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

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Electronic Supplementary Information

Crystal structure determinations

X-ray diffraction experiments for 2,3-bis(*p*-fluorophenyl)cyclopropenone (abbreviated as ***p*-FC$_3$=O** in table S1), **13**, **14**·CHCl$_3$ and **15** were carried out at 100 K on a Bruker Kappa Apex II CCD diffractometer, using Mo-Ka radiation (λ = 0.71073 Å). Crystal data for **1** was collected at 173 K on a Bruker SMART CCD diffractometer, using Mo-Ka radiation (λ = 0.71074 Å). A single crystal was coated in inert oil and mounted on a glass fibre. Intensities were integrated [1] from several series of exposures in φ and ω calculated by the Apex II[2] program, whilst for **1** several series of exposures measuring 0.3° in ω, after unit cell determination. Absorption corrections were based on equivalent reflections using SADABS,[3] and structures were refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL.[4] Crystal structure and refinement data are given in Table S1.

Table S1 Crystallographic data

Compound	**1**	***p*-FC$_3$=O**	**13**	**14**·CHCl$_3$	**15**
Colour, habit	colourless block	colourless needle	brown lathe	colourless plate	yellow needle
Size/mm	0.40×0.40×0.10	1.26×0.14×0.08	0.38×0.10×0.10	0.56×0.15×0.06	0.67×0.24×0.20
Empirical Formula	$C_{15}H_{10}Cl_2$	$C_{15}H_8F_2O$	$C_{33}H_{43}Cl_2PPd$	$C_{36}H_{30}Cl_5O_2PPd$	$C_{33}H_{23}Cl_2F_2PPd$
M	261.13	242.21	647.94	809.22	665.78
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P\ mn2_1$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a/Å	14.3776(13)	24.758(2)	9.4214(3)	11.911(3)	9.9931(6)
b/Å	7.8923(7)	3.7984(3)	17.6389(5)	28.476(8)	14.9088(9)
c/Å	11.2349(10)	6.0626(5)	18.9653(5)	10.962(3)	18.2358(10)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	105.465(2)	90.00	108.913(2)	110.442(2)	90.00
γ/°	90.00	90.00	90.00	90.00	90.00
V/A^3	1228.69(19)	570.13(13)	2981.56(15)	3483.79(16)	2716.9(3)
Z	4	2	4	4	4
μ/mm^{-1}	0.500	0.110	0.876	0.994	0.975
T/K	173	100	100	100	100
Reflections: total/independent	12378/2803	3695/724	57537/11600	104658/11422	19524/6782
R_{int}	0.0392	0.0251	0.0541	0.0640	0.0448
Final *R*1 (observed data)	0.0314	0.0275	0.0361	0.0333	0.0332
Largest peak, hole (eA^{-3})	0.230, -0.240	0.181, -0.150	1.225, -1.125	0.87, -1.05	0.714, -0.418
ρ_{calc}/g cm^{-3}	1.412	1.411	1.443	1.54	1.628
Flack parameter	-	1(10)[a]	-	-	-0.02(2)

[a] Friedel pairs merged, because structure was measured with Mo radiation, but the heaviest atom present in the molecule is fluorine, so correct identification of Friedel pairs would not be reliable.

Results and discussion

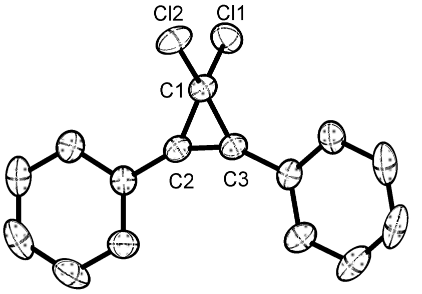


Fig. S1 Thermal ellipsoid plot of **1**. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

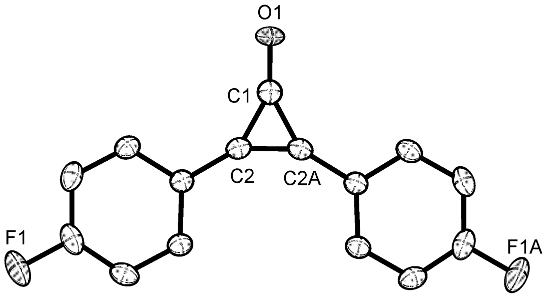


Fig. S2 Thermal ellipsoid plot of ***p*-FC$_3$=O**. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

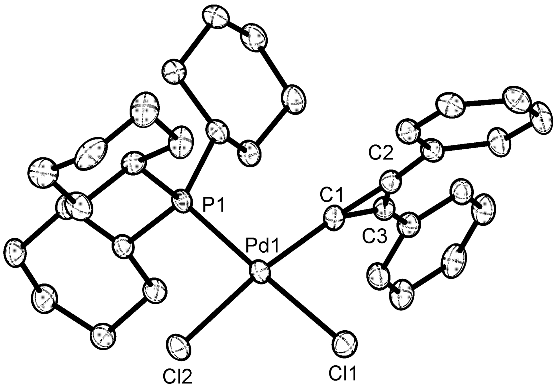


Fig. S3 Thermal ellipsoid plot of **13**. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

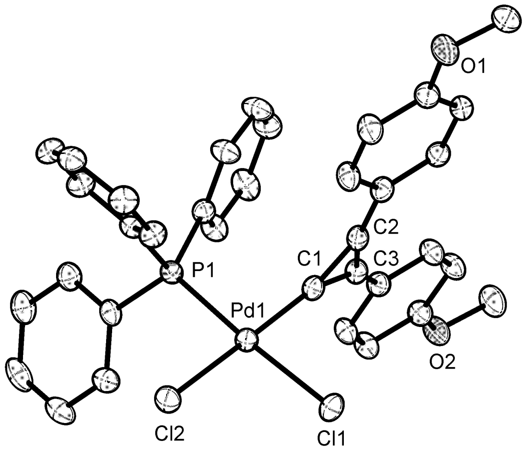


Fig. S4 Thermal ellipsoid plot of **14**. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

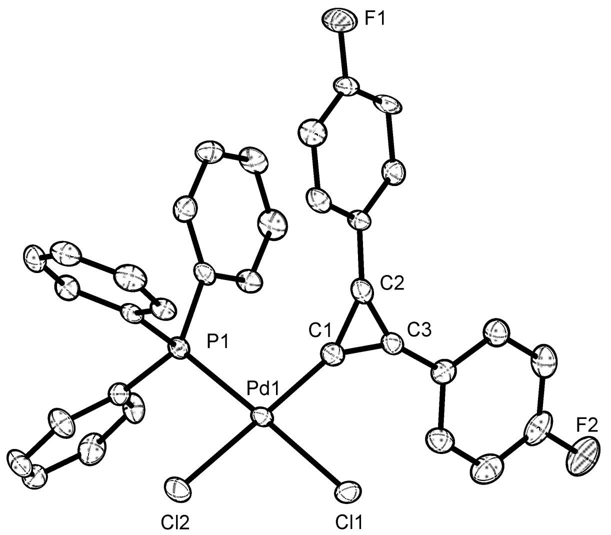


Fig. S5 Thermal ellipsoid plot of **15**. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been removed for clarity.

Table S2a Selected bond distances (Å) and angles (°) for **1** and ***p*-FC**$_3$**=O**

	1	***p*-FC**$_3$**=O**
C1-C2	1.429(2)	1.416(3)
C1-C3	1.423(2)	-
C2-C3	1.305(2)	1.369(3)
C1-Cl1	1.7869(16)	-
C1-Cl2	1.7775(16)	-
C1-O1	-	1.228(3)
C3-C1-C2	54.29(10)	57.83(15)
C1-C-C-C (Ph tilt)	-6.4(3), 11.1(3)	-1.6(4)

Table S2b Selected bond distances (Å) and angles (°) for **13**, **14**·CHCl$_3$ and **15**.

	13	**14**·CHCl$_3$	**15**
Pd1-C1	1.9347(18)	1.933(18)	1.942(3)
Pd1-P1	2.2803(5)	2.250(5)	2.2579(7)
Pd1-Cl1 (*trans* P1)	2.3716(5)	2.373(5)	2.3603(8)
Pd1-Cl2 (*trans* C1)	2.3566(5)	2.359(5)	2.3367(8)
C1-C2	1.399(2)	1.388(3)	1.382(4)
C1-C3	1.393(3)	1.387(2)	1.381(4)
C2-C3	1.358(3)	1.373(3)	1.367(4)
C1-Pd1-Cl1	81.69(6)	86.49(5)	87.16(9)
C1-Pd1-P1	95.70(6)	89.20 (5)	93.75(9)
Cl1-Pd1-Cl2	91.472(17)	92.22 (17)	92.48(3)
C2-C1-Pd1	152.88(15)	145.41(15)	152.6(3)
C3-C1-C2	58.20(13)	59.34(13)	59.3(2)
Cl1-Pd1-C1-C2	-63.8(3)	-85.0(2)	-132.7(5)
C1-C-C-C (Ph tilt)	-21.5(4), -10.7(4)	-9.1(4) / 3.9(4)	22.6(7), -3.0(7)

Discussion

Selected bond lengths and angles are given in Table S2a and S2b.

Crystals of **1** (Fig. S1) crystallised from a saturated solution of cyclohexane in space group $P2_1/c$. The bond lengths in the cyclopropenylidene three-membered ring (C1, C2 and C3) indicate that the C=C double bond is partly localised, as the C2-C3 bond length is 0.12 Å shorter than C1-C2 and C1-C3.

Crystals of the ***p*-FC$_3$=O** (Fig. S2) crystallised from a saturated solution of diethyl ether and methanol in non-centrosymmetric space group $Pmn2_1$. The planar molecule has exact mirror symmetry that bisects the cyclopropenyl ring along C1, between the double C2-C2A bond (Z' = ½). The bond lengths in the cyclopropenylidene three-membered ring (C1, C2 and C3) indicate that the C=C double bond is partly localised, as the C2-C3 bond length is 0.05 Å shorter than C1-C2 and C1-C3.

Crystals of **13** (Fig. S3) crystallised from a saturated solution of acetonitrile and diethyl ether and in space group $P2_1/n$. The Pd(II) centre has square planar geometry and is coordinated by the cyclopropenylidene ligand *cis* to a phosphine ligand PCy_3, both of which are *trans* to a chloride ligand. The chlorine bond length *trans* to the carbene (Pd-Cl2) is slightly shorter than that *trans* to the phosphine, by 0.015 Å, which is the same trend as the previously reported structure when the phosphine was PPh_3,[5] this confirms that the *trans* influence of the phosphine ligand is marginally stronger than that of the cyclopropenylidene. The cyclopropenylidene ligand plane is approximately perpendicular to the coordination plane (torsion angle Cl1-Pd1-C1-C2 = -63.8°). The structure is similar to CSD ref. XIKGOO, which is a dichloromethane solvate.

Crystals of **14**·$CHCl_3$ (Fig. S4) crystallised from a saturated solution of chloroform in space group $P2_1/c$. The Pd(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. The chlorine bond length *trans* to the carbene (Pd-Cl2) is slightly shorter than that *trans* to the phosphine, by 0.014 Å, as for **13,** confirming that the *trans* influence of the phosphine ligand is slightly stronger than that of the cyclopropenylidene. The cyclopropenylidene ligand plane is again approximately perpendicular to the coordination plane (torsion angle Cl1-Pd1-C1-C2 = - 85.0°). The structure includes a molecule of chloroform (from the solvent) which is weakly hydrogen bonded to the two chloride ligands (H…Cl 2.67 and 2.86 Å).

Crystals of **15** (Fig. S5) crystallised from a saturated solution of dichloromethane and hexane in space group $P2_12_12_1$. The Pd(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. The chlorine bond length *trans* to the carbene (Pd-Cl2) is slightly shorter than that *trans* to the phosphine, by 0.024 Å, confirming that the *trans* influence of the phosphine ligand is stronger than that of the carbene. The cyclopropenylidene ligand plane is out of the coordination plane (torsion angle Cl1-Pd1-C1-C2 = -132.7°). This may be affected by π-stacking interactions between the phenyl substituents of the phosphine ligand and the *para* fluorinated aryl of the cyclopropenylidene.

Table S3 Relative energy values for rotation of cyclopropenylidene ligands about the Pd-C1 bond in complexes **10**, **11** and **12** (Fig.4 in paper)

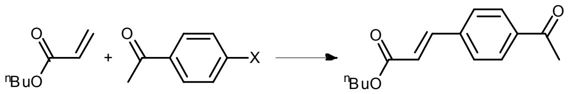
Restrained Torsion (Cl-Pd-C1-C2°)	**10**	**11**	**12**
0	1.69	1.53	1.63
15	1.33	1.11	1.25
30	0.17	0.01	0.00
45	0.13	0.00	0.06
60	1.03	1.06	1.23
75	2.14	2.18	2.36
90	2.69	2.43	3.36
Optimised value	0.00 (40°)	0.02 (39°)	0.22 (37°)

Catalysis Data

The catalytic procedures below are representative examples of each reaction and specifically detail Entry 1 in each table (Tables S4-S6). 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.

Mizoroki-Heck Reaction. A Schlenk flask was charged with sodium acetate (246 mg, 3.00 mmol), bromoacetophenone (398 mg, 2.00 mmol) and the internal standard, diethylene glycol di-*n*-butyl ether (100 mg, 0.45 mmol). *n*-Butyl acrylate (385 mg, 3.00 mmol) and degassed *N,N*-dimethylacetamide (2 mL) were added and the reaction was heated to 145 °C. Catalyst **7** (1×10^{-3} mol%) was then added and the reaction was stirred for 18 h. After this time, the reaction mixture was allowed to cool, washed with dilute hydrochloric acid, extracted with dichloromethane and the organic phase was 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.

Table S4 Catalytic activity of cyclopropenylidene palladium(II) complexes in Mizoroki-Heck reactions

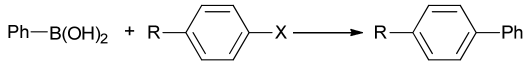


[a]Entry	X	Cat.	[b]phosphine	mol % Pd	[c]conversion (yield) / %	TON
1	Br	**7**	none	10^{-3}	99(99)	99000
2	Br	**7**	PPh_3	10^{-3}	100(99)	99000
3	Br	**7**	P^tBu_3	10^{-3}	100(99)	99000
4	Br	**8**	none	10^{-3}	99(97)	97000
5	Br	**8**	PPh_3	10^{-3}	100(99)	99000
6	Br	**8**	P^tBu_3	10^{-3}	100(99)	99000
7	Br	**9**	none	10^{-3}	100(79)	79000
8	Br	**9**	PPh_3	10^{-3}	100(99)	99000
9	Br	**5**	none	10^{-3}	98(90)	90000
10	Br	**6**	none	10^{-3}	96(69)	69000
11	Cl	**7**	none	0.01	97(3)	300
12	Cl	**9**	P^tBu_3	0.01	98(5)	500
13	Cl	**5**	none	0.01	98(4)	400
14	Cl	**6**	none	0.01	97(4)	400

[a] Conditions: 2.0 mmol aryl halide, 3.0 mmol *n*-butyl acrylate, 3.0 mmol NaOAc, 2 ml *N,N*-dimethylacetamide diluent, 145 °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 diethylene glycol di-*n*-butyl ether. Products were checked by NMR spectroscopy against authentic samples.

Suzuki-Miyaura Reaction. A Schlenk flask was charged with potassium carbonate (415 mg, 3.00 mmol), bromoacetophenone (398 mg, 2.00 mmol), and the internal standard, diethylene glycol di-*n*-butyl ether (100 mg, 0.45 mmol). Phenylboronic acid (293 mg, 2.40 mmol) and degassed xylene (2 mL) were added and the reaction was heated to 130 °C. Catalyst **7** (1 mol%) was then added and the reaction stirred for 18 h. After this time, the reaction mixture was allowed to cool, washed with dilute hydrochloric acid, extracted with dichloromethane and the organic phase was 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.

Table S5 Catalytic activity of cyclopropenylidene palladium(II) complexes in Suzuki-Miyaura reactions

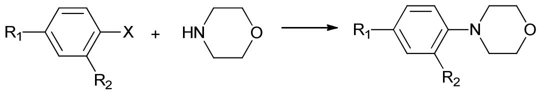


[a]Entry	X	Cat.	R	[b]phosphine	mol % Pd	[c]conversion (yield) / %	TON
1	Br	**7**	C(O)Me	none	1	100(94)	94
2	Br	**7**	C(O)Me	P^tBu_3	1	100(99)	99
3	Br	**8**	C(O)Me	none	1	98(80)	80
4	Br	**8**	C(O)Me	PPh_3	1	100(90)	90
5	Br	**9**	C(O)Me	none	1	99(71)	71
6	Br	**5**	C(O)Me	none	1	100(78)	78
7	Br	**6**	C(O)Me	none	1	100(98)	98
8	Cl	**7**	C(O)Me	P^tBu_3	1	95(30)	30
9	Cl	**5**	C(O)Me	none	1	91(4)	4
10	Cl	**6**	C(O)Me	none	1	97(1)	1

[a] Conditions: 2.0 mmol aryl halide, 2.4 mmol $PhB(OH)_2$, 3.0 mmol K_2CO_3, 2 ml xylenes diluent, 130 °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 diethylene glycol di-*n*-butyl ether. Products were checked by NMR spectroscopy against authentic samples.

Buchwald-Hartwig Amination. A Schlenk flask was charged with sodium-*t*-butoxide (135 mg, 1.40 mmol), 4-bromobenzotrifluoride (225 mg, 1.00 mmol), and the internal standard, hexadecane (100 mg, 0.40 mmol). Morpholine (87 mg, 1.00 mmol), triphenylphosphine (8 mg, 0.04 mmol) and toluene (15 mL) were added and the reaction was heated to 100 ºC. Catalyst **7** (2 mol%) was then added and the reaction stirred for 18 h. After this time, the reaction mixture was allowed to cool, washed with water, extracted with toluene and the organic phase was dried over magnesium sulfate. Conversion was determined by GC relative to the internal standard. Yield was determined by integration of ^{1}H NMR peaks against additional standard 1,3,5-trimethoxybenzene.

Table S6 Catalytic activity of cyclopropenylidene palladium(II) complexes in Buchwald-Hartwig amination reactions



[a]Entry	X	Cat.	R^1, R^2	[b]phosphine	mol% Pd	[c]conversion (yield) / %	TON
[d]1	Br	**7**	CF_3, H	none	2	50(30)	15
[d]2	Br	**7**	CF_3, H	PPh_3	2	100(62)	31
[d]3	Br	**7**	CF_3, H	P^tBu_3	2	100(89)	45
4	Br	**7**	CF_3, H	$P(Mes)_3$	2	48(22)	11
5	Br	**7**	CF_3, H	$P(OPh)_3$	2	82(52)	26
6	Br	**8**	CF_3, H	none	2	91(7)	4
8	Br	**9**	CF_3, H	none	2	91(10)	5
[d]9	Br	**5**	CF_3, H	none	2	100(54)	27
10	Br	**6**	CF_3, H	none	2	94(34)	17
[d]11	Cl	**7**	CF_3, H	none	2	7(0)	0
[d]12	Cl	**7**	CF_3, H	PPh_3	2	88(0)	0
[d]13	Cl	**7**	CF_3, H	P^tBu_3	2	100(85)	43
14	Cl	**7**	OMe,H	PPh_3	2	89(3)	2
15	Cl	**7**	CF_3, H	$P(Mes)_3$	2	8(1)	1
16	Cl	**7**	CF_3, H	$P(OPh)_3$	2	69(48)	24
[d]17	Cl	**7**	H, OMe	P^tBu_3	2	100(97)	49
18	Cl	**11**	H, OMe	P^tBu_3	2	100(96)	48
19	Cl	**12**	H, OMe	P^tBu_3	2	88(86)	43
20	Cl	**11**	OMe, H	P^tBu_3	2	100(100)	50

[a] Conditions: 1.0 mmol aryl halide, 1.0 mmol morpholine, 1.4 mmol NaO^tBu, 100°C, 18h. [b] 1 mol equiv. of phosphine with respect to amount of palladium used. [c] Conversions were determined by GC relative to the internal standard hexadecane and yields were determined by integration of ^{1}H NMR peak vs trimethoxybenzene standard. [d] Previously published results, conversion and yield were determined by GC relative to the internal standard hexadecane.[6]

References

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[1] Bruker SAINT V7.06A (**1**) or v7.34A (***p*-FC$_3$=O**, **13**, **14**, **15**), Siemens Analytical X-ray Instruments Inc., Madison, WI, 2003 or 2007.

[2] SMART v5.054 or Apex2, Bruker-AXS, 1998 or 2007.

[3] G. M. Sheldrick, SADABS V2.10 (**1**) or V2008/2 (***p*-FC$_3$=O**, **13**, **14**, **15**), Bruker AXS Inc., Madison, Wisconsin, USA, or 2008.

[4] SHELXTL program system version V6.14, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.

[5] D. F. Wass, M. F. Haddow, T. W. Hey, A. G. Orpen, C. A. Russell, R. L. Wingad and M. Green, *Chem. Comm.*, 2007, 2704-2706.

[6] D. F. Wass, T. W. Hey, J. Rodriguez-Castro, C. A. Russell, I. V. Shishkov, R. L. Wingad and M. Green, *Organometallics*, 2007, **26**, 4702-4703.