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Catalysis of CC-coupling reactions by cyclopropenylidene palladium complexes

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Abstract

Several mixed palladium(II) complexes bearing 2,3-diarylcyclopropenylidene ligands (aryl = phenyl, mesityl, naphthyl) and triaryl- and trialkylphosphines have been prepared. Single crystal structure details of one of the dimeric chloro-bridged complexes as well as of two monomeric phosphine substituted complexes are presented and compared with appropriate structural features of similar 2,3-diaminocyclopropenylidene- and cycloheptatrienylidene complexes. The new complexes were tested as catalysts in Suzuki–Mijaura coupling reactions with bromo- and chloroarenes and their catalytic activity compared with that of analogous NHC- and cycloheptatrienylidene complexes.

Keywords: CC-coupling; Carbenes; Carbocycles; Homogeneous catalysis; Palladium

1. Introduction

In a recent publication we have shown that new palladium complexes **1** containing the carbocyclic carbene ligand cycloheptatrienylidene (CHT) (Fig. 1) represent effective catalysts in CC-coupling reactions. The activities of the easily available complexes $C_7H_6PdX_2PR_3$ are comparable or even superior to the well established corresponding NHC-complexes [1]. We have extended our ongoing efforts to explore and optimize this new class of catalysts also to include the analogous palladium complexes bearing the smallest carbocyclic carbene ligand cyclopropenylidene. Comparing the IR-data and carbonyl force constants of cycloheptatrienylidene and diphenylcyclopropenylidene metal complexes, W.M. Jones proposed that there is no significant difference in the σ-donating/π-accepting properties of both ligands which are important for the catalytic activity [2]. The synthesis of cyclopropenylidene palladium complexes has been reported at first 30 years ago [3]. Since then several articles have been published [4], focusing on the variation of the substituents at the cyclopropene ring, alternative preparation methods of cyclopropenylidene complexes, investigation of their reactivity, and discussion of structure and bonding. Analogous platinum complexes have also been described [5]. Hitherto cyclopropenylidene palladium complexes have only been employed for the isomerization of quadricyclane to norbornadiene [6]. In this context the recently reported isolation of a stable diaminocyclopropenylidene derivative and its corresponding lithium adduct by Bertrand [7] has to be mentioned which probably may stimulate the complex chemistry of such carbene ligands.

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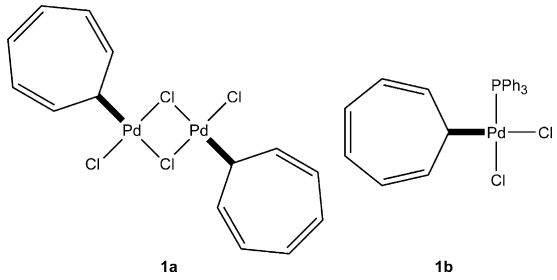


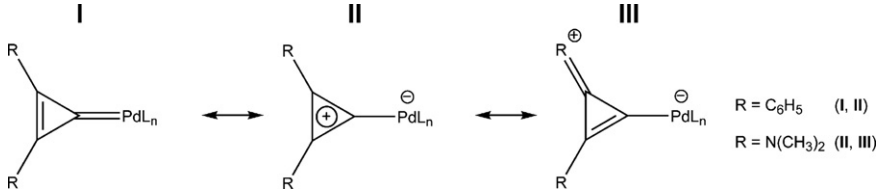
Fig. 1. Catalytically active CHT-palladium complexes.

2. Results and discussion

2.1. Synthesis and characterization

For our catalytic experiments we choose the palladium complexes **3**, **4** and **5**, respectively with aryl substituted cyclopropenylidene ligands. As starting compounds the corresponding 1,1-dichlorocyclopropenes **2** were used, which are readily accessible in large variety by *Friedel-Crafts* reactions with tetrachlorocyclopropene. The substituted dichlorocyclopropenes are transformed by reaction with palladium-black in good yield into the catalyst precursors **3**, which can be converted with phosphines almost quantitatively into the catalytically active compounds **4** and **5** respectively (Scheme 1).

Complexes **3**, **4** and **5** are stable against air and moisture; below 185 °C no decomposition could be observed.



Compounds **4** and **5** are readily soluble in polar solvents such as CH_2Cl_2, THF, acetonitrile and DMF. The dimeric mesitylcyclopropenylidene complex **3b** is very soluble in CH_2Cl_2, unlike **3a**, **3c** and all previously reported analogous cyclopropenylidene palladium complexes [3,4], including the CHT-Komplex **1a**. Crystals of **3b** suitable for X-ray analysis could be prepared enabling the first structural analysis of a dimeric chloro-bridged palladium complex with carbocyclic carbene ligands. The monomeric complexes **4**, **5a** and **5c** could be isolated only in the *cis*-configuration, whereas **5b** hitherto was obtained as a mixture of *cis*- and *trans*-isomers as indicated in the NMR-spectra by two different ^{31}P signals for coordinated phosphines [1] and a double data set in the carbon NMR including two ^{13}C resonances in the carbene region.

[1] ^{31}P resonances with appreciable different chemical shifts have also been reported for the *cis*- and *trans*-isomers of NHC–phosphane–platinum complexes by Lappert et al. in J. Organomet. Chem. 72 (1974) 139.

2.2. Structural and spectroscopic details

The monomeric complexes **4** and **5a** were characterized by single crystal X-ray diffraction. A comparison of the molecular structure of **5a** (Fig. 2) with that of the corresponding diaminocyclopropenylidene palladium complex **6** [4c] (Fig. 3) revealed significant differences (Table 1).

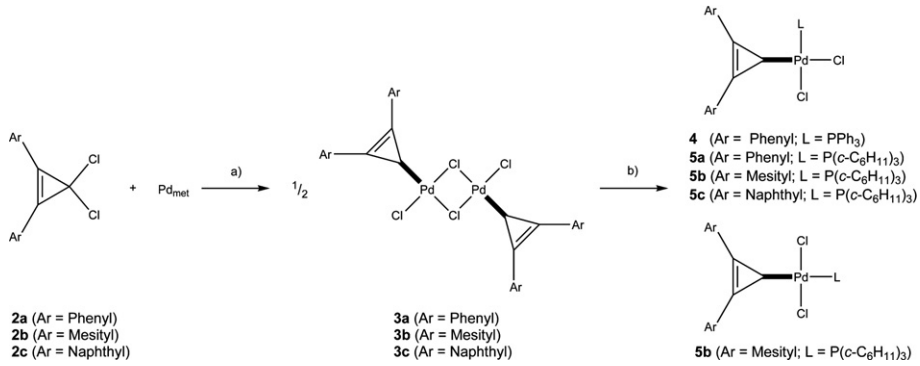
The Pd–C_1 bond distance in **5a** is somewhat shorter (0.03 Å) than in **6**, indicating a higher π-charge acceptability of the phenyl substituted cyclopropenylidene ligand compared to the amino substituted carbene.

The cyclopropenylidene moiety in **5a** shows different bond lengths among the carbon atoms of the ring: the C_2–C_3 distance is shorter (0.03 and 0.05 Å) than the C_1–C_2 and C_1–C_3 distances respectively. The bond angle C_2–C_1–C_3 is 58.1° (Table 2). In the three-membered ring of complex **6,** all bond distances are equal, the three bond angles measuring almost exactly 60°. These structural features confirm previous suggestions according to which the canonical forms **I** and **II** are predominant in diphenylcyclopropenylidene complexes, whereas complexes with diaminocyclopropenylidene ligands are best represented by forms **II** and **III** [4d]. The cyclopropene-shaped stretching of the three-membered ring in **5a** is not as pronounced as in several 2,3-diphenylcyclopropenylidene complexes of manganese and chromium bearing strong donating cyclopentadienyl or π-arene ligands [8] which obviously enhance back bonding to the carbene ligand.

The stronger π-acceptor character of the dipenylcyclopropenylidene ligand in **4** compared to that of the CHT ligand in **1b** is demonstrated by a slightly shorter Pd–C_1 distance and a considerably strengthened Pd–Cl_{trans} bond in **4** relative to **1b**. The *trans*-influence of the carbene ligand in the CHT-complex **1b** is even stronger than in complex **6** bearing the strong donating diaminocyclopropenylidene ligand, as indicated by the longer Pd–Cl_{trans} distance in **1b** compared to that in **6** (see Table 1).

The dimeric complex **3b** crystallizes in a triclinic and a less soluble monoclinic modification. The molecular structures of the compound in both modifications are different (Fig. 4).

In the triclinic cell the molecules are packed more densily resulting in two disparate coordination centers at both palladium atoms (see Tables 1 and 2). Especially the palladium–cyclopropenylidene units show different bond distances and shapes of the three-membered rings. The torsion angles between the cyclopropenylidene and the Pd_2Cl_2-



Scheme 1. Synthesis of cyclopropenylidene palladium complexes: (a) toluene, 80 °C; (b) toluene, 1 equiv L = PPh_3 or P(c-C_6H_{11})$_3$.

core differ considerably (cf. Table 2). In the monoclinic modification the dimeric molecules show both a symmetrical structure with a centre of inversion and without any molecular symmetry. The two cyclopropenylidene–palladium fragments are identical. Deviation of the cyclopropenylidene ligand from an equilateral triangle is less distinct and the dihedral angle between the C_3-ring and the coordination plane is appreciably smaller (about 40°) than in the phosphine substituted complexes **4** and **5a**. The latter may be explained by the absence of bulky phosphine ligands in the chloro-bridged complex. Differing molecular solid state structures of **3b**, found in the monoclinic and the triclinic polymorphs demonstrate the influence of packing effects on the molecular shape of the ligands.

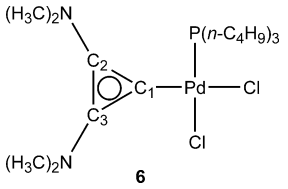


Fig. 3. Diaminocyclopropenylidene palladium complex.

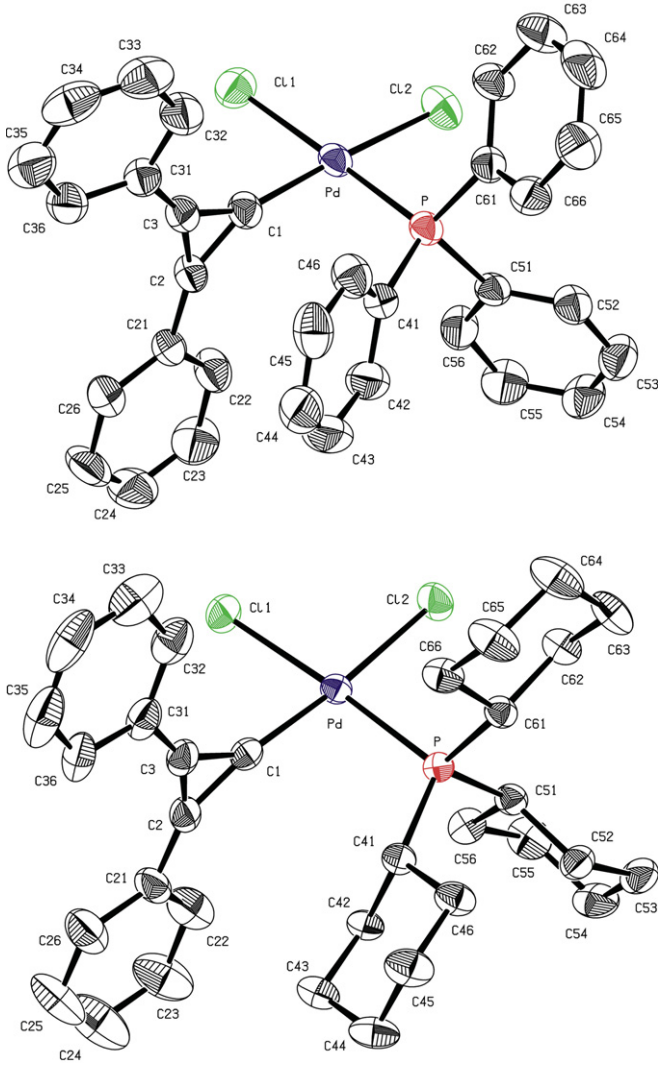


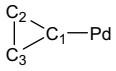
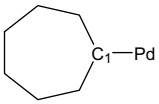
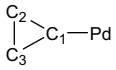
Fig. 2. ORTEP style plot of compound **4** (top) and **5a** (bottom) in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

^{13}C NMR signals for the carbon atoms directly bonded to palladium in the dimeric chlorine bridged complexes **3a** and **3b** were observed at 174 and 183 ppm. The corresponding resonances in the phosphine substituted monomeric complexes **4** and **5a**–**c** appear at 196–210 ppm (Table 4). A similar deshielding of the carbene carbon center has been mentioned at phosphine substituted Pd(II) NHC complexes compared to their dimeric parent compounds. It was explained by a lower electron density on the carbene carbon atom due to an electron poorer Pd(II) center because of the phosphine ligand's capability to accept π-electron density [9].

The ^{13}C NMR resonances of the carbene carbon atoms in dimesitylcyclopropenylidene complexes **3b** and **5b** are shifted to lower field by ca. 10 ppm relative to the analogous diphenylcyclopropenylidene (**3a**, **5a**) and the dinaphthylcyclopropenylidene compound (**5c**). The same effect is observed when phenyl substituents at the cyclopropenylidene ligands in Pd(II) complexes are replaced by stronger σ-electron donating alkyl groups [4d].

It was not possible to compare the ^{13}C NMR spectra of the new cyclopropenylidene complexes with those of the CHT complexes **1a** and **1b** due to the low solubility of the latter. In DMSO they decompose under formation of tropone (cf. [2]).

Table 1
Selected bond lengths (Å) of palladium complexes with carbocyclic carbene ligands

		$Pd–C_1$	$C_1–C_2$	$C_1–C_3$	$C_2–C_3$	$Pd–Cl_{trans}$	$Pd–Cl_{cis}$
4		1.945(2)	1.377(4)	1.381(3)	1.363(3)	2.3444(8)	2.3620(8)
5a		1.931(4)	1.380(5)	1.366(5)	1.333(6)	2.3439(10)	2.3615(10)
6[4c]		1.961(3)	1.385(5)	1.380(4)	1.384(5)	2.361(1)	2.385(1)
1b[1]		1.968(2)	–	–	–	2.3884(7)	2.3697(6)
3b[m]		A: 1.919(4)	1.384(6)	1.395(6)	1.372(6)	–	–
		B: 1.908(4)	1.376(6)	1.377(6)	1.368(6)	–	–
		1.921(4)	1.378(6)	1.392(6)	1.375(6)	–	–
3b[t]		1.907(7)	1.405(10)	1.400(11)	1.384(11)	–	–
		1.910(7)	1.397(11)	1.419(10)	1.402(11)	–	–

[m] Monoclinic.
[t] Triclinic.

Table 2
Selected bond angles (°) of cyclopropenylidene palladium complexes

	4	**5a**	**6** [4c]	**3b**[m]		**3b**[t]	
$\angle C_2–C_1–C_3$	59.2(2)	58.1(3)	60.1(2)	**A**: 59.2(3)	–	59.1(5)	59.7(5)
				B: 59.6(3)	59.5(3)		
$\angle Cl_{cis}–Pd–C_1–C_2$	88.4(3)	79.6(7)	76.6	**A**: 40.8(7)	–	43(1)	46(1)
				B: 34.0(8)	45.6(7)		

[m] Monoclinic.
[t] Triclinic.

Table 3
Crystallographic data for **3b**[t] · (C_7H_8), **3b**[m], **4**, and **5a** · (CH_2Cl_2)

	3b[t] · (C_7H_8)	**3b**[m]	**4**	**5a** · (CH_2Cl_2)
Formula	$C_{49}H_{52}Cl_4Pd_2$	$C_{42}H_{44}Cl_4Pd_2$	$C_{33}H_{25}Cl_2PPd$	$C_{34}H_{45}Cl_4PPd$
F_w	995.55	903.41	629.82	732.89
Color/habit	Colorless/needle	Colorless/fragment	Colorless/fragment	Colorless/fragment
Crystal dimensions (mm^3)	$0.02 \times 0.05 \times 0.20$	$0.10 \times 0.20 \times 0.30$	$0.10 \times 0.30 \times 0.40$	$0.15 \times 0.30 \times 0.33$
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (Å)	8.389(3)	13.445(3)	11.9490(3)	9.4348(6)
b (Å)	15.362(5)	36.781(7)	12.4010(3)	21.5832(16)
c (Å)	18.655(6)	14.516(3)	12.8655(4)	17.1777(12)
α (°)	100.88(3)	90	112.8573(10)	90
β (°)	99.88(3)	110.79(3)	92.5077(9)	104.871(6)
γ (°)	103.73(3)	90	101.5672(14)	90
V ($Å^3$)	2233.7(14)	6711(3)	1705.33(8)	3380.8(4)
Z	2	6	2	4
T (K)	150	150	233	173
D_{calcd} ($g\,cm^{-3}$)	1.480	1.341	1.227	1.440
μ (mm^{-1})	1.077	1.068	0.765	0.935
$F(000)$	1012	2736	636	1512
θ Range (°)	2.95–20.86	2.91–25.31	1.73–25.33	2.92–25.37
Index ranges (h, k, l)	±8, ±15, ±18	±16, ±44, ±17	±14, ±14, ±15	±11, ±26, ±20
Number of reflections collected	17226	80439	38714	21941
Number of indepenndent reflections/R_{int}	4670/0.084	12166/0.030	6234/0.047	6185/0.037
Number of observed reflections [$I_o > 2\sigma(I_o)$]	2386	7334	5342	4043
Number of data/restraints/parameters	4670/0/509	12166/0/667	6234/0/334	6185/0/361
$R_1/wR_2[I_o > 2\sigma(I_o)]$[a]	0.0325/0.0444	0.0322/0.0778	0.0325/0.0699	0.0342/0.0830
R_1/wR_2 (all data)[a]	0.0880/ 0.0508	0.0562/ 0.0850	0.0409/0.0721	0.0610/0.0887
Goodness-of-fit (on F^2)[a]	0.732	0.861	1.043	0.943
Largest difference in peak and hole (e $Å^{-3}$)	+0.55/−0.32	+0.68/−0.61	+0.48/−0.29	+0.94/−0.45

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

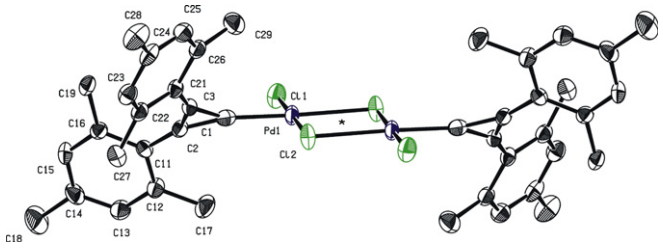


Fig. 4. ORTEP style plot of compound **3b**[m] (molecule **A**) in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. A centre of inversion is indicated by a ∗. The symmetry operation to equivalent atom positions is defined by $(-x, 2-y, -z)$.

Table 4
^{13}C-chemical shifts of the carbene carbons of diarylcyclopropenylidene palladium(II) complexes

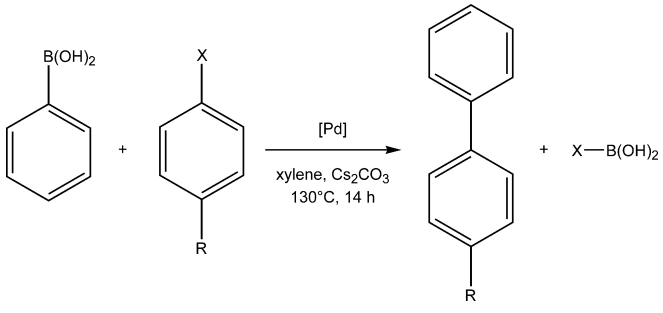
Complex	δ (ppm)	Solvent
3a	174.0	DMF-d_7
3b	182.9	$CDCl_3$
3c	not observed	$CDCl_3$
4	196.1	$CDCl_3$
5a	197.7	$CDCl_3$
5b	209.2/202.4[a]	$CDCl_3$
5c	200.3	$CDCl_3$

[a] Mixture of *cis*- and *trans*-isomers.

2.3. Catalytic properties

Complexes **3a** and **4** were tested as catalysts in Suzuki coupling reactions of bromo and chloroarenes and compared with the CHT-complexes **1** and with corresponding NHC-complexes. Unlike NHC-catalysts [9], but similar to the CHT-catalyst **1b** catalyst **4** did not exhibit an induction period (Fig. 5).

However, as shown in Table 5 cyclopropenylidene complex **4** does not approach the catalytic activity of the corresponding CHT-complex **1b** [1], especially at the coupling of chloroarenes and deactivated bromoarenes (entries 5–10 in Table 5). The best cyclopropenylidene catalysts **3b** and **5b** (entry 10 in Table 5 and entry 12 in Table 6) are even less active than the most effective NHC-phosphane system (entry 11 in Table 5). This may be due to a supposed lower σ-donating ability of the diphenylcyclopropenylidene ligand compared to the cycloheptatrienylidene. However, there is too little data as yet to reliably explain this effect.



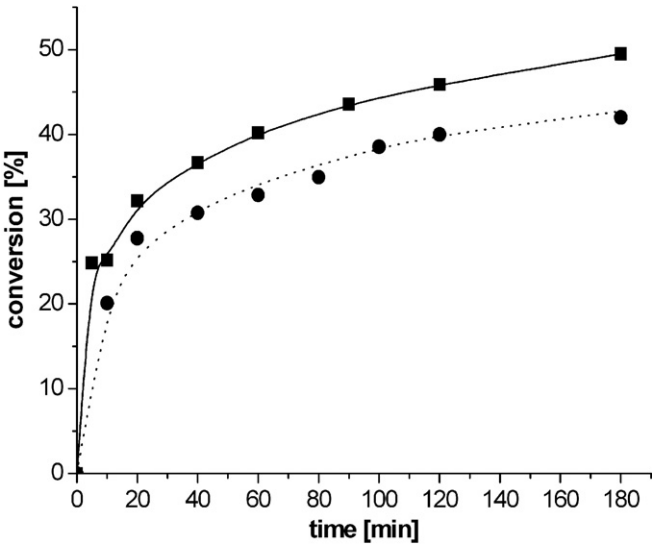


Fig. 5. Conversion-time plot for the Suzuki coupling of *p*-bromoanisole with phenylboronic acid; catalysts **1b** (■, —; 0.1 mol %) and **4** (●, ···; 0.1 mol %) are compared.

Table 5
Comparison of the catalytic activity of cyclopropenylidene- and CHT-complexes in Suzuki coupling reactions.

Entry	R	X	Cat.	mol % [Pd]	Yield (%) [a]	TON
1	H	Br	**4**	10^{-3}[b]	98	9.8×10^4
2	H	Br	**1b**	10^{-3}[b]	100	10^5
3	H	Br	**4**	10^{-4}[b]	55	5.5×10^5
4	H	Br	**1b**	10^{-4}[b]	89	8.9×10^5
5	OCH_3	Br	**4**	0.01[b]	21	2100
6	OCH_3	Br	**1b**	0.01[b]	43	4300
7	$C(O)CH_3$	Cl	**4**	0.01	1	100
8	$C(O)CH_3$	Cl	**1b**	0.01	11	1100
9	OCH_3	Cl	**1a**[c]	1	93	93
10	OCH_3	Cl	**3b**[c]	1	55	55
11	OCH_3	Cl	NHC[d]	1	69[e]	69

[a] GC yield with diethylene glycol di-*n*-butyl ether as the internal standard.
[b] K_2CO_3 as base.
[c] *In situ* with 1 equiv P(*c*-C_6H_{11})$_3$.
[d] Diiodo{1,3-di[(R)-1-phenylethyl]imidazolin-2-ylidene}(tricyclohexylphosphino)-palladium(II).
[e] After 32 h.

In Table 6 the influence of different substituents at the cyclopropenylidene ligand on the catalytic efficiency is depicted. As demonstrated by entries 9, 12 and 15 the complex with the mesityl substituted cyclopropenylidene ligand **5b** shows a somewhat higher activity in the coupling reaction of chloroanisole compared to the corresponding phenyl- and naphthyl-substituted carbene complexes **5a** and **5c**. This result may be explained by a greater effect of the bulkier mesityl substituents on the metal environment (cf. Fig. 4). Catalyst **5a** with the stronger donating phosphine P(*c*–C_6H_{11})$_3$ gives significantly better results than the analogous complex **4** with P(C_6H_5)$_3$ (cf. entries 5 and 7 in Table 5 with 2 and 7 in Table 6).

Table 6
Catalytic activities of palladium complexes with different diarylcyclopropenylidene ligands

Entry	R	X	Cat.	mol % [Pd]	Yield [%][a]	TON
1	H	Br	**5a**	10^{-3}	82[b]	8.2×10^4
2	OCH_3	Br	**5a**	0.01	46[b]	4600
3	H	Br	**5b**	10^{-3}	94[b]	9.4×10^4
4	OCH_3	Br	**5b**	0.01	28[b]	2800
5	H	Br	**5c**	10^{-3}	85[b]	8.5×10^4
6	OCH_3	Br	**5c**	0.01	23[b]	2300
7	$C(O)CH_3$	Cl	**5a**	0.01	28	2800
8	H	Cl	**5a**	0.01	14	1400
9	OCH_3	Cl	**5a**	1	18	18
10	$C(O)CH_3$	Cl	**5b**	0.01	33	3300
11	H	Cl	**5b**	0.01	16	1600
12	OCH_3	Cl	**5b**	1	29	29
13	$C(O)CH_3$	Cl	**5c**	0.01	38	3800
14	H	Cl	**5c**	0.01	13	1300
15	OCH_3	Cl	**5c**	1	16	16

[a] GC yield with diethylene glycol di-*n*-butyl ether as the internal standard.
[b] K_2CO_3 as base.

3. Conclusion

Palladium complexes with arylsubstituted cyclopropenylidene ligands are readily accessible in large variety by reaction of 2,3-diaryl-1,1-dichlorocyclopropenes with palladium black. Their phosphine substituted derivatives differ significantly from analogous 2,3-diaminocyclo-propenylidene complexes with regard to structural features. As deduced from palladium–carbene bond lengths and from their *trans*-influence on Cl_{trans} in *cis*-carbene(phosphine)–palladium dichlorides the diarylcyclopropenylidene ligands reveal appreciably higher π-acceptor qualities compared to cycloheptatrienylidene. This may be the reason why the diarylcyclopropenylidene palladium(II) complexes are less active catalysts in CC-coupling reactions than the corresponding cycloheptatrienylidene complexes. But, similar to the latter they do not exhibit an induction period.

4. Experimental

General comments: Tetrachlorocyclopropene [10] and the diarylcyclopropenones [11] were prepared according to literature. All experiments were carried out under dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and stored under argon. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JMX-GX 400 spectrometer (frequencies: ^1H 399.8 MHz, ^{13}C 100.5 MHz, ^{31}P 161.8 MHz) at room temperature and referenced to the residual ^1H and ^{13}C signals of the solvents or 85% H_3PO_4 as an external standard (^{31}P). NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were carried out by the Microanalytical Laboratory at TU München. Mass spectra were performed on a Finnigan MAT 90 spectrometer using the FAB technique (Mass Spectrometry Laboratory, TU München). GC spectra were measured on a Hewlett–Packard gas chromatograph GC 6890 equipped with a FID detector. Melting points were measured with a Büchi melting point apparatus system.

4.1. Synthesis of the 1,1-dichloro-2,3-diarylcyclopropenes

General procedure: The 1,1-dichloro-2,3-diarylcyclopropenones were prepared following the method of Föhlisch and Bürgle [12]. An excess of oxalylchloride was added dropwise to a stirred solution of the arylcyclopropenone (dichloromethane/−78 °C). The mixture was allowed to reach room temperature and was stirred until gas evolution ceased. Volatile components were removed in vacuo and the crude product was purified by recrystallization.

1,1-Dichloro-2,3-diphenylcyclopropene (**2a**) [12].

4.1.1. 1,1-Dichloro-2,3-dimesitylcyclopropene (*2b*)

Dimesitylcyclopropenone (2.75 g, 9.47 mmol, 1.0 equiv); oxalylchloride (3.15 g, 24.8 mmol, 2.6 equiv); recrystallization from hexane/dichloromethane; colorless needles; yield: 3.04 g (93%); $C_{21}H_{22}Cl_2$ ($M = 345.31$). Anal. Calc. C, 73.04; H, 6.42. Found: C, 75.21; H, 6.73%. ^1H NMR ($CDCl_3$): δ [ppm] = 6.95 (s, 8H, Ar–H), 2.33 (m, 18H, CH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ [ppm] = 140.5, 139.1, 130.0, 128.8, 122.8, 21.3 (*p*-CH_3), 21.2(*o*-CH_3).

4.1.2. 1,1-Dichloro-2,3-dinaphthylcyclopropene (*2c*)

Dinaphthylcyclopropenone (1.75 g, 5.71 mmol, 1.0 equiv); oxalylchloride (2.00 g, 15.6 mmol, 2.8 equiv); recrystallization from dichloromethane; yellow needles; yield: 1.84 g (89%); $C_{23}H_{14}Cl_2$ ($M = 361.26$). Anal. Calc. C, 76.47; H, 3.91. Found: C, 76.56; H, 3.79%.

^1H NMR ($CDCl_3$): δ [ppm] = 8.54 (d, $^3J = 8.0$ Hz, 2H), 8.16 (d, $^3J = 7.2$ Hz, 2H), 8.07 (d, $^3J = 8.0$ Hz, 2H), 7.98 (d, $^3J = 7.6$ Hz, 2H), 7.66 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ [ppm] = 133.9, 132.2, 131.5, 130.4, 128.7, 127.8, 126.9, 126.2, 125.8, 125.5, 125.3, 122.3.

4.2. Synthesis of the chloro bridged complexes

General procedure: Pd black and the 1,1-dichloro-2,3-diarylcyclopropene were stirred in 5–10 mL toluene for 24–30 h at 80 °C. The product mixture was then extracted in two portions for 8–48 h in a small Soxhlet apparatus with 25–50 mL of boiling dichloromethane in each case. The combined extracts were concentrated under reduced pressure to 20–40 mL and cooled to −10 °C. The precipitated crystalline product was filtered off, washed with diethyl ether and dried in vacuo.

4.2.1. Bis[dichloro(diphenylcyclopropenylidene) palladium(II)] (*3a*)

Pd black 776 mg (7.29 mmol, 1.0 equiv); 1,1-dichloro-2,3-diphenylcyclopropene 1.56 g (5.97 mmol, 1.2 equiv); yellow powder; yield: 1.37 g (51%); $^{30}H_{22}Cl_4Pd_2$ ($M = 737.15$). Anal. Calc. C, 48.88; H, 3.01; Pd, 28.87. Found: C, 48.73; H, 2.80; Pd, 28.8%.

^{1}H NMR (DMF-d_7): δ [ppm] = 8.75 (m, 8H, Ar–H), 8.01(m, 4H, Ar–H), 7.87 (m, 8H, Ar–H). ^{13}C{^{1}H} NMR (DMF-d_7): δ [ppm] = 177.1 (backbond carbons), 174.0 (carbene C), 137.0, 135.0, 130.5, 122.5 (assignment by Inverse Gated ^{1}H-Decoupling; relaxation time: 10 s).

4.2.2. Bis[dichloro(dimesitylcyclopropenylidene) palladium(II)] (**3b**)

Pd black 995 mg (9.35 mmol, 1.2 equiv); 1,1-dichloro-2,3-dimesitylcyclopropene 2.67 g (7.73 mmol, 1.0 equiv); yellow-orange powder; yield: 2.38 g (68%); $C_{42}H_{44}Cl_4Pd_2$ (M = 903.41). Anal. Calc. C, 55.84; H, 4.91; Pd, 23.56. Found: C, 55.79; H, 4.78; Pd, 23.4%.

^{1}H NMR ($CDCl_3$): δ [ppm] = 7.04 (s, 8H, Ar–H), 2.56 (s, 24H, *o*-CH_3), 2.39 (s, 12H, *p*-CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ [ppm] = 182.9 (carbene C), 180.9, 145.4, 141.6, 129.5, 120.6, 21.7 (*p*-CH_3), 21.5 (*o*-CH_3).

4.2.3. Bis[dichloro(dinaphthylcyclopropenylidene) palladium(II)] (**3c**)

Pd black 436 mg (4.10 mmol, 1.3 equiv); 1,1-dichloro-2,3-dinaphthylcyclopropene 1.19 g (3.28 mmol, 1.0 equiv); yellow powder; yield: 0.53 g (34%); $C_{46}H_{30}Cl_4Pd_2$ (M = 937.38). Anal. Calc. C, 59.07; H, 3.02; Pd, 22.75. Found: C, 56.33; H, 3.67; Pd, 20.0%.

^{1}H NMR ($CDCl_3$): δ [ppm] = 8.88 (d, ^3J = 8.8 Hz, 2H), 8.52 (d, ^3J = 8.0 Hz, 2H), 8.33 (d, ^3J = 7.2 Hz, 2H), 8.2–7.6 (m, 22H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ [ppm] = 171.1, 146.5, 134.0, 132.3, 130.5, 128.8, 127.9, 127.0, 125.9, 125.6, 122.4 (carbene C not observed).

4.3. Synthesis of the phosphine complexes

General procedure: Complex **3a/b/c** and the concerning phosphine was dissolved in toluene and stirred at 80 °C for 2–3 h. The resulting solid was filtered off, washed with toluene and pentane and dried in vacuo.

4.3.1. cis-Dichloro(diphenylcyclopropenylidene) (triphenylphosphine)palladium(II) (**4**)

2a 103 mg (0.14 mmol, 1.0 equiv); PPh_3 77 mg (0.29 mmol, 2.1 equiv); yellowish microcrystalline powder; mp: 185 °C (dec.); yield: 160 mg (91%); $C_{33}H_{25}Cl_2PPd$ (M = 629.82). Anal. Calc. C, 62.93; H, 4.00; Pd, 16.90. Found: C, 61.88; H, 3.97; Pd, 17.0%.

^{1}H NMR ($CDCl_3$): δ [ppm] = 8.5–7.0 (m, 25H, Ar–H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ [ppm] = 196.1 (carbene C), 173.5, 135.8, 134.6, 134.5, 133.5, 133.2, 131.1, 130.5, 130.0, 129.6, 128.5, 128.4, 121.8. ^{31}P{^{1}H} NMR ($CDCl_3$): δ [ppm] = 27.6 (s).

MS (FAB): *m*/*z* (%): 595 (15, $[M-Cl]^+$), 557 (2, $[M-2Cl]^+$), 191 (13, [carbene]).

4.3.2. cis-Dichloro(diphenylcyclopropenylidene) (tricyclohexylphosphine)palladium(II) (**5a**)

2a 128 mg (0.17 mmol, 1.0 equiv); P(*c*-C_6H_{11})$_3$ 98 mg (0.35 mmol, 2.1 equiv); yellowish microcrystalline powder; mp: 205 °C (dec.); yield: 261 mg (93 %); ^{1}H NMR ($CDCl_3$): δ [ppm] = 8.40 (m, 4H, Ar–H), 7.72 (m, 6H, Ar–H), 2.1–0.8 (m, 33H, *c*-C_6H_{11}).

^{13}C{^{1}H} NMR ($CDCl_3$): δ [ppm] = 197.7 (carbene C), 175.4, 136.0, 133.2, 129.9, 122.3, 35.9 (*c*-C_6H_{11}), 35.6 (*c*-C_6H_{11}), 29.9 (*c*-C_6H_{11}), 27.3 (*c*-C_6H_{11}), 27.2 (*c*-C_6H_{11}), 26.0 (*c*-C_6H_{11}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ [ppm] = 51.4 (s). MS (FAB): *m*/*z* (%): 611 (18, $[M-Cl]^+$), 575 (10, $[M-2Cl]^+$), 191 (100, [carbene]). $C_{33}H_{44}Cl_2PPd$ (M = 649.00); Anal. Calc. C, 61.07; H, 6.83; Pd, 16.40. Found: C, 59.38; H, 6.36; Pd, 15.1%.

4.3.3. cis/trans-Dichloro(dimesitylcyclopropenylidene) (tricyclohexylphosphine)palladium(II) (**5b**)

2b 173 mg (0.19 mmol, 1.0 equiv); P(*c*-C_6H_{11})$_3$ 113 mg (0.40 mmol, 2.1 equiv); yellowish microcrystalline powder; mp: 200 °C (dec.); yield: 261 mg (93%); $C_{39}H_{56}Cl_2PPd$ (M = 733.16). Anal. Calc. C, 63.89; H, 7.70; Pd, 14.52. Found: C, 64.30; H, 7.80; Pd, 13.9%.

^{1}H NMR ($CDCl_3$): δ [ppm] = 7.01 (s, 4H, Ar–H), 2.55 (s, 12H, *o*-CH_3), 2.36 (s, 6H, *p*-CH_3), 2.1–1.0 (m, 33H, *c*-C_6H_{11}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ [ppm] = 209.2 (d, $^2J_{PC}$ = 191 Hz, *trans* carbene C), 202.4 (s, *cis* carbene C), 180.3, 180.2, 179.3, 144.6, 144.0, 141.3, 141.1, 141.0, 129.5, 129.2, 121.9, 121.7, 36.2 (*c*-C_6H_{11}), 35.9 (*c*-C_6H_{11}), 32.0 (*c*-C_6H_{11}), 31.2 (*c*-C_6H_{11}), 31.0 (*c*-C_6H_{11}), 30.0 (*c*-C_6H_{11}), 29.7(*c*-C_6H_{11}), 29.6(*c*-C_6H_{11}), 27.7 (*c*-C_6H_{11}), 27.6 (*c*-C_6H_{11}), 27.2 (*c*-C_6H_{11}), 27.1 (*c*-C_6H_{11}), 26.6 (*c*-C_6H_{11}), 26.0 (*c*-C_6H_{11}), 21.6 (CH_3), 21.3 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ [ppm] = 49.2 (s), 25.1 (s).

MS (FAB): *m*/*z* (%): 695 (8, $[M-Cl]^+$), 659 (4, $[M-2Cl]^+$), 275 (100, [carbene]).

4.3.4. cis-Dichloro(dinaphthylcyclopropenylidene) (tricyclohexylphosphine)palladium(II) (**5c**)

2c 135 mg (0.14 mmol, 1.0 equiv); P(*c*-C_6H_{11})$_3$ 95 mg (0.34 mmol, 2.4 equiv); yellow-green microcrystalline powder; mp: 205 °C (dec.); yield: 174 mg (81%); $C_{41}H_{48}Cl_2PPd$ (M = 749.12). Anal. Calc. C, 65.74; H, 6.46; Pd, 14.21. Found: C, 65.78; H, 6.26; Pd, 13.3%.

^{1}H NMR ($CDCl_3$): δ [ppm] = 9.83 (d, ^3J = 8.4 Hz, 2H, Ar–H), 8.44 (d, ^3J = 7.2 Hz, 2H, Ar–H), 8.15 (d, ^3J = 8.0 Hz, 2H, Ar–H), 7.93 (m, ^3J = 7.8/8.4 Hz, 4H, Ar–H), 7.71 (m, ^3J = 7.6/8.0 Hz, 4H, Ar–H), 2.0–0.7 (m, 33H, *c*-C_6H_{11}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ [ppm] = 200.3 (carbene C), 174.6, 136.7, 133.8, 132.7, 129.6, 128.8, 128.2, 127.9, 126.7, 125.3, 119.9, 36.0 (*c*-C_6H_{11}), 35.8 (*c*-C_6H_{11}), 29.7 (*c*-C_6H_{11}), 27.2 (*c*-C_6H_{11}), 27.1 (*c*-C_6H_{11}), 25.8 (*c*-C_6H_{11}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ [ppm] = 51.1 (s).

MS (FAB): *m*/*z* (%): 711 (2, $[M-Cl]^+$), 675 (7, $[M-2Cl]^+$), 291 (68, [carbene]).

4.4. Suzuki coupling

Inside a glove box a Schlenk flask was charged with potassium or cesium carbonate (3.0 mmol), aryl halide

(2.0 mmol), phenylboronic acid (2.4 mmol), and the internal standard diethylene glycol di-*n*-butyl ether (100 mg).

Then (outside the glove box) degassed xylene (2 mL) was added against a stream of argon, and the reaction mixture was heated to 130 °C. When the reaction temperature had been reached the catalyst solution was added against a stream of argon. At the end of the reaction solution was cooled to 25 °C, treated with water (3 mL), and extracted with diethyl ether (3 × 2 mL). The organic phase was dried over $MgSO_4$. Conversions and yields were determined GC analysis.

Catalyst solutions for the catalysts **3** and **4a**, **4b**, **4c**: A solution of catalyst (0.02 mmol) in DMF (10 mL) was stored in the freezer. The concentration was selected such that 0.1 mL of the solution corresponds to a catalyst/substrate ratio of 0.01 mol% catalyst. For experiments with extremely low catalyst concentrations the catalyst solution was diluted further. Catalyst solutions for the catalyst **2b**: The solution was prepared by stirring the phosphane with **2b** (P/Pd ratio 1:1) in DMF (0.5 mL) for 10 min at 25 °C.

4.5. Single crystal X-ray structure determination of compounds $3b^{[t]} \cdot (C_7H_8)$, $3b^{[m]}$, 4, and $5a \cdot (CH_2Cl_2)$

General: Crystal data and details of the structure determination are presented in Table 3. Suitable single-crystals for the X-ray diffraction study were grown with standard cooling techniques. Crystals were stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collections were performed at low temperatures (OXFORD CRYOSYSTEMS cooling device). Each crystal was measured with a couple of data sets in rotation scan modus. Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and aromatic d_{C-H} distances of (1.00, 0.99 Å) and (0.95 or 0.94 Å), respectively, and $U_{iso(H)} = 1.2U_{eq(C)}$. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.008. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed with the WINGX system, including the programs PLATON, SHELXL-97, and SIR92[13]. *Specials*: $\mathbf{3b}^{[t]} \cdot (C_7\mathbf{H}_8)$: (OXFORD DIFFRACTION, XCALIBUR, κ-CCD; sealed tube, Enhance X-ray Source, SPELLMAN, DF3; five data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 2.00°$; d$x = 50$; $T = 150$ K). Low quality of the crystal forced us to cut the data set at $\theta = 20.86°$. $\mathbf{3b}^{[m]}$: (OXFORD DIFFRACTION, XCALIBUR, κ-CCD; sealed tube, Enhance X-ray Source, SPELLMAN, DF3; five data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 0.75°$; d$x = 60$; $T = 150$ K). The asymmetric unit contains two crystallographic independent molecules **A** and **B** of the target compound **3b**. **A** is located around a centre of symmetry in contrast to **B**. One molecule of the solvent CH_2Cl_2 could not be resolved and modeled without a doubt. This problem was solved be using the PLATON "calc squeeze" procedure. **4**: (NONIUS, MACH3, κ-CCD; rotating anode, NONIUS, FR591; nine data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 2.00°$, d$x = 40$; $T = 233$ K). Two molecules of the solvent CH_2Cl_2 could not be resolved and modeled without a doubt. This problem was solved be using the PLATON "calc squeeze" procedure. $\mathbf{5a} \cdot \mathbf{(CH_2Cl_2)}$ (OXFORD DIFFRACTION, XCALIBUR, κ-CCD; sealed tube, Enhance X-ray Source, SPELLMAN, DF3; four data sets in rotation scan modus with $\Delta\omega = 1.0°$; d$x = 50$; $T = 173$ K).

Note added in proof

Very recently in a later submitted paper Duncan F. Wass et al. (Chem. Commun., 2007, doi:10.1039/b702827j) published the molecular structure of compound **4**. These X-ray results confirm our findings and we conclude a minor influence of packing effects on the solid state structure for this organometallic compound.

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Appendix A. Supplementary material

CCDC 650964, 650965, 650963 and 650962 contain the supplementary crystallographic data for $\mathbf{3b}^{[t]} \cdot (C_7\ \mathbf{H}_8)$, $(\mathbf{3b}^{[m]})$, **4** and $\mathbf{5a} \cdot (\mathbf{CH_2Cl_2})$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.050.

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