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Cyclopropenylidene carbene ligands in palladium C–C coupling catalysis

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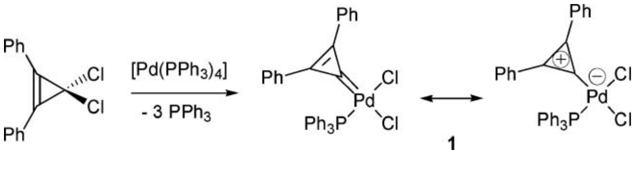
A palladium complex supported by a 2,3-diphenylcyclopropenylidene carbene ligand is a highly active and robust catalyst for Heck and Suzuki coupling reactions.

In recent years, *N*-heterocyclic carbenes have emerged as 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 coupling.[2] Numerous variations to the structure of *N*-heterocyclic carbene ligands have been investigated. By contrast, carbocyclic carbene ligands, *i.e.* with no heteroatom, are much rarer; the only use of such ligands in catalysis is a recent report concerned with ligands based on 7-membered rings by Herrmann and co-workers.[3] It is noteworthy that this catalyst shows superior performance to even *N*-heterocyclic carbene systems in many respects.

In 1968, Öfele reported the stable complex [Cr(CO)$_5$(2,3-diphenylcyclopropenylidene)].[4a] We were attracted to this result, particularly the reported CO stretching frequencies of the complex which suggest the 3-membered ring carbene ligand to be an exceptionally strong σ-donor and poor π-acceptor. Data presented by Kawada and Jones[4b] supports this thesis and also suggests that such ligands are more robust to thermal and chemical decomposition compared to other carbene ligands. 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). Certain palladium complexes of related ligands have been reported;[5] however, the potential of cyclopropenylidene carbene complexes in catalysis remains unrealised to date. We describe here the synthesis and structural characterisation of such a complex, together with its performance in C–C coupling catalysis.

In a simple and high yielding reaction (70% isolated yield), complex **1** was prepared by the oxidative addition of 1,1-dichoro-2,3-diphenylcyclopropene to [Pd(PPh$_3$)$_4$] in toluene at room temperature (Scheme 1), the product precipitating from the reaction mixture. Single crystals of **1** suitable for X-ray diffraction study were obtained from chloroform.‡



Scheme 1 Synthesis of **1**.†

The chloroform solvate of **1** crystallises in the space group $P\bar{1}$ with one molecule of complex and 1.5 molecules of chloroform in the asymmetric unit (one of the chloroform molecules is disordered over an inversion centre). The molecular geometry in the crystal structure is shown in Fig. 1. The complex adopts approximate (not crystallographic) mirror symmetry, with the plane of symmetry being the square planar moiety consisting of Pd1, P1, Cl1, Cl2 and C1. The carbene ligand ring is approximately orthogonally orientated to the square plane of the complex and examination of the C–C bond lengths of the three-membered ring indicate that the ligand is best described as a delocalised 2π aromatic cyclopropenium ring, albeit C2–C3 is slightly shorter than the other C–C bonds of this moiety [1.363(5) Å *vs.* 1.387(5) Å and 1.390(5) Å]. The chlorine bond length *trans* to the carbene (Pd–Cl2) is slightly shorter [2.3449(11) Å] than that *trans* to the phosphine [2.3617(11) Å], which suggests that the *trans* influence of the phosphine ligand is stronger than that of the carbene. The same effect is seen in the crystal structure of [PdCl$_2${PBu$^n_3$}{2,3-di(dimethylamino)cyclopropenylidene}] reported by Ibers and co-workers,[6] whose 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 (Pd–C1) is slightly shorter than the equivalent

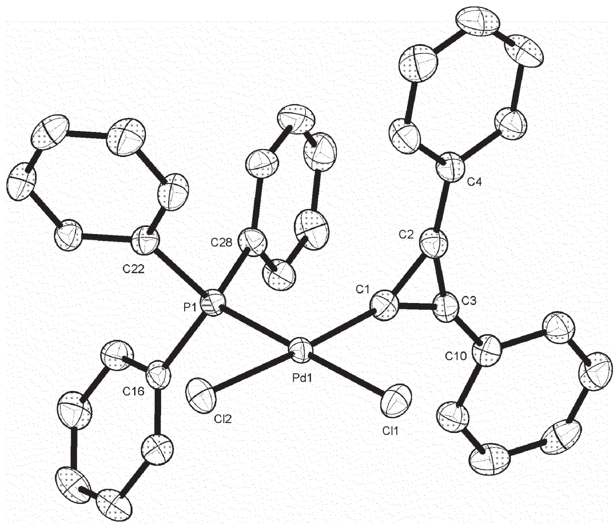


Fig. 1 Molecular structure of **1** (H atoms and solvent of crystallisation omitted for clarity. ORTEP plot created at 50% probability). Selected bond lengths (Å) and angles (°): Pd1–C1 1.939(3); Pd1–P1 2.2430(10), Pd1–Cl1 2.3617(11), Pd1–Cl2 2.3449(11), C1–C2 1.387(5), C1–C3 1.390(5), C2–C3 1.363(5), C2–C4 1.435(5), C3–C10 1.443(5); C2–C1–C3 58.8(2), C3–C2–C1 60.7(3), C2–C3–C1 60.5(3), P1–Pd1–C1–C2 94.0(5).

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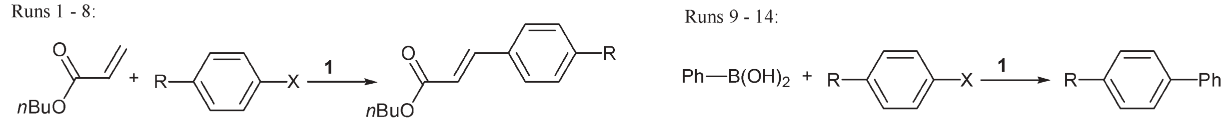
Table 1 Catalysis data



Run	R	X	Base	Mol% Pd	Conversion %	TON
1[a]	C(O)Me	Br	NaOAc	0.01	100	10 000
2[a]	C(O)Me	Br	NaOAc	10^{-3}	99	99 000
3[a]	C(O)Me	Br	NaOAc	10^{-4}	94	940 000
4[a]	H	Br	NaOAc	10^{-3}	80	80 000
5[a]	OMe	Br	NaOAc	10^{-3}	54	54 000
6[a]	C(O)Me	Cl	NaOAc	1	98	98
7[a]	C(O)Me	Cl	K_2CO_3	1	100	100
8[a]	C(O)Me	Cl	K_2CO_3	10^{-4}	31	310 000
9[b]	H	Br	K_2CO_3	1	96	96
10[b]	H	Br	Cs_2CO_3	1	99	99
11[b]	OMe	Br	K_2CO_3	1	97	97
12[b]	C(O)Me	Br	K_2CO_3	1	100	100
13[b]	C(O)Me	Cl	K_2CO_3	1	14	14
14[b]	OMe	Cl	K_2CO_3	1	6	6

[a] Experimental conditions unless stated otherwise: A Schlenk flask was charged with sodium acetate (3.0 mmol), aryl halide (2.0 mmol) and the internal standard diethylene glycol di-*n*-butyl ether (100 mg); *n*-butyl acrylate (3.0 mmol) and degassed *N*,*N*-dimethylacetamide (DMA) (2 ml) were added and the reaction heated to 145 °C. **1** was then added and the reaction stirred for 18 h. After this time, the reaction mixture was allowed to cool, washed with dilute HCl (aq), extracted with dichloromethane and the organic phase dried over $MgSO_4$. Conversion and yield were determined by GC relative to the internal standard. Products were checked by NMR spectroscopy against authentic samples. [b] Essentially the same procedure was followed, only DMA diluent was replaced with xylenes and the temperature was 130 °C.

bond length in both Ibers's complex [1.939(3) Å in this study *vs.* 1.961(3) Å], and Herrmann's cycloheptatrienylidene complex [1.968(2) Å].[3]

As typical palladium complex-catalysed reactions, we tested complex **1** in Heck and Suzuki coupling reactions. Excellent results were obtained with a range of substrates (Table 1). For Heck reactions (runs 1–8), essentially quantitative conversion is seen within 18 h with 4-bromoacetophenone, even at low (10^{-4} mol%) catalyst loadings (runs 1–3). Similar results are seen with other aryl bromide substrates (runs 4 and 5). Remarkably, 4-chloroacetophenone is converted with similar activity under analogous conditions (run 8), achieving turnover numbers as high as 310 000. Suzuki reactions are also successful (runs 9–14), albeit higher catalyst concentrations are required as is usual for such reactions. However, even with relatively deactivated chloro substrates, catalytic conversion is observed. These figures of merit are superior to both analogous *N*-heterocyclic carbene and cycloheptatrienylidene catalysts in every case,[3] demonstrating an advantage particularly for the more challenging chloro substrates.

A plot of % conversion with time reveals no induction period in either reaction (Fig. 2). This suggests very rapid initiation and implies a homogeneous reaction. A similar observation is made by Herrmann and co-workers for cycloheptatrienylidene catalysts,[3] where good performance is attributed to the high thermal stability of the metal–carbene unit in their systems. We suggest the same rationale here, although the potential for electronic flexibility of the ligand between the illustrated resonance forms (Scheme 1) depending on the requirements of catalytic intermediates may also be a factor.

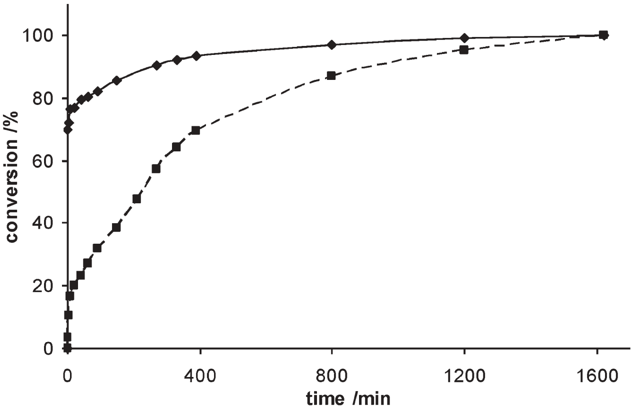


Fig. 2 Conversion *vs.* time plot for Heck coupling (- -■- -: conditions as run 1) and Suzuki coupling (—♦—: conditions as run 12).

In conclusion, our new cyclopropenylidene carbene catalyst shows excellent activity for C–C coupling reactions. Work is underway to further modify this ligand type and fully map structure–property relationships.

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Notes and references

† Compound **1** has been fully characterised by NMR spectroscopy and elemental analysis.

‡ Crystal data for $\mathbf{1}\cdot 1.5CHCl_3$. $Pd_1P_1C_{33}H_{25}Cl_2\cdot 1.5CHCl_3$, colourless block, size (mm) 0.22 × 0.16 × 0.10, M = 808.9, triclinic, space group $P\bar{1}$, a = 11.959(4) Å, b = 12.039(4) Å, c = 13.082(5) Å, α = 110.973(14)°, β = 95.71(2)°, γ = 99.735(18)°, V = 1707.0(11) A^3, Z = 2, μ = 1.124mm^{-1}, T 173 K, reflections: total/independent/R_{int} = 11715/7631/0.0240, Final $R1$ and w$R2$: 0.0395, 0.1083, largest peak, hole: 1.562, −0.674, ρ_{calc}1.574 g cm^{-3}. Programs: Bruker SMART and SAINT control and integration software, Bruker SHELXTL.[7] CCDC 637980. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702827j

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