

Chiral diaminocarbene palladium(II) complexes: Synthesis, reduction to Pd(0) and activity in the Mizoroki–Heck reaction as recyclable catalysts

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Abstract

A preparation of chiral palladium(II) bis-diaminocarbene complexes was developed from the corresponding silver(I) diaminocarbenes and bis(acetonitrile)dichloropalladium(II). Crystal structure details of *trans*-diiodo bis[(4*R*,5*R*)-1,3-dibenzyl-4,5-di-*tert*-butylimidazolin-2-ylidene] palladium(II) are presented. Mixed diaminocarbene–phosphine complexes were also prepared in two steps from the corresponding imidazolidinium salts and palladium acetate. The very high air, moisture and thermal stability of such complexes were confirmed. These two families of complexes were tested in the Mizoroki–Heck reaction. Their ability to be reduced into Pd(0) which undergoes oxidative addition with aryl halides was studied by cyclic voltammetry. The ability of different agents to generate Pd(0) complexes and the reactivity of these latter with aryl halides were also studied *in situ*. The obtained results allowed us to perform Heck reactions at temperatures starting from 40 °C in DMF, by activation of the palladium(II) catalyst precursor. Moreover, in the case of the bis-diaminocarbene complexes, the Pd(0) catalysts were totally re-oxidized during the work-up and the starting Pd(II) complexes could be quantitatively recovered.

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1. Introduction

N-heterocyclic carbenes (NHC) have recently emerged as an important family of ligands with strong σ -donor electronic properties [1–4]. In contrast to the widely used phosphines complexes, most of the complexes formed with these ligands are exceptionally stable toward heat, air and moisture. Indeed, NHC are tightly bound to the metal thereby avoiding decomposition pathway or deposition of free (and inactive) metal under catalytic conditions.

Herrmann et al. reported for the first time in 1995 the use of palladium(II) NHC complexes in the Heck

reaction [5]. This group postulated that the Pd(II) species, a stable catalyst precursor, might be activated into Pd(0) for the coupling to occur. Since then, carbene complexes of Pd(II) or Pd(0) have been widely used as catalysts or catalyst precursors for Heck [6–23] or Suzuki [10,11,17,18,20,24–31] reactions, α -arylations of ketones or amides [32–35], and other C–C couplings [20,36–40], as well as *N*-arylations of amines or imines [34,41–44], allylic alkylations [45] and oxidative kinetic resolution of alcohols [46].

Generally, Heck reactions conducted with these complexes required high temperatures (higher than 120 °C) and polar solvents. These drastic conditions, that seemed to be necessary to get good conversions, have highlighted the stability of many of these Pd species. For instance, couplings of aryl chlorides could be performed at 140 °C by stabilizing the active Pd(0) complex in ionic liquids [7].

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Several syntheses of chiral NHC complexes of palladium have been reported in the literature [16,20,22,47–49]. But, to our knowledge, the only example of asymmetric catalysis with Pd carbene complexes, giving good selectivities, was reported by Hartwig and co-workers in 2001 in the α -arylation of amides [32] with enantiomeric excesses up to 76%. However, maybe as a consequence of the harsh conditions required for the Heck reaction, only one example of an asymmetric version, with a low asymmetric induction (e.e. = 8%), was mentioned by Enders et al. [16].

The generation of the active species and its exact nature and reactivity, was not precisely determined even though, as cited above, Herrmann et al. reported increased activities in the presence of a reducing agent [5]. In order to develop an asymmetric version of the Heck reaction with NHC complexes of palladium, it would be of interest to be able to perform the reaction under conditions as mild as possible. Therefore, the determination of the limitant steps of the coupling reaction is of great importance.

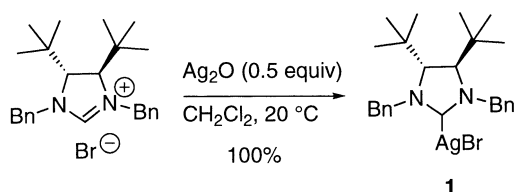
Another important point concerns the regeneration and re-use of the catalyst. Polymer-supported carbene complexes of Pd(II) as recyclable catalysts for the Heck reaction were recently reported [19]. The possibility to recycle non-supported palladium(II) carbene complexes was also already considered by Enders et al. [16]. However, this opportunity was not widely studied in homogeneous catalysis but could be of particular interest in the case of chiral catalysts whose preparations are often expensive and require multi-step syntheses.

We wish to report here the synthesis of several chiral imidazolin-2-ylidene palladium(II) complexes, their activity in the Mizoroki–Heck reaction, their reduction into Pd(0) and the re-oxidation of the Pd(0) species. We also wish to present the possible use of some of these Pd(II) complexes as recyclable chiral catalysts.

2. Results and discussion

2.1. Synthesis of bis-carbene palladium(II) complexes

Recently, we have reported the preparation of various chiral silver(I) diaminocarbenes such as **1** [50], using the method described by Wang and Lin [51] (Scheme 1). These chiral complexes were used for the in situ

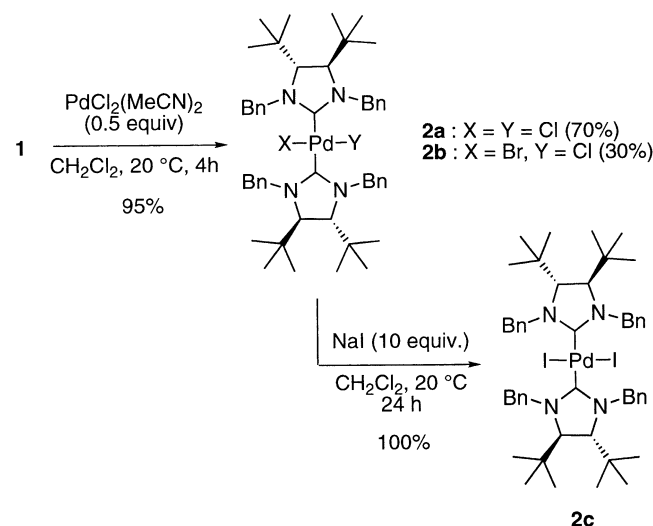


Scheme 1. Preparation of silver(I) diaminocarbene complexes.

preparation of several imidazolin-2-ylidene copper complexes which were found to be efficient catalysts for the enantioselective conjugate addition of diethylzinc to enones [52,53], affording enantioselectivities up to 88%. In addition to the fact that these silver(I) carbene complexes are generally air-stable and easy to handle, they could often act as effective carbene transfer agents towards various transition metals, including palladium [51]. This property was recently exploited by several groups for the synthesis of palladium(II) imidazol-2-ylidene complexes. [10,15,47].

Thus, we first examined the ability of the chiral silver complex **1** to act as a carbene transfer agent towards Pd(II) complexes. Indeed, treatment of **1** by 0.5 equivalent of $\text{PdCl}_2(\text{MeCN})_2$ in CH_2Cl_2 at 20 °C, led after 4 h, to a mixture of the bis-carbene complexes **2a** and **2b** in 95% yield (Scheme 2).

These two complexes were easily isolated by filtration of the silver salts and concentration. The yellow solid obtained was air-stable and non-sensitive to water. These complexes were also stable on silica gel and could be separated by flash-chromatography. This purification allowed the full characterization of each complex and the determination of their ratio in the crude mixture by NMR (**2a/2b** = 70:30). A *trans* configuration was attributed to the major isomer **2a** since its NMR spectrum was characteristic of a symmetrical complex (C_2 symmetry). The ^1H -NMR signals of **2b** were representative of a non-symmetrical complex. The ^{13}C -NMR chemical shift of the carbene carbon (C-Pd) in the minor isomer **2b** (198.4 ppm) was very similar to the one of **2a** (198.6 ppm). Since the difference of chemical shifts of the carbene carbon between *trans* or *cis* palladium diaminocarbene complexes was shown to be generally important [11], we assumed that **2b** was the *trans* diaminocarbene complex with one bromide and one chloride on the palladium and not the *cis* complex.



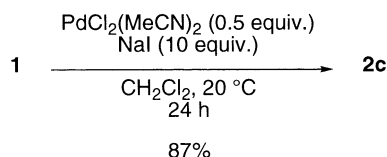
Scheme 2. Preparation of Pd(II) bis-diaminocarbene complexes.

Although the separation of the complexes **2a** and **2b** was necessary to determine their exact structure, it was rather delicate and arduous. Therefore, the mixture of **2a/2b** was quantitatively transformed into the *trans* diiodo complex **2c** by treatment with an excess of sodium iodide in CH_2Cl_2 at 20°C (Scheme 2). This halogen exchange at room temperature allowed the one step synthesis of complex **2c** in 87% yield from the silver carbene **1** and $\text{PdCl}_2(\text{MeCN})_2$, in the presence of an excess of sodium iodide (Scheme 3).

The structure of **2c** was determined by X-ray spectroscopy (Fig. 1). The crystallographic data are shown in Table 1. Selected bond lengths and angles are given in Table 2. This *trans* bis-square planar complex of Pd(II) shows a high degree of symmetry. The diaminocarbenes planes are both oriented of 69.3° and -68.1° towards the coordination plan of the palladium and the dihedral angle between the two diaminocarbene subunits is of 42.6° . The palladium–carbene bond length is of about $2.03 \text{ \AA}$.

2.2. Synthesis of mixed phosphine–carbene palladium(II) complexes

Herrmann et al. and Nolan and co-workers have reported the superior activity of mixed phosphine–carbene complexes compared to their bis-carbene analogues [20,21]. To synthesize such complexes we first attempted, by analogy with the preparation of complexes **2**, to transfer only one diaminocarbene unit from the silver complex **1** to one equivalent of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$. Unfortunately, by this procedure, the bis-carbene **2a** was obtained in poor yield together with a mixture of non-characterized species. We turned then towards the alternative methodology described by Herrmann et al. [20]. The equimolar reaction of the imidazolinium salt **4** with $\text{Pd}(\text{OAc})_2$ in THF at 20°C , in the presence of potassium *tert*-butoxide and sodium iodide (four equivalents), led to the stable and isolable Pd(II) dimeric complex **5** (Scheme 4) which was obtained in 72% yield as a red–brown crystalline solid. This dimer was easily and rapidly cleaved by triphenylphosphine at 20°C in CH_3CN or CH_2Cl_2 . The orange crystalline solid thus obtained was also air and moisture stable and was meticulously purified by silica gel chromatography to remove possible traces of PPh_3 and other residual palladium complexes. The mixed



Scheme 3. Preparation of complex **2c**.

Table 1
Crystallographic data for compound **2c**

Compound	2c
Formula	$\text{C}_{50}\text{H}_{68}\text{PdI}_2\text{N}_4$
Colour	Yellow
Crystal class	Orthorhombic
Space group	$P2_12_12_1$
Z	4
Unit cell parameters	
<i>a</i> (Å)	16.300 (12)
<i>b</i> (Å)	17.607 (9)
<i>c</i> (Å)	17.780 (9)
Volume (Å ³)	5103 (5)
Radiation type	Mo–K α
Wavelength (Å)	0.71069
Density (g cm ^{−3})	1.41
<i>M</i> (g mol ^{−1})	1085.34
μ (cm ^{−1})	16.08
Temperature (K)	295
Shape	Parallelepiped
Diffractometer	Enraf-Nonius Mach-3
Reflections measured	4983
Independent reflections	4952

phosphine–carbene complex **6** was obtained in 82% yield.

2.3. Catalytic activities of the palladium(II) carbene complexes **2c** and **6** in the Heck reaction

We first tested the activity and stability of **2c** in the classical Heck coupling of phenyl iodide with butylacrylate (Scheme 5) [54]. The reaction performed at 120°C in DMF, in the presence of 2% mol of catalyst **2c**, led after 16 h to a complete conversion into (*E*)-

Table 2
Selected bond lengths (Å) and angles (°) for **2c**

Compound	2c
<i>Bond lengths</i>	
Pd(1)–C(2)	2.027(8)
Pd(1)–C(102)	2.038(8)
N(1)–C(2)	1.36(1)
N(101)–C(102)	1.34(1)
N(3)–C(2)	1.33(1)
N(103)–C(102)	1.32(1)
N(1)–C(5)	1.49(1)
N(3)–C(4)	1.477(11)
<i>Bond angles</i>	
C(2)–Pd(1)–C(102)	177.0(3)
N(1)–C(2)–N(3)	108.4(7)
N(101)–C(102)–N(103)	108.9(7)
Pd(1)–C(2)–N(1)	125.5(5)
Pd(1)–C(2)–N(3)	126.1(6)
C(2)–N(3)–C(4)	113.8(7)
C(2)–N(1)–C(5)	111.8(6)
C(2)–N(3)–C(14)	122.0(7)
C(2)–N(1)–C(15)	122.0(6)

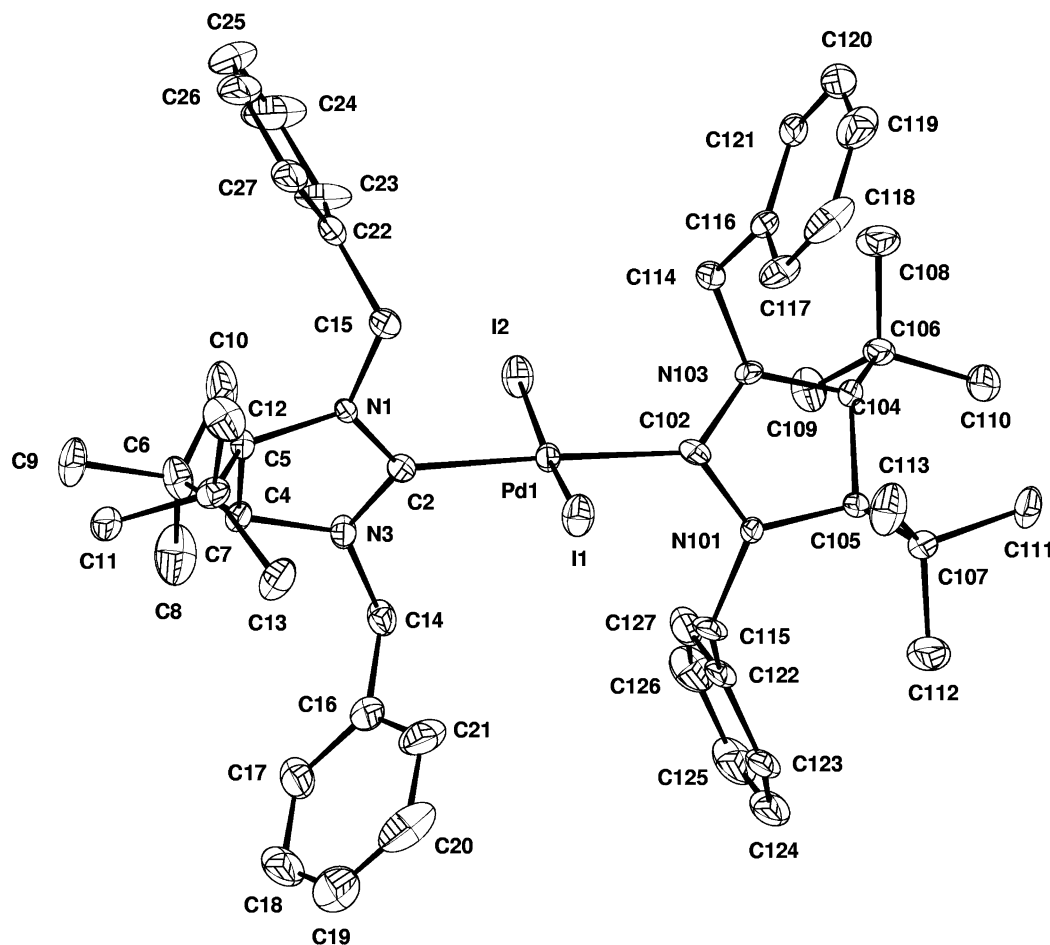
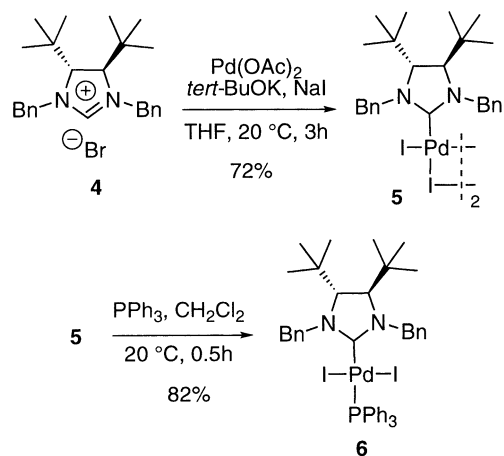


Fig. 1. ORTEP view of complex **2c**.

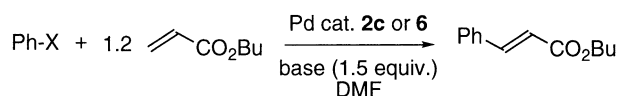
butylcinnamate (Table 3, entries 1–2). To test further the long-term stability of **2c**, very small amounts of catalyst were used (0.05 and 0.005% mol) in the presence of either sodium acetate or diisopropylethylamine. After 96 h at 120 °C, turn-over numbers up to 14 600 were

obtained without palladium metal deposit, demonstrating the stability of the catalyst in these conditions (entries 3–5). Moreover, in the standard conditions using 2% of catalyst **2c** (21.7 mg), we were surprised to detect by ^1H -NMR the presence of the initial Pd(II) catalyst in the crude mixture after work-up. More than 90% of **2c** could be recovered by simple precipitation in MeOH and drying. As mentioned before, Enders et al. already reported the possibility to recover their bis-carbene Pd(II) catalysts after the Heck reaction and they suggested, that a Pd(IV) intermediate may be involved in the catalytic cycle [16].

Heck reactions were then attempted at lower temperatures. At 80 °C, still with phenyl iodide, the reactivity decreased dramatically and only poor conversions were obtained with both bases tested (Table 3, entries 6 and 7).



Scheme 4. Preparation of the mixed phosphine–carbene complex **6**.



Scheme 5. Heck reactions with complexes **2c** and **6**.

Table 3
Heck reactions with complexes **2c** and **6**

Entry	Catalyst ^a % mol	PhX ^a	Base ^a	T (°C)	t (h)	Conv. (%) ^b	TON
1	2c 2%	PhI	<i>i</i> Pr ₂ EtN	120	16	100	50
2	2c 2%	PhI	AcONa	120	16	100	50
3	2c 0.05%	PhI	<i>i</i> Pr ₂ EtN	120	96	93	1860
4	2c 0.05%	PhI	AcONa	120	96	100	2000
5	2c 0.005%	PhI	AcONa	120	96	73	14 600
6	2c 2%	PhI	<i>i</i> Pr ₂ EtN	80	16	1	
7	2c 2%	PhI	AcONa	80	16	10	
8	2c 2%	PhBr	AcONa	120	16	2	
9	6 2%	PhI	AcONa	120	16	96	
10	6 2%	PhI	AcONa	80	16	5	
11	6 2%	PhI	<i>i</i> Pr ₂ EtN	80	16	0	

^a 1 mmol of PhX, 1.5 mmol of base, % mol of catalyst based on the amount of PhX.

^b Dodecane as internal reference.

The bis-carbene catalyst **2c** was also ineffective, even at 120 °C, to promote the coupling reaction of phenyl bromide and butylacrylate (entry 8).

Using the mixed NHC–phosphine complex **6**, the reaction proceeded rapidly at 120 °C with no traces of Pd metal deposit (entry 9). However, contrary to the bis-carbene complex **2c**, the mixed complex **6** was not recovered after the usual work-up but was only detected as traces together with traces of **2c** by ¹H-NMR of the crude reaction mixture.

At 80 °C, a very low, or no conversion, was obtained with both bases (entries 10 and 11).

In order to explain the lack of reactivity of our catalysts at 80 °C, even with PhI, and to understand how a Pd(II) complex could be recovered at the end of the reaction, we decided to investigate the reduction of complexes **2** and **6** into Pd(0) and the re-oxidation of the latter.

2.4. Reduction of palladium(II) complexes **2** and **6** to palladium(0) and re-oxidation of the generated palladium(0) complexes

2.4.1. Electrochemical reduction of palladium(II) complexes **2** and **6** to palladium(0) complexes: determination of the rate constant of the oxidative addition of aryl halides to the electrogenerated palladium(0) complexes

The electrochemical reduction of palladium(II) to palladium(0) complexes allows the characterization of the electrogenerated palladium(0) complexes in terms of nucleophilic properties by the determination of their oxidation potential, as well as the characterization of their reactivity in oxidative addition of aryl halides by the determination of the rate constants [55,56].

The electrochemical reduction of complexes **2a**, **2c** and **6** (3 mM) was investigated in DMF. Whatever the

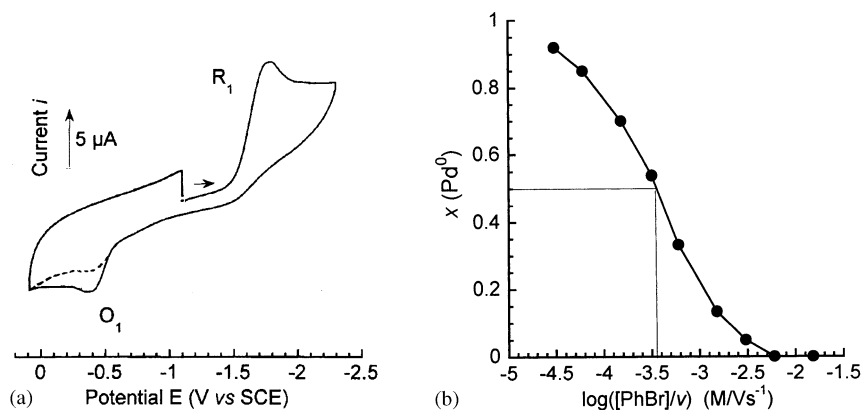


Fig. 2. (a) (—) Reduction of complex **2c** (3 mM) in DMF (containing *n*-Bu₄NBF₄, 0.3 M): cyclic voltammetry at a steady gold disk electrode (i.d. = 0.5 mm) with a scan rate $v = 10 \text{ V s}^{-1}$, at 20 °C. (---) In the presence of PhBr (3 mM). (b) Kinetics of the oxidative addition of PhBr (3 mM) with the bis(carbene)Pd(0) (3 mM) generated by the reduction of complex **2c** in DMF at 20 °C: plot of the molar fraction x of the unreacted Pd(0) complex versus $\log([\text{PhBr}]/v)$ ($x = i_{\text{ox}}^0/i_{\text{ox}}$; i_{ox} : oxidation peak current of the electrogenerated Pd(0) in the presence of PhBr at O₁; i_{ox}^0 : oxidation peak current of the electrogenerated bis(carbene)Pd(0) at O₁ in the absence of PhBr, at a given scan rate v , determined as in Fig. 2a).

Table 4

Reduction peak potentials E_{R1}^b of **2a**, **2c**, **6** and oxidation peak potentials E_{O1}^b of the electrogenerated Pd(0) complexes

Entry	Pd(II) complex ^a	E_{R1}^b (V versus SCE) ^b	E_{O1}^b (V versus SCE) ^b electrogenerated Pd(0)	k (M ⁻¹ s ⁻¹) PhI	k (M ⁻¹ s ⁻¹) PhBr
1	Bis(carbene)PdCl ₂ 2a	-2.03	-0.49	n.d. ^c	–
2	Bis(carbene)PdI ₂ 2c	-1.58	-0.48	> 1180	1180
3	(carbene)(PPh ₃)PdI ₂ 6	-1.20	-0.15	830	2
4	(PPh ₃) ₂ PdCl ₂ [58]	-0.91	-0.03	540 ^d	–

Rate constant k of the oxidative addition of aryl halides to the electrogenerated Pd(0) (DMF, 20 °C).^a [Pd(II)] = 3 mM in DMF containing *n*-Bu₄NBF₄ (0.3 M).^b Peak potentials were determined at a steady gold disk electrode (i.d. 1 mm) versus a saturated calomel electrode at a scan rate of 0.5 V s⁻¹.^c Not determined because the reduction potential of complex **2a** is close to that of PhI (-2.1 V). Consequently, it is not possible to reduce **2a** without reducing PhI.^d In THF.

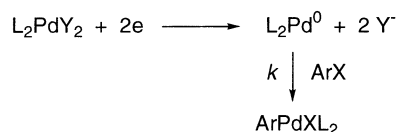
scan rate (in the range 0.2–100 V s⁻¹), the three complexes exhibited a single irreversible reduction peak R₁ with similar reduction peak current intensities (Fig. 2a, Table 4). An irreversible oxidation peak O₁ was observed on the reverse scan which characterized the complexes generated by the reduction of complexes **2a**, **2c** and **6** at R₁ (Fig. 2a, Table 4).

The determination of the absolute number n of electron(s) [57] involved in the electrochemical reduction of complex **2c** at R₁ revealed a two-electron reduction ($n = 1.8 \pm 0.1$) in the time scale of the cyclic voltammetry. Consequently the electrochemical reduction of palladium(II) complexes **2a**, **2c** and **6** generates palladium(0) complexes characterized by their oxidation peaks O₁. From the reduction potentials of the palladium(II) complexes investigated here, one observes that, for a given halide, the introduction of carbene ligands onto the Pd(II) complexes resulted in more negative potentials (Table 4, entries 1,4 and 2,3). This shows that the carbene ligand is more electron donor than PPh₃ and consequently the Pd(II) ligated by one or two carbene ligands is less easily reduced than complexes ligated by PPh₃. For a given ligand, the Pd(II) complex ligated by two iodides is more easily reduced than that ligated by two chlorides, as already observed for PPh₃ ligands [56].

Even if we are comparing peak potentials and not standard potentials, the great similarity observed for the oxidation peak potentials of the Pd(0) generated by the reduction of **2a** and **2c** (Table 4, entries 1,2) suggests that a similar complex was generated: a neutral bis(carbene)Pd(0) (Scheme 6) not ligated by the halide [59], in contrast to what is reported for PPh₃ with formation of anionic (PPh₃)₂Pd(0)Y⁻ (Y = I, Br, Cl) complexes [56]. This is probably due to the fact that the bis(carbe-

ne)Pd(0) is more electron rich and consequently less incline to coordinate anionic halides. Since the carbene ligand is more electron donor than PPh₃, the electrogenerated Pd(0) complexes ligated by carbene(s) were found to be more easily oxidized (Table 4).

Pd(0) complexes ligated by the carbene being more electron rich than those ligated by PPh₃, they should be more reactive in the oxidative addition of aryl halides (ArX). The rate constant k of the oxidative addition of the electrogenerated Pd(0) complex (Scheme 6) was determined by performing cyclic voltammetry at various scan rates v , taking the opportunity that the oxidation current of Pd(0) at O₁ is proportional to its concentration [55,56]. At low scan rate ($v = 0.2$ V s⁻¹), the Pd(0) complex electrogenerated by the reduction of complex **2c** (3 mM) had totally disappeared in the presence of PhBr (3 mM) due to the oxidative addition, as attested by the absence of the oxidation peak O₁ on the reverse scan. When the scan rate was progressively increased, the oxidation peak O₁ of Pd(0) was progressively restored (Fig. 2a, $v = 10$ V s⁻¹). The time allotted to the Pd(0) for its reaction with PhBr was that which was spent between the generation of Pd(0) by reduction of the Pd(II) complex at R₁ and its oxidation at O₁ (e.g. in Fig. 2a, $t = \Delta E/v$ with $\Delta E = 2.4$ V). This time was shorter and shorter when the scan rate was increased and the oxidation peak current of Pd(0) at O₁ progressively increased. At 100 V s⁻¹, the oxidation peak current of the Pd(0) was 92% of that obtained in the absence of PhBr, corresponding to a conversion of only 8%. Since the oxidation current is proportional to the Pd(0) concentration, the molar fraction x of the electrogenerated Pd(0) which had not reacted with PhBr (for a given scan rate v) was: $x = i_{ox}/i_{ox}^0$ (i_{ox} : oxidation peak current of the electrogenerated Pd(0) in the presence of PhBr, i_{ox}^0 : oxidation peak current of the electrogenerated Pd(0) in the absence of PhBr). The plot of x versus $\log([PhBr]/v)$ is shown in Fig. 2b. This allows the determination of the scan rate $v_{1/2}$ corresponding to the half reaction (Fig. 2b) and then $t_{1/2} = \Delta E/v_{1/2}$. The rate constant k of the oxidative addition is determined



Scheme 6. Electrochemical reduction of Pd(II) complexes.

by the kinetic law: $1/x = kC_0t + 1$ ($C_0 = 3 \text{ mM} = [\text{PhBr}] = [\text{Pd(0)}]$).

The rate constants of the oxidative addition of aryl halides with the Pd(0) complexes generated by reduction of complexes **2c** and **6** are collected in Table 4. One observes that the bis(carbene)Pd(0) is the most reactive complex and that the substitution of one and then two carbenes by PPh₃ results in less and less reactive Pd(0) complexes.

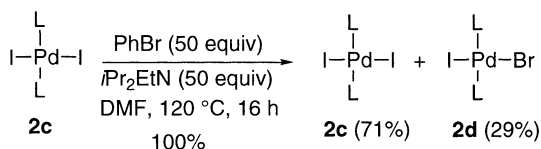
As a conclusion, the Pd(II) complexes ligated to the carbene(s) are less easily reduced than those ligated by PPh₃. The Pd(0) complexes ligated to the carbene(s) are more easily oxidized than those ligated by PPh₃ and thus more reactive in oxidative additions with aryl halides. It is worthwhile to note that PhBr undergoes the oxidative addition at room temperature.

Taking into account the high reactivity of the bis(carbene)Pd(0) complex in oxidative addition, it is of great interest to introduce a chemical reducing agent in any catalytic reaction, so that to decrease any induction period in which the Pd(II) complex is transformed into the active Pd(0) complex and to increase the concentration of the active Pd(0) complex.

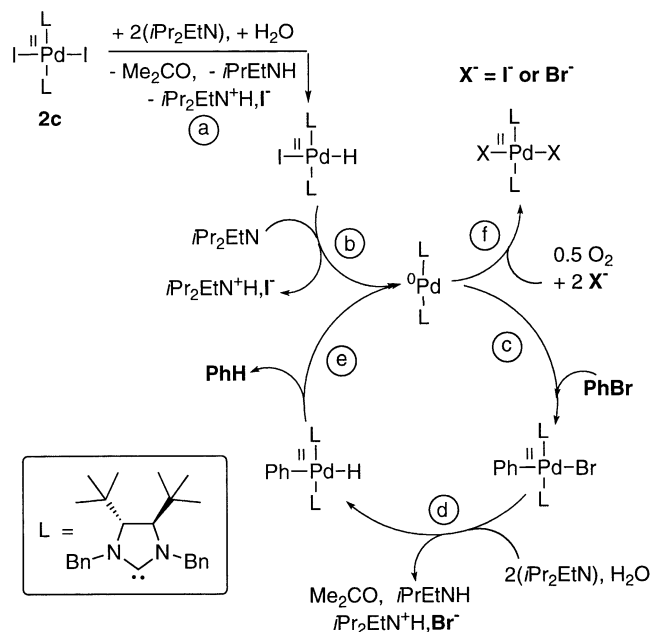
2.4.2. In situ reduction of palladium(II) complexes **2** and **6** to palladium(0) complexes and re-oxidation of the palladium(0) complexes

To evaluate the ability of the base to reduce **2c** in situ during the Heck reaction, 0.02 mmol of the complex was dissolved in DMF. After addition of *i*Pr₂EtN (1 mmol) and PhBr (1 mmol), the mixture was heated for 16 h at 120 °C. After work-up, the Pd(II) complex was quantitatively recovered as a 71/29 mixture of **2c** and **2d** (Scheme 7).

The generation of **2d** that results from a halogen exchange on the palladium indicated that bromide ions were generated during the reaction. This is only possible if **2c** is first reduced into Pd(0) by the base (Scheme 8, steps a and b), followed by oxidative addition of the Pd(0) with PhBr (step c). The reduction of the resulting complex, by a second equivalent of base, generated one equivalent of *i*Pr₂EtN⁺H, Br[−] and a palladium hydride (step d) that was recycled into Pd(0) by reductive elimination (step e). During the work-up, the Pd(0) complex might be easily re-oxidized by oxygen in the presence of iodides or bromides (R₃NH⁺, I[−] or R₃NH⁺, Br[−]) to give **2c** or **2d** (step f) [30]. Therefore,



Scheme 7. Reduction of **2c** by *i*Pr₂EtN in the presence of PhBr.

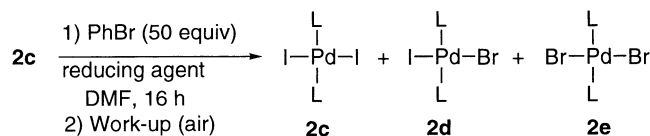


Scheme 8. Reduction of **2c** by *i*Pr₂EtN in the presence of PhBr.

the formation of the complex **2d** from **2c** gives evidence of the reduction into Pd(0).

To confirm that **2d** was really the bromo-iodo complex, the dibromo complex **2e** was quantitatively prepared by treatment of **2c** with an excess of NaBr in DMF at 120 °C and fully characterized. The reaction of the dibromo complex with one equivalent of NaI at 20 °C gave a mixture of three complexes **2c**, **2d** and **2e**. The complex **2d** was not separable from the mixture. By comparison with the ¹H-NMR spectrum of the diiodo complex **2c** and of the dibromo complex **2e**, it was possible to determine the signals corresponding to the bromo-iodo complex, which chemical shifts were identical to those of **2d**, obtained by the experiment described in Scheme 7. The detection of complexes **2d** and **2e** was used as a qualitative test to determine the ability of various agents to reduce the Pd(II) complexes (Scheme 9). The results are presented in Table 5. First of all, we observed that the reduction of **2c** by AcONa at 120 °C in DMF, seems to be more efficient than the reduction by *i*Pr₂NEt (entries 1 and 2). Indeed, with AcONa, a 24/50/26 mixture of **2c**, **2d** and **2e** was obtained (entry 2). No halogen exchange occurred in the absence of base at 120 °C (Table 5, entry 3).

The mechanism of the reduction of the Pd(II) complex by *i*Pr₂NEt could occur by an hydride transfer

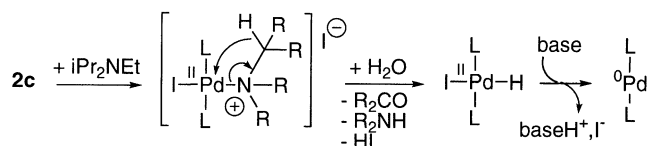


Scheme 9. Reduction of **2c** in the presence of PhBr.

Table 5

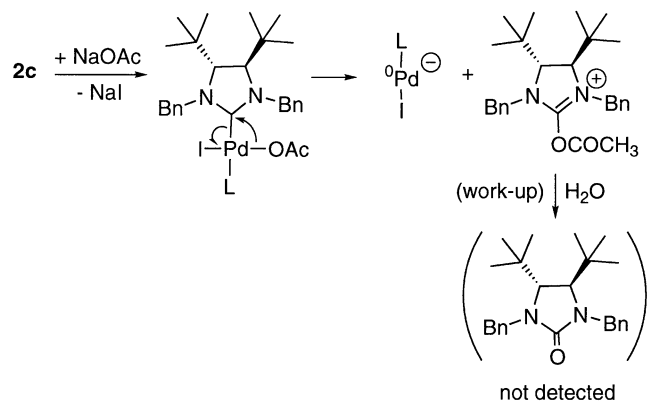
Reduction of complex **2c** and oxidation of the resulting Pd(0) complex

Entry	Reducing agent (equivalent)	Aryl halide	<i>T</i> (°C)	2c (%) ^a	2d (%) ^a	2e (%) ^a
1	<i>i</i> Pr ₂ EtN (50)	PhBr	120	71	29	0
2	AcONa (50)	PhBr	120	24	50	26
3	—	PhBr	120	100	0	0
4	<i>i</i> Pr ₂ EtN (50)	PhBr	80	91	9	0
5	AcONa (50)	PhBr	80	88	11	1
6	HCO ₂ Na (10)	PhI	80	100	0	0
7	HCO ₂ Na (10)	PhBr	80	11	42	47
8	HCO ₂ Na (1)	PhBr	80	45	43	12
9	HCO ₂ Na (10)	PhBr	20	85	15	0
10	HCO ₂ Na (47.5)	1-Iodonaphthalene	80	100	0	0
11	HCO ₂ Na (47.5)	1-Bromonaphthalene	80	6	40	54

^a Ratio determined by ¹H-NMR after work-up. No loss of Pd: **2c** gave quantitatively a mixture of **2c**, **2d** and **2e**.Scheme 10. Reduction of **2c** by *i*Pr₂EtN.

from the amine to the palladium, followed by reductive elimination (Scheme 10) [54,60]. It is more delicate in the case of sodium acetate since the usual mechanism proposed for PPh₃ ligands, involved, after substitution of an halogen by an acetate, the reductive elimination between the acetate and the ligand of the Pd(II) (Scheme 11) [61]. Since our catalyst **2c** was recovered unchanged, and since no modified form of the carbene ligand was detected by ¹H-NMR of the crude, the reduction of the carbene complex by NaOAc remains ambiguous.

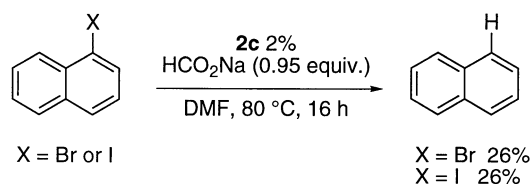
After 16 h at 80 °C, the reaction from **2c** afforded only 12% of the modified complexes **2d** and **2e** using NaOAc as the reducing agent and 9% of **2d** using *i*Pr₂EtN (Table 5, entries 4 and 5). At this temperature, the reduction of the Pd(II) complex by both bases seemed to be less efficient than at 120 °C. It is noteworthy that the rate of

Scheme 11. Reduction of **2c** by AcONa.

the oxidative addition may also be affected by the decrease of the temperature. These first observations could explain to a great extent the results obtained above in the Mizoroki–Heck reaction. The Pd(II) pre-catalyst must be reduced in situ by the base for the coupling reaction to occur. This operation is effective at 120 °C where good conversions were obtained, but not at 80 °C (low conversions).

Then, we tested the use of sodium formate in order to determine under which conditions this additive was able to reduce the Pd(II) pre-catalyst. We demonstrated, that at 80 °C in DMF, this reduction was much more efficient than with the bases. Indeed, the use of ten equivalents of HCO₂Na gave a 11/42/47 mixture of **2c**, **2d** and **2e** (Table 5, entry 7). A decrease in the quantities of HCO₂Na to one equivalent, also led to an important amount of transformed catalysts (entry 8). At 20 °C, a non-negligible amount of **2d** (15%) was formed after 16 h (entry 9), suggesting that the oxidative addition may occur at room temperature.

The reduction of the aryl bromide showed in Scheme 8 was confirmed by performing the reaction with 1-bromonaphthalene (1 mmol), in the presence of 0.95 mmol of sodium formate (Scheme 12). After 16 h at 80 °C with 2% mol of **2c**, naphthalene was obtained in 26% yield together with 74% of starting material (ratio determined by ¹H-NMR). The catalyst was recovered as a mixture of **2c**, **2d** and **2e** in a 6/40/54 ratio (Table 5, entry 11). Surprisingly, 1-iodonaphthalene was reduced within the same yield in these conditions. The dehalo-

Scheme 12. Reduction of 1-bromo and 1-iodonaphthalene with **2c** and HCO₂Na.

generation of aryl halides mediated by Pd/imidazolium salt system was reported by Nolan and co-workers [63].

In all the reactions described above (Section 2.4.2), we never noticed precipitation of Pd black and the Pd(II) catalyst was always quantitatively recovered by precipitation with methanol. We also never observed the complex formed in the oxidative addition of Pd(0) with the aryl halide. This is probably due to a fast reduction of the $(\text{NHC})_2\text{PhPdBr}$ species, the bis-carbene Pd(0) complex obtained being probably rapidly oxidized into **2c**, **2d** or **2e** during the work-up, and thus not observed (Scheme 8, steps c and f). However, oxidative addition products were isolated recently by Cavell et al., from a bis-carbene Pd(0) complex [64–66].

In the case of phenyl chloride, the oxidative addition occurred very slowly at 80 °C in DMF since only 11% of complex **2g** was detected after 16 h (Scheme 13). Moreover, at this temperature, the carbene ligands in the $(\text{NHC})_2\text{Pd}(0)$ species formed, was reduced by the excess of sodium formate to generate the aminor **7** and palladium black which precipitates.

2.5. Optimisation of the Mizoroki–Heck reaction conditions

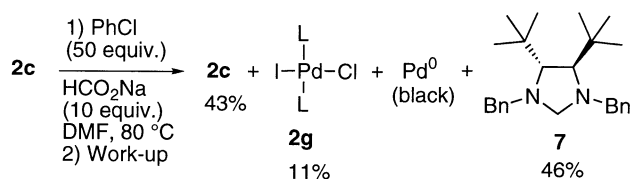
With all these observations in hand, we tested again the activity of the carbene complexes in the Mizoroki–Heck reaction, in the presence of reducing agents to activate the Pd(II) pre-catalyst. The results are presented in Table 6. First, when the coupling of PhI and butylacrylate, using **2c** at 80 °C, was not possible without reducing agent (Table 3, entries 6 and 7), the addition of 10% mol of sodium formate led to a complete conversion into (*E*)-butylcinnamate (Table 6, entry 1). Moreover, the reaction was also effective at 40 °C leading to 52% of conversion after 16 h (entry 2). Prolonging the reaction time to 48 h afforded quantitatively the Heck coupled product (entry 3). We have shown by cyclic voltammetry (Section 2.4.1), that the oxidative addition of the Pd(0) bis-carbene complex to PhI was fast even at 20 °C. However, no conversion was obtained at this temperature with 10% of HCO_2Na (entry 4). The stability of the catalyst, generated from **2c** in the presence of HCO_2Na , was demonstrated by performing the Heck reaction with phenyl iodide at 120 °C, using 10^{−3}% mol of **2c**. A turn-over number of 31 000 was obtained after 96 h at this temperature (entry

5). It is noteworthy that, in all reactions using PhI (entries 1–6), no precipitation of Pd metal was observed and the complex **2c** could be recovered by precipitation and recycled.

However, the coupling of phenyl bromide tested in various conditions failed. The use of 10% of HCO_2Na in the presence of *i*Pr₂EtN or Cs_2CO_3 as the base, led to no conversion at 80 °C. Moreover, the catalyst was not stable in these conditions since an important palladium black deposit was observed after 16 h (entries 7 and 8). The catalyst could be stabilized by performing the reaction in the presence of NaI [67]. In this case, no degradation was observed but still without conversion (entry 9). From these observations, we can assume that the efficiency of the oxidative addition of the active Pd(0) complex to phenyl bromide may be dramatically altered by the presence of the alkene. Indeed, in the presence sodium formate but without alkene, we have demonstrated that the Pd(0) species generated was able to undergo the oxidative addition with PhBr, even at 80 °C (Table 5, entries 4 and 5). In the same way, at 120 °C in the absence of sodium formate, only traces of coupled product were observed with PhBr and butylacrylate (Table 3, entry 8) although we have shown that the base is able to reduce **2c** and that the oxidative addition occurred in these conditions without alkene (Table 5, entry 1). Therefore, we presume that the lack of reactivity with PhBr in the coupling reaction with butylacrylate is probably due to a competitive complexation of the bis-carbene Pd(0) species by the alkene, that inhibits the oxidative addition [62] and allows the degradation of the carbene ligand by the hydride. We can not exclude either that the low reactivity with PhBr comes from the difficulty for the alkene to carry out the substitution of the bromide which is present on the palladium after the oxidative addition had occurred.

For the same reasons, the coupling of PhCl using **2c**, even in the presence of sodium formate proved to be inefficient. The use of only 1.8% mol of formate for 2% mol of **2c** did not prevent from the degradation of the catalyst and precipitation of Pd metal was observed (entries 11,12).

The mixed complex **6** gave also good results in the coupling of phenyl iodide and butylacrylate in the presence of a reducing agent. The use of 10% mol of HCO_2Na afforded quantitatively (*E*)-butylcinnamate after 16 h at 80 °C, without precipitation of Pd metal (entry 13). This reaction could be performed at 40 °C with a complete conversion after 48 h (entry 14). Surprisingly, the use of 4% mol of PPh_3 with 2% of the mixed complex **6**, but without HCO_2Na , led to a total conversion after 16 h at 80 °C (entry 15). We have shown previously that the coupling reaction of PhI and butylacrylate did not occur at 80 °C using **6** without excess of PPh_3 (Table 3, entries 10 and 11). The exact role of the phosphine is not obvious. It might be either



Scheme 13. Reduction of **2c** by HCO_2Na in the presence of PhCl.

Table 6

Heck reactions with complexes **2c**, **6** and **5** in the presence of reducing and stabilizing agents

Entry	Catalyst (% mol) ^a	PhX ^a	Additives (% mol) ^a	Base ^a	T (°C)	t (h)	Conv. (%) ^b	Precipitation of Pd black
1	2c 2%	PhI	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	80	16	100	No
2	2c 2%	PhI	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	40	16	52	No
3	2c 2%	PhI	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	40	48	100	No
4	2c 2%	PhI	HCO ₂ Na (10)	NEt ₃	20	16	2	No
5	2c 0.001%	PhI	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	120	96	31	No ^d
6	2c 2%	PhI	PPh ₃ (4)	<i>i</i> Pr ₂ EtN	80	16	0	No
7	2c 2%	PhBr	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	80	16	2	Yes
8	2c 2%	PhBr	HCO ₂ Na (10)	CS ₂ CO ₃	80	16	0	Yes
9	2c 2%	PhBr	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	80	16	0 ^c	No
10	2c 2%	PhBr	PPh ₃ (4)	<i>i</i> Pr ₂ EtN	120	16	0	No
11	2c 2%	PhCl	HCO ₂ Na (1.8)	<i>i</i> Pr ₂ EtN	120	16	0	Yes
12	2c 2%	PhCl	HCO ₂ Na (1.8)	AcONa	80	16	0	Yes
13	6 2%	PhI	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	80	16	100	No
14	6 2%	PhI	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	40	48	100	No
15	6 2%	PhI	PPh ₃ (4)	<i>i</i> Pr ₂ EtN	80	16	100	No
16	6 2%	PhBr	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	80	16	0	Yes
17	5 1%	PhI	PPh ₃ (4)	<i>i</i> Pr ₂ EtN	80	16	100	No
18	5 1%	PhBr	PPh ₃ (4)	<i>i</i> Pr ₂ EtN	120	16	70	Yes
19	5 1%	PhBr	PPh ₃ (4)	<i>i</i> Pr ₂ EtN	120	16	96^c	Tiny
20	5 1%	PhBr	PPh ₃ (4)	<i>i</i> Pr ₂ EtN	100	16	3	Yes
21	5 1%	PhBr	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	60	16	0	Yes
22	5 1%	PhBr	HCO ₂ Na (10)	<i>i</i> Pr ₂ EtN	80	16	3 ^c	Tiny

^a 1 mmol of PhX, 1.5 mmol of base, 1.2 mmol of butylacrylate, % mol of catalyst and additives based on the amount of PhX.^b Dodecane as internal reference.^c The reaction was performed with 1 mmol of NaI.^d The precipitation of Pd metal was not detectable.

to stabilise the active catalytic species (NHCPd(0)PPh₃), or to generate a more active species by ligand exchange, or to reduce **6** into a Pd(0) species. To confirm one of these hypotheses, a solution of 0.02 mmol of **6** was stirred with 0.08 mmol of PPh₃ and 1 mmol of PhBr for 16 h at 80 °C in DMF. After usual work-up, the analysis of the crude by ¹H-NMR revealed the presence of **6** and of a new complex, in a 1:1 ratio. The same experiment performed with PhI instead of PhBr led exclusively to **6**. Noteworthy, in these two experiments, we never detected the bis-carbene complex **2c**, this is probably an indication of the absence of ligand exchange. The new complex obtained in the first reaction was separated from **6** by silica gel chromatography. The ¹H-NMR spectrum of this isolated complex was characteristic of a non-symmetrical complex [68]. However, when the signals of the diaminocarbene ligand were effectively present, those of PPh₃ were not visible and it seemed that the phosphine has been replaced by one molecule of water. According to this spectrum, we suggested that this compound could be either the (NHC)PdI₂(H₂O) complex with the two iodides in a *cis* position or the (NHC)PdIBr(H₂O) complex. According to Scheme 8, only the second complex could come from the reduction of **6** by PPh₃, followed by oxidative addition of the Pd(0) with PhBr. Since we were not able to obtain supplementary analyses of this complex [69], we could not conclude on the exact role of PPh₃.

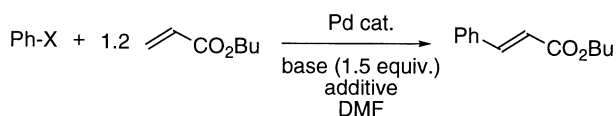
By comparison, the use of 4% PPh₃ without sodium formate was totally ineffective to activate **2c** in the same conditions: no Heck coupled product was obtained from PhI and butylacrylate at 80 °C (entry 6). The use of 4% PPh₃ was also ineffective in the coupling of PhBr using **2c** at 120 °C (entry 10).

The coupling of phenyl bromide, in the presence of HCO₂Na, was not effective with **6**. At 80 °C, we only observed the degradation of the catalyst with formation of Pd black (entry 16). As previously reported by Herrmann et al., the mixed phosphine–carbene complex **6** could be generated in situ starting from its dimeric precursor **5** and PPh₃ at 20 °C [20]. We attempted then the Heck reaction, with 1% mol of **5** and an excess of PPh₃ (4% mol), in order to generate **6** and to activate this latter with the excess of phosphine. In such conditions, the coupling of PhI occurred with a complete conversion at 80 °C (entry 17). Moreover, this procedure allowed the coupling of PhBr at 120 °C. A conversion of 70% was obtained after 16 h (entry 18). Nevertheless, precipitation of Pd metal was still observed. The active catalytic species was stabilized in the presence of an excess of NaI [67]. In this case, still at 120 °C and with 4% mol of PPh₃, a conversion of 96% was reached with little or no degradation of the catalyst (entry 19). The fact that this reaction failed using sodium formate as the reducing agent, is probably due to a competitive reduction of the carbene ligand by the

excess of formate that destroys the catalyst (entry 16). No conversion was obtained with PhBr at temperatures inferior to 120 °C using the dimer **5** and PPh₃ (entry 20). After 16 h at 100 °C, we only observed precipitation of Pd metal. Likely, in these conditions, the oxidative addition with PhBr does not occur. This could be ascribed, once more, to the competitive complexation of the active Pd(0) species by the alkene. Finally, the dimeric Pd(II) complex **5** was inactive in the Heck reaction in the absence of phosphine (entry 21). In this reaction, the carbene complex was rapidly degraded by the formate and precipitation of Pd metal was observed after 15 min at 20 °C. The Pd(0) species generated directly from **5** and HCO₂Na could be stabilized by an excess of NaI even though no conversion was obtained after 16 h at 80 °C (entry 22) Scheme 14.

3. Conclusion

Chiral bis-diaminocarbene complexes of palladium(II) are readily accessible from the corresponding silver(I) diaminocarbene complexes and PdCl₂(MeCN)₂. Mixed carbene–phosphine complexes are also easily prepared from Pd(OAc)₂ and the corresponding chiral imidazolium salts. These two families of complexes are air and moisture stable and can be purified by silica gel chromatography. These Pd(II) complexes are not easily reduced into the active Pd(0) species but the generated Pd(0) complexes undergo facile re-oxidation. In the classical conditions of the Mizoroki–Heck reaction, the pre-catalyst is probably reduced by the base but only at high temperature and coupling products are exclusively obtained with phenyl iodide in DMF at 120 °C. The in situ reduction of the Pd(II) complexes by addition of sodium formate allows the coupling reaction of PhI and butylacrylate at 40 °C instead of 120 °C. The mixed carbene–phosphine Pd(II) complex is more easily reduced than the bis-carbene complex and can be activated by PPh₃. This activation allows the coupling of PhBr with butylacrylate at 120 °C. The bis-carbene complex **2c** is particularly interesting since it is quantitatively regenerated by re-oxidation of the active Pd(0) species during the work-up. In summary, these complexes are very efficient catalysts for the Mizoroki–Heck reaction with aryl iodides but their activity is lower for the coupling of aryl bromides. The use of these chiral palladium carbene complexes in asymmetric coupling reactions is under investigation.



Scheme 14. Heck reactions with complexes **2c**, **6** and **5** in the presence of reducing agents.

4. Experimental

All experiments were carried out under argon. Solvents were of analytical grade type and used without special drying or distillation. NMR spectra were recorded on a Bruker ARX 400 or AC 200 Q instrument, in CDCl₃ or DMSO-*d*₆ as the solvent. Optical rotations were measured on a Perkin–Elmer 343.

4.1. Synthesis of (**2a**) and (**2b**)

A mixture of *N,N'*-dibenzylimidazolin-2-ylidene silver(I) bromide **1** (550 mg, 1.0 mmol) and PdCl₂(CH₃CN)₂ (130 mg, 0.5 mmol) in CH₂Cl₂ was stirred for 2 h at 20 °C. Discoloration of the solution and apparition of a white precipitate of silver salt was observed. The crude mixture was filtered over celite and concentrated to give a 2/1 mixture of palladium complexes **2a** and **2b** (430 mg, 95% yield). The two complexes were separated by chromatography over silica gel (cyclohexane/AcOEt; 95:5).

4.1.1. Complex (**2a**)

253mg (56%) of a white solid were obtained after chromatography (*R*_f 0.45). M.p. dec. 248 °C. [α]_D²⁰ = +50.1 (*c* 0.38, CHCl₃). Anal. Calc. for C₅₀H₆₈N₄Cl₂Pd (*M*_w = 902.43): C, 66.55; H, 7.60; N, 6.21. Found: C, 66.28; H, 7.67; N, 5.90. Exact MS (FAB+): 830.4533 for C₅₀H₆₈N₄Pd [M⁺–2Cl], 865.4219 for C₅₀H₆₈N₄PdCl [M⁺–Cl]. ¹H-NMR (400 MHz) δ 0.76 (s, 36H), 3.06 (s, 4H), 4.68 (d, 4H, *J* 14.7 Hz), 6.58 (d, 4H, *J* 14.7 Hz), 7.23–7.34 (m, 12H), 7.75 (d, 8H, *J* 7.4 Hz). ¹³C-NMR (50 MHz) δ 27.8, 36.2, 54.8, 69.3, 128.0, 128.5, 130.7, 136.0, 198.6 (N–C–N).

4.1.2. Complex (**2b**)

122mg (25%) of a white solid were obtained after chromatography (*R*_f 0.5). M.p. dec. 259 °C. [α]_D²⁰ = +168 (*c* 0.21, CH₂Cl₂). Anal. Calc. for C₅₀H₆₈N₄BrClPd (*M*_w = 946.88): C, 63.42; H, 7.24; N, 5.92. Found: C, 63.72; H, 7.31; N, 5.62. ¹H-NMR (400 MHz) δ 0.76 (s, 18H), 0.77 (s, 18H), 3.06 (s, 4H), 4.63 (d, 2H, *J* 14.7 Hz), 4.68 (d, 2H, *J* 14.7 Hz), 6.58 (bd, 4H, *J* 14.7 Hz), 7.22–7.32 (m, 12H), 7.75 (d, 8H, *J* 7.4 Hz). ¹³C-NMR (50 MHz) δ 27.7, 36.0, 36.2, 54.6, 56.1, 69.0, 69.2, 127.8, 128.3, 130.7, 135.7, 135.8, 198.4 (N–C–N). MS (ESI): 865.42 for C₅₀H₆₈N₄PdCl [M⁺–Br], 911.41 for C₅₀H₆₈N₄PdBr [M⁺–Cl].

4.2. Synthesis of (**2c**)

4.2.1. Method A

A mixture of **2a** and **2b** (220 mg, 0.24 mmol) and sodium iodide (ten equivalent) in DMF (5 ml) was stirred for 12 h at 120 °C. The solution was cooled to ambient temperature, diluted with Et₂O (30 ml) and

washed with H₂O (4 × 3 ml). The organic layer was dried over MgSO₄, filtered and concentrated to give complex **2c** as a pale yellow solid (260 mg, 100% yield). Purification over silica gel (cyclohexane/AcOEt; 95: 5; *R_f* 0.55) afforded analytically pure **2c**. The complex was crystallised by slow evaporation in a mixture of CH₂Cl₂ and cyclohexane.

4.2.2. Method B

To a solution of PdCl₂(CH₃CN)₂ (72 mg, 0.278 mmol) in CH₂Cl₂ (5 ml) were added the silver carbene **1** (306 mg, 0.555 mmol) and NaI (2.78 mmol). The mixture was stirred for 20 h at 20 °C then filtered over celite and concentrated. The crude solid was washed with MeOH and dried to afford 264 mg (87%) of **2c** as a pale yellow–green solid.

M.p. 307 °C. $[\alpha]_D^{20} = +52$ (*c* 0.3, CHCl₃). Exact MS (FAB+): 830.4516 for C₅₀H₆₈N₄Pd [M⁺–2I], 957.3570 for C₅₀H₆₈N₄PdCl [M⁺–I]. Anal. Calc.: C, 55.33; H, 6.32; N, 5.16; Found: C, 55.72; H, 6.65; N, 5.09. ¹H-NMR (400 MHz) δ 0.87 (s, 36H), 3.12 (s, 4H), 4.60 (d, 4H, *J* 14.8 Hz), 6.30 (d, 4H, *J* 14.8 Hz), 7.25–7.34 (m, 12H), 7.77 (d, 8H, *J* 7.4 Hz). ¹³C-NMR (100 MHz) δ 28.5, 37.2, 56.1, 69.8, 128.2, 128.5, 131.4, 135.8, 198.2 (N–C–N).

4.3. Synthesis of (2e)

A mixture of **2a** and **2b** (351 mg, 0.723 mmol) and sodium bromide (ten equivalents) in DMF (5 ml) was stirred for 12 h at 120 °C. The solution was cooled to ambient temperature, diluted with Et₂O (30 ml) and washed with H₂O (4 × 3 ml). The organic layer was dried over MgSO₄, filtered and concentrated to give complex **2e** as a pale yellow solid (360 mg, 100% yield from 0.723 mmol of **1**). Purification over silica gel (cyclohexane/AcOEt; 95:5) afforded analytically pure **2e** as a white solid.

Anal. Calc. for C₅₀H₆₈N₄Br₂Pd (*M_w* = 991.33): C, 60.58; H, 6.91; N, 5.65; Found: C, 60.61; H, 6.91; N, 5.59. ¹H-NMR (400 MHz) δ 0.78 (s, 36H), 3.05 (s, 4H), 4.64 (d, 4H, *J* 14.8 Hz), 6.48 (d, 4H, *J* 14.8 Hz), 7.22–7.36 (m, 12H), 7.75 (d, 8H, *J* 7 Hz). ¹³C-NMR (100 MHz) δ 28.1, 36.6, 55.4, 69.6, 128.1, 128.6, 131.1, 136.0, 198.8 (N–C–N).

4.4. Determination of the ¹H-NMR chemical shifts of (2d). Synthesis of a reference

99mg (0.1 mmol) of **2e** and 15 mg (0.1 mmol) of NaI in CH₂Cl₂ (2 ml) were stirred for 20 h at 20 °C. The mixture was diluted with Et₂O (10 ml) and washed with water (3 × 2 ml). The organic layer was dried over MgSO₄, filtered and concentrated to give 102 mg of a mixture of **2c**, **2d** and **2e** in a 8/40/52 ratio. The ¹H-NMR reference of **2d** was determined from the spectrum

of the mixture by removal of the known signals of **2c** and **2e**.

¹H-NMR (400 MHz) δ 0.81 (s, 18H), 0.85 (s, 18H), 3.09 (m, 4H), 4.58 (d, 2H, *J* 14.7 Hz), 4.67 (d, 2H, *J* 14.7 Hz), 6.40 (d, 2H, *J* 14.7 Hz), 6.43 (d, 2H, *J* 14.7 Hz), 7.2–7.34 (m, 12H), 7.77 (d, 8H, *J* 7 Hz).

4.5. Synthesis of (5)

Pd(OAc)₂ (112 mg, 0.5 mmol), imidazolinium bromide **4** (222 mg, 0.5 mmol), potassium *tert*-butoxide (67 mg, 0.6 mmol) and sodium iodide (300 mg, 2 mmol) were dissolved in dry THF (40 ml) and the solution was stirred at 20 °C for 5 h. After filtration and evaporation to dryness, purification by silica gel chromatography (cyclohexane/AcOEt; 1: 1; *R_f* 0.9) afforded **5** as a red–brown powder (130 mg, 72% yield).

M.p. dec. > 280 °C, $[\alpha]_D^{20} = +218$ (*c* 0.07, CH₂Cl₂). Anal. Calc. for C₅₀H₆₄I₄N₄Pd₂ (*M_w* = 1445.56): C, 41.54; H, 4.74; N, 3.88; Found: C, 41.50; H, 4.81; N, 3.70. ¹H-NMR (400 MHz) δ 0.80 (s, 18H), 0.84 (s, 18H), 3.23 (s, 2H), 3.29 (s, 2H), 4.60 (m, 4H), 6.42 (d, 2H, *J* 14.7 Hz), 6.63 (d, 2H, *J* 14.7 Hz), 7.30–7.46 (m, 16H), 7.74–7.81 (m, 8H, Haro). ¹³C-NMR (100 MHz) δ 27.8, 28.0, 36.6, 36.9, 56.5, 56.8, 69.6, 70.8, 128.4, 128.7, 130.9, 131.2, 134.1, 134.5, 186.8 (N–C–N).

4.6. Synthesis of (6)

To a solution of complex **5** (85 mg, 0.058 mmol) in CH₂Cl₂ (2 ml) was added triphenylphosphine (22 mg, 0.116 mmol). The solution was stirred at 20 °C for 30 min and concentrated. The orange solid obtained (107 mg) was purified by silica gel chromatography (cyclohexane/AcOEt; 95: 5; *R_f* 0.3) to give **6** as an orange solid (93 mg, 82% yield).

M.p. 98 °C. $[\alpha]_D^{20} = +120$ (*c* 0.08, CH₂Cl₂). Anal. Calc. for C₄₃H₅₀N₂I₂PPd₂ (*M_w* = 985.07): C, 52.43; H, 5.01; N, 2.84; Found: C, 51.98; H, 5.42; N, 2.43. ¹H-NMR (400 MHz, CDCl₃) δ 0.91 (s, 18H), 3.24 (s, 2H), 4.63 (d, 2H, *J* 14.8 Hz), 6.17 (d, 2H, *J* 14.8 Hz), 7.23–7.37 (m, 15H), 7.54–7.58 (m, 10H). ¹H-NMR (400 MHz, DMSO-*d*₆) δ 0.85 (s, 18H), 3.35 (s, 2H), 4.65 (d, 2H, *J* 14.9 Hz), 5.88 (d, 2H, *J* 14.9 Hz), 7.35–7.40 (m, 15H), 7.54–7.58 (m, 5H), 7.72–7.74 (m, 5H). ³¹P-NMR (162 MHz, DMSO-*d*₆) δ 15.68. ¹³C-NMR (50 MHz, DMSO-*d*₆) δ 28.5, 37.5, 56.4, 70.7, 128.7, 128.9, 129.0, 131.0, 131.3, 132.9, 133.8, 135.4, 135.6, 135.7, 189.2 (N–C–N).

4.7. Typical procedure for the in situ reduction and oxidative addition with palladium(II) complex 2c

To a solution of **2c** (21.7 mg, 0.02 mmol) in DMF (1 ml) were added the aryl halide (1 mmol) and the appropriate amount of reducing agent. The mixture

was degassed under vacuum then stirred under argon at the indicated temperature. After cooling, the solution was diluted with Et₂O (10 ml), washed with water (4 × 2 ml), dried over MgSO₄, filtered and concentrated. The catalyst was recovered almost quantitatively by precipitation with MeOH. After drying, the residue was analyzed by ¹H-NMR.

4.8. Typical procedure for the Mizoroki–Heck reaction

To a solution of Pd(II) complex (0.02 mmol) in DMF (1 ml) were added, the reducing agent (as indicated in Table 3), the aryl halide (1 mmol), the base (1.5 mmol) and butylacrylate (173 μl, 1.2 mmol). Dodecane (230 μl, 1 mmol) can be added as an internal reference for GC. The mixture was degassed under vacuum then stirred under argon at the indicated temperature. After cooling, the solution was diluted with Et₂O (10 ml) and washed with water (4 × 2 ml). The solution was analyzed by GC. After drying over MgSO₄, filtration and concentration, the catalyst, in the case of **2c**, can be separated from the coupling product by precipitation with MeOH. The crude coupling product was purified by silica gel chromatography (cyclohexane/AcOEt; 95: 5).

(*E*)-Butyl-cinnamate: ¹H-NMR (400 MHz) δ 0.99 (t, 3H, *J* 7.4 Hz), 1.45 (tq, 2H, *J* 6.7 and 7.4 Hz), 1.71 (tt, 2H, *J* 6.7 Hz), 4.23 (t, 2H, *J* 6.7 Hz), 6.47 (d, 1H, *J* 16 Hz), 2H), 7.40–7.41 (m, 3H), 7.52–7.54 (m, 2H), 7.70 (d, 1H, *J* 16 Hz).

4.9. Typical procedure for the electrochemical reduction of complex **2c** and for the determination of the rate constant of the oxidative addition of aryl halides with the electrogenerated Pd(0)

Cyclic voltammetry was performed with a wave-form generator PAR Model 175. The voltammograms were recorded with a digital oscilloscope Nicolet 3091. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1 cm² apparent surface area; the reference was a saturated calomel electrode (Radiometer Analytical) separated from the solution by a bridge (3 ml) filled with 2 ml of DMF containing *n*-Bu₄NBF₄ (0.3 M). The working electrode was a steady gold disk electrode whose diameter was adapted to the scan rate (i.d. 1 mm for 0.2 < *v* < 5 V s^{−1} and i.d. 0.5 mm for 10 < *v* < 100 V s^{−1}). In a solution in 8 ml of DMF containing *n*-Bu₄NBF₄ (0.3 M) was added 26 mg (0.024 mmol, 3 mM) of complex **2c**. The cyclic voltammetry was performed at different scan rates (0.2 < *v* < 100 V s^{−1}) in the absence of PhBr and then in the presence of PhBr (2.5 μl, 3 mM) with the same range of scan rates.

The absolute number of electron *n* involved in the reduction of complex **2c** (0.3 mM in DMF) was determined using chronoamperometry at a steady gold

disk electrode (i.d. 0.5 mm for step durations *θ* = 100 and 200 ms) and cyclic voltammetry at a steady gold disk electrode (i.d. 25 μm, *v* = 0.02 V s^{−1}) as reported in Ref. [57]. The resulting reduction currents were compared to the oxidation currents obtained in both techniques for ferrocene (0.3 mM in DMF) as an internal standard (monoelectronic oxidation).

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 200814 for compound **2c**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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- [69] Less than 4 mg of complex were obtained after purification.