction mixture was passed through Celite/sand and the filter was washed with acetonitrile. The volatiles were removed *in vacuo*, and the crude solid was recrystallised from acetonitrile, to give the $[PdCl_2(MeCN)(cyclo\text{-}C_3(Ar)_2)]$ complex (**10–12**).

$[PdCl_2(MeCN)(cyclo\text{-}C_3(Ph)_2)]$ (10). Reaction of 1,1-dichloro-2,3-diphenylcyclopropene (**1**) (136.0 mg, 0.52 mmol) with $[Pd(dba)_2]$ (300.0 mg, 0.52 mmol) gave **10** as yellow crystals (200.0 mg, 94%) δ_H(300 MHz, CD_3CN) 8.58 (4 H, d, $^3J_{HH}$ = 8.4 Hz, *o*-Ar*H*), 7.90 (2 H, t, $^3J_{HH}$ = 7.5 Hz, *p*-Ar*H*), 7.79 (4 H, t, $^3J_{HH}$ = 7.7 Hz, *m*-Ar*H*), 1.97 (3 H, s, CH_3CN).

$[PdCl_2(MeCN)(cyclo\text{-}C_3(p\text{-}(OMe)C_6H_4)_2)]$ (11). Reaction of 1,1-dichloro-2,3-bis(*p*-methoxyphenyl)cyclopropene (**3**) (100.0 mg, 0.31 mmol) with $[Pd(dba)_2]$ (178.0 mg, 0.31 mmol) gave **11** as yellow crystals (36.0 mg, 25%) (Found: C, 48.1; H, 3.8; N, 2.9. Calc. for $C_{19}H_{17}Cl_2NO_2Pd$: C, 48.6; H, 3.7; N, 3.0%); δ_H(300 MHz, CD_3CN) 8.50 (4 H, d, $^3J_{HH}$ = 8.8 Hz, *o*-Ar*H*), 7.25 (4 H, d, $^3J_{HH}$ = 8.8 Hz, *m*-Ar*H*), 3.97 (6 H, s, OCH_3), 2.14 (3 H, s, CH_3CN).

$[PdCl_2(MeCN)(cyclo\text{-}C_3(p\text{-}(F)C_6H_4)_2)]$ (12). Reaction of 1,1-dichloro-2,3-bis(*p*-fluorophenyl)cyclopropene (**4**) (500.0 mg, 1.70 mmol) with $[Pd(dba)_2]$ (970.0 mg, 1.70 mmol) gave **12** as yellow crystals (60.0 mg, 19%) δ_H(300 MHz, CD_3CN) 8.65 (4 H, dd, $^3J_{HH}$ = 5.3, 9.0 Hz, *o*-Ar*H*), 7.50 (4 H, t, $^3J_{HH}$ = 8.8 Hz, *m*-Ar*H*); δ_F(283 MHz, CD_3CN) 100.3 (s).

Synthesis of $[PdCl_2(cyclo\text{-}C_3(Ph)_2)(PCy_3)]$ (13). The bimetallic palladium complex **7** (37.0 mg, 0.05 mmol) and tricyclohexylphosphine (34.0 mg, 0.12 mmol) were dissolved in acetonitrile in a small vial. The reaction mixture was stirred for 30 min in the glovebox and then filtered through a glass filter. The product was recrystallised with hexane as a co-solvent to give **13** as brown crystals (7.0 mg, 45%) (Found: C, 61.7; H, 7.3. Calc. for $C_{33}H_{44}Cl_2PPd$: C, 61.1; H, 6.8%); δ_H(300 MHz, CD_2Cl_2) 8.45 (4 H, d, $^3J_{HH}$ 6.9 Hz, *o*-Ar*H*), 7.99 (2 H, t, $^3J_{HH}$ 7.7 Hz, *p*-Ar*H*), 7.89 (4 H, t, $^3J_{HH}$ 7.7 Hz, *m*-Ar*H*), 2.3–1.8 (33 H, m, (*cyclo*-$C_6H_{11})_3$; δ_P(121 MHz, CD_2Cl_2) 51.2 (s); HRMS (ESI): Calc. for $[C_{33}H_{43}PClPd]^+$: 611.1845, found 611.1890.

Synthesis of $[PdCl_2(cyclo\text{-}C_3(p\text{-}(OMe)C_6H_4)_2)(PPh_3)]$ (14). Complex **11** (24.0 mg, 0.05 mmol) and triphenylphosphine (16.0 mg, 0.06 mmol) were dissolved in chloroform in an NMR tube. The tube was shaken and gently heated with a heat gun to give a yellow solution. The solution was left overnight to give complex **14** as colourless crystals (17 mg, 50 %) (Found: C, 59.7; H, .4.1. Calc. for $C_{35}H_{30}Cl_2O_2PPd$: C, 60.8; H, 4.4%); δ_H(300 MHz, $CDCl_3$) 8.50 (1 H, d, $^3J_{HH}$ = 8.6 Hz, *o*-Ar*H*), 8.10 (4 H, d, $^3J_{HH}$ = 8.6 Hz, *m*-Ar*H*), 7.72 (6 H, m, Ar*H*), 7.50 (3 H, m, Ar*H*), 7.29 (6 H, m, Ar*H*), 7.17 (4 H, d, $^3J_{HH}$ = 8.6 Hz, *m*-Ar*H*), 3.95 (6 H, s, OCH_3); δ_P(121 MHz, $CDCl_3$) 27.7 (s, *P*Ph_3); HRMS (ESI): Calc. for $[C_{35}H_{29}PClO_2Pd]^+$: 653.0623, found 653.0645.

Synthesis of $[PdCl_2(cyclo\text{-}C_3(p\text{-}(F)C_6H_4)_2)(PPh_3)]$ (15). Complex **12** (23 mg, 0.05 mmol) and triphenylposphine (16 mg, 0.06 mmol) were dissolved in acetonitrile (1 mL) in a small vial. The reaction mixture was stirred for 10 min. The solution was kept in the fridge overnight to give **15** as yellow crystals (14 mg, 42%) (Found: C, 59.1; H, 3.3. Calc. for $C_{33}H_{24}Cl_2F_2PPd$: C, 59.4; H, 3.6%); δ_H(300 MHz, CD_2Cl_2); 8.15 (4 H, d, $^3J_{HH}$ = 5.5 Hz, *o*-Ar*H*), 8.12 (4 H, d, $^3J_{HH}$ = 5.5 Hz, *m*-Ar*H*), 7.68 (6 H, m, Ar*H*), 7.36 (6 H, m, Ar*H*), 7.27 (6 H, m, Ar*H*); δ_P(121 MHz, CD_2Cl_2) 27.7 (s, *P*Ph_3); δ_F(283 MHz, CD_2Cl_3) – 98.6 (s); HRMS (ESI); Calc. for $[C_{33}H_{23}PClF_2Pd]^+$: 629.0223, found 629.0229.

Catalytic experiments

The catalytic procedure is given for entry 1 in Table 3. Catalysts were added either as complex (**5–9**) or a mixture of complex (**7–9**) with one equivalent (based on palladium) of the appropriate phosphine ligand.

Stille reaction.[17] A Schlenk flask was charged with cesium fluoride (334 mg, 1.10 mmol), 4-bromoanisole (187 mg, 1.00 mmol), and the internal standard, hexadecane (100 mg, 0.40 mmol). Phenyltributyltin (404 mg, 1.10 mmol) and degassed dioxane (2 mL) were added and the reaction was heated to 90 °C. Catalyst **7** (2 mol%) and triphenylphosphine (1 equiv. based on Pd) was then added and the reaction stirred for 18 h. After this time, the reaction mixture was allowed to cool, diluted with diethyl ether and filtered through a pad of silica gel. The silica gel was washed thoroughly with diethyl ether. The combined organic layers were dried over magnesium sulfate. Conversion and yield were determined by GC relative to the internal standard. Products were checked by NMR spectroscopy against authentic samples.

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