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Palladium complexes with ethylene-bridged bis(*N*-heterocyclic carbene) for C–C coupling reactions

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Abstract—A series of new ethylene-bridged bis(imidazolium) halides with various *N*-substitutions were synthesized. Complexation of these imidazolium halides with Pd(OAc)$_2$ produced new Pd(II) ethylene-bridged bis(carbene) complexes. Crystallographic analyses of some of the new imidazolium salts and Pd(II) complexes were determined. Applications of these seven-member palladacycles in Suzuki and Heck coupling reactions produced comparable catalytic activities to those of six-member analogs.

1. Introduction

Recently, it has been shown that palladium complexes of *N*-heterocyclic carbene ligands offer distinctive advantages as possible alternatives for Pd/phosphine systems in the C–C coupling reactions.[1] Some highly active palladium systems with monodentate carbene ligands for the activation of aryl chlorides were developed.[2] Preparation of chelating ligands of *N*-heterocyclic carbene, which would provide extra air and moisture stability for the palladium centers, are receiving much attention.[3] For examples, some methylene-bridged bis(imidazolium) salts, in combination with Pd(OAc)$_2$, were equally efficient in Suzuki coupling with aryl chlorides as substrates.[4] Of all the reported *cis*-chelating bidentate ligands containing *N*-heterocyclic carbene, the palladium centers involved are exclusively of five- or six-member palladacycles.[3] To the best of our knowledge, there has been no report in employing seven-member palladacycles of bidentate carbene ligands in C–C coupling reactions. The reason is partly because the seven-member palladacycles were proven to be difficult to prepare.[3a,5] It has also been established that for monodentate or chelating ligands with *N*-heterocyclic carbene, bulky *N*-substitutions were essential for high catalytic activity in Suzuki–Miyaura coupling reactions.[6]

In view of the easy condensation of substituted benzyl chlorides with imidazoles, which provide availability of a large variety of *N*-substituted imidazoles, we report on the synthesis of a series of new methylene- and ethylene-bridged bis(imidazolium) salts and the successful preparations of their corresponding Pd(II) halide complexes. These Pd(II) complexes crystallized very readily in DMF/diethyl ether mixture and their molecular structures were determined by single-crystal X-ray crystallography. Crystallographic analyses on the ethylene-bridged bis(imidazolium) salts also reveal a possible conformation change stabilized by the presence of hydrogen bonding with an incorporated water molecule in the asymmetric unit. The activities of some of the palladium-catalyzed reactions, for example, co-polymerization of carbon monoxide and ethylene,[7] depend remarkably on the chelate size. As Pd(II) complexes of methylene-bridged bis(carbene) have already been demonstrated to be effective in C–C coupling reactions,[4a] we were interested to see if seven-member palladacycle can also mediate the catalytic reactions. Recently, research in functionalized *N*-heterocyclic carbene ligands is receiving much attention,[8] the study will contribute to the modular design strategies of employing seven-member palladacycle with *N*-heterocyclic carbene. Our results shows that the use of Pd(II) complexes with ethylene-bridged bis(carbene) in Suzuki and Heck coupling reactions produced comparable activities to the methylene-bridged analogs.

2. Results and discussion

2.1. Chelating bidentate ligand precursors

The ligand precursors of bis(carbene) employed are shown in Scheme 1. A series of substituted *N*-benzylimidazoles

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Keywords: C–C Coupling reactions; Chelating *N*-heterocyclic carbenes; Palladium(II) complexes.

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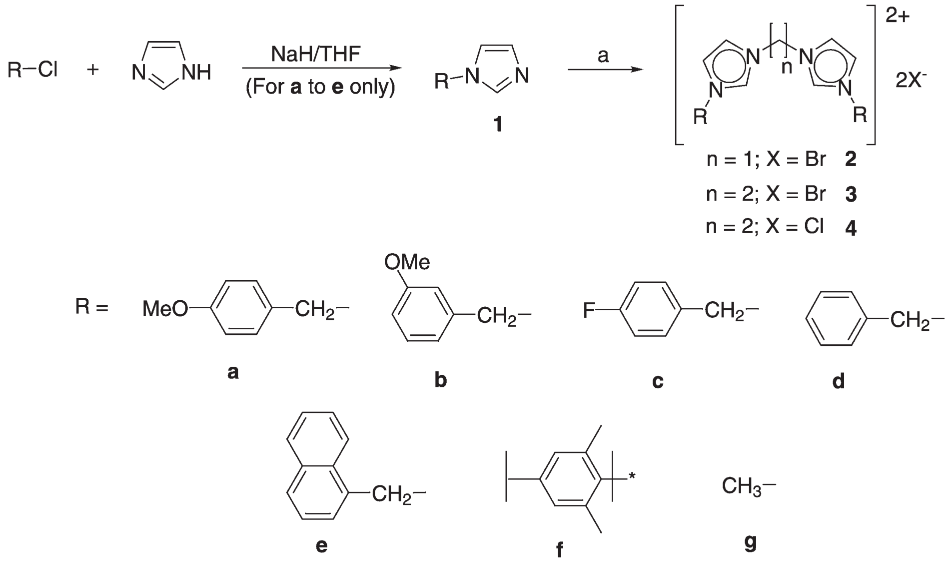


Conditions: (a) For **2a-2e**, neat dibromomethane, 70-80 °C, 1-2 d; for **3a-3g**, 1,2-dibromoethane/THF, 70-80 °C, 2-3 d; for **4a-4e**, 1,2-dichloroethane/THF, reflux, 2-3 d.

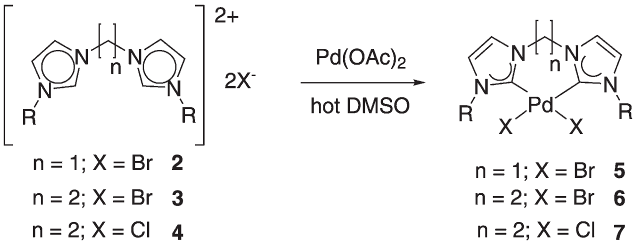
Scheme 1. Ligand precursors of bis(carbene).

1a–**1e** were firstly prepared by heating the corresponding substituted benzyl chloride and imidazole with 4 equiv. of NaH in THF overnight. Quantitative yields were achieved with our modified procedures and the products could be used for the next step without further purifications.[9] Previously, methylene-bridged bis(imidazolium) salts were obtained by reactions of 2 equiv. of *N*-substituted imidazole with an equivalent of CH_2Br_2 or CH_2I_2 in toluene or xylene.[10] The new methylene-bridged bis(imidazolium) bromides **2a**–**2e** were obtained with an alternative method of heating a solution of **1a**–**1e** in neat CH_2Br_2 at 70–80 °C for 1–2 d affording comparable yields. The bis(imidazolium) salts were slowly precipitated as white solids which were isolated in high purity after washing with THF. Interestingly, even though CH_2Br_2 was used in large excess, no mono-imidazolium salt was obtained. However, treatment of a solution of **1a**–**1g** in hot 1,2-dibromoethane did not result in the anticipated ethylene-bridged bis(imidazolium) bromides. Only mono-imidazolium bromides were obtained instead. Therefore, the ethylene-bridged bis(imidazolium) bromides **3a**–**3g** were synthesized by reacting 2 equiv. of **1a**–**1g** with an equivalent of 1,2-dibromoethane in refluxing THF. The ethylene-bridged bis(imidazolium) chlorides **4a**–**4g** were prepared similarly but with lower yields obtained.

2.2. Preparation and characterization of chelating bidentate palladium(II) complexes

Pd(II) complexes **5a**–**5e** were smoothly synthesized in high yields by following the reported protocol of treating the methylene-bridged bis(imidazolium) salt with $Pd(OAc)_2$ in hot DMSO (Scheme 2).[3b] Most remarkably, we applied the same methodology for the corresponding ethylene-bridged bis(imidazolium) halides and were able to obtain Pd(II) complexes **6** and **7**. It is likely that the successful application of the $Pd(OAc)_2$ protocol with bis(imidazolium) salts of ethylene spacer depends very much on the *N*-substitution as both previous attempts by Herrmann et al with *N*-^{t}Bu and our effort with *N*-Me substitutions were unsuccessful. Green et al. had already demonstrated that Ni(II) complexes with ethylene-bridged relative to methylene-bridged bis(carbene) ligands were sterically more congested.[11a] Consistently, the Pd(II) complex **5f** with bulky mesityl groups could be obtained from **2f**,[3b] but similar preparation from the ethylene-bridged analog **3f** was not successful. Only with bis(imidazolium) halides of *N*-benzyl or naphthylmethyl substitution, the corresponding Pd(II) complexes could be achieved with the $Pd(OAc)_2$ protocol. However, in general, lower yields compared with the methylene analogs were obtained. In fact, palladium black were observed during the course of reaction and filtration of the DMSO solution had to be done in the workup procedure. All the Pd(II) halide complexes obtained are stable in air and form crystals very readily (vide infra).

The ethylene-bridged bis(carbene) ligands were coordinated in chelating fashion around the palladium centers as evidenced by the fact that in the ^{1}H NMR spectrum of **6a**, for example, the resonance for the acidic protons of the organic ancillary at ca. δ 9.3 was no longer observed and the imidazole rings were symmetry-related. The ^{13}C signal for the carbene carbons was observed as a broad signal at ca. δ 157. In addition, the ethylene protons were split into two



Scheme 2. Synthesis of palladium complexes with chelating *N*-heterocyclic carbenes.

Table 1. Crystallographic data for **2a**, **4d**, and **4e**

	2a	**4d**	**4e**·H_2O
Empirical formula	$C_{23}H_{26}Br_2N_4O_2$	$C_{22}H_{24}Cl_2N_4$	$C_{30}H_{28}Cl_2N_4\cdot H_2O$
Formula weight	550.30	415.35	533.48
Color and Habit	Colorless needle	Colorless prism	Colorless parallelpipe
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$
a (Å)	37.952(11)	5.941(3)	7.976(3)
b (Å)	5.2200(14)	12.728(6)	8.668(3)
c (Å)	12.383(3)	13.843(4)	19.359(7)
α (deg)	90	90	92.081(10)
β (deg)	99.929(5)	98.05(2)	90.37(2)
γ (deg)	90	90	99.961(19)
V (Å^3)	2416.4	1036.3(8)	1317.2(9)
T (K)	150(2)	150(2)	150(2)
Z	4	2	2
D_{calcd} (Mg/m^3)	1.513	1.331	1.345
μ (mm^{-1})	3.381	0.329	0.278
Range of transm. factor	1.00–0.68	0.81–0.80	0.96–0.81
No. of unique data	2397	2385	5800
No. of parameters refined	141	127	342
$R1[I>2\sigma I]$	0.0471	0.0284	0.0503
$wR2$ (all data)	0.1671	0.0782	0.1240
Residuals (eÅ^{-3})	0.429, −0.458	0.299, −0.211	0.364, −0.243

separate broad signals at δ 4.55 and 5.28, as a result of ligand coordination. The broadening of resonances could be attributed to the fluxionality of the seven-member palladacycle. Also, the benzylic protons were observed as two sets of AB doublets with geminal coupling of 14.6 Hz at δ 4.94 and 5.35, indicating hindered rotation of the *N*-substitutions around the C–N bonds. Similar phenomena were also observed for the *N*-substitutions in the methylene analogs **5a–5e**.

2.3. Molecular structures of ligand precursors 2a, 4d, and 4e

Crystals of **2a**, **4d**, and **4e** suitable for X-ray crystallographic analysis were obtained by slow diffusion of diethyl ether into a DMF solution of the corresponding salts. In all cases, colorless crystals were obtained after few days. The crystallographic data of **2a**, **4d**, and **4e** are listed in Table 1 and their molecular structures are shown in Figures 1–3 respectively. The ethylene-bridged imidazolium chloride **4d** crystallizes in the monoclinic space group $P2_1/c$ with one half of the cationic molecule and a chloride anion per asymmetric unit. The second half and the other chloride anion are generated by inversion through a center of symmetry. As a result, the two imidazole rings are parallel and in *anti* relationship to each other. Each of the chloride ions are situated on one side of the molecular cation. The separation between the two imidazole planes is 1.510 Å. The head to tail stacking of the π systems of phenyl rings is propagated by the screw axis forming infinite chains of molecular cation along *b*-axis (Fig. 4). The interplanar distance is 3.6316 Å. For the anion coordination environment of the compound, Figure 4 also clearly shows that in the crystal lattice the chloride anion interacts with the hydrogen atoms on the C(1) and C(4) (the carbenic hydrogen and the hydrogen of ethylene linkage), those on the C(2) and C(5) (the imidazole ring proton and the benzylic hydrogen) of a proximal molecule, and also the hydrogen atom on the C(4) of a third molecule, thus linking three molecular cations together. The contact distance of

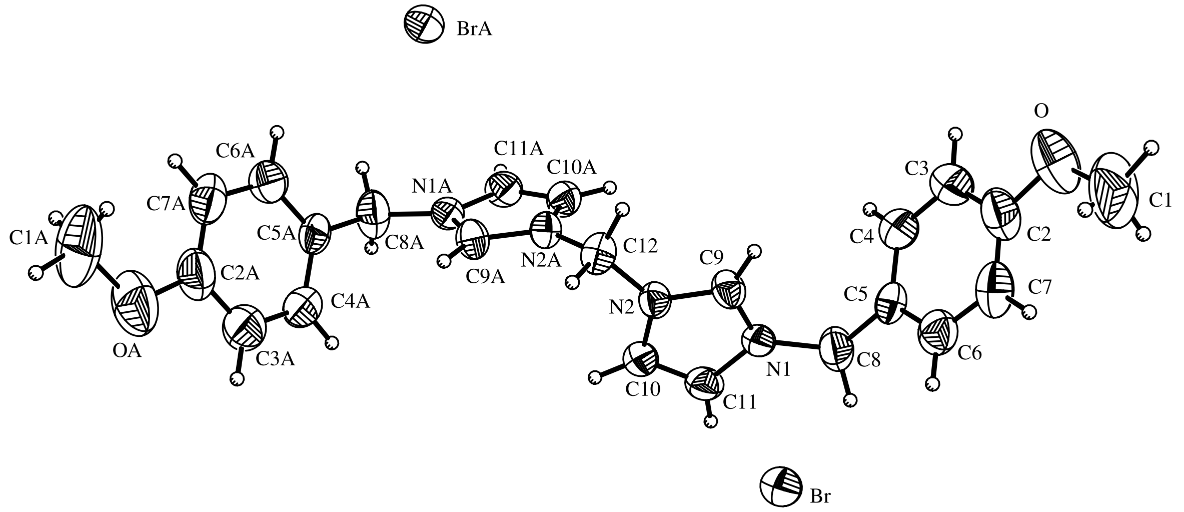


Figure 1. Molecular structure of **2a**.

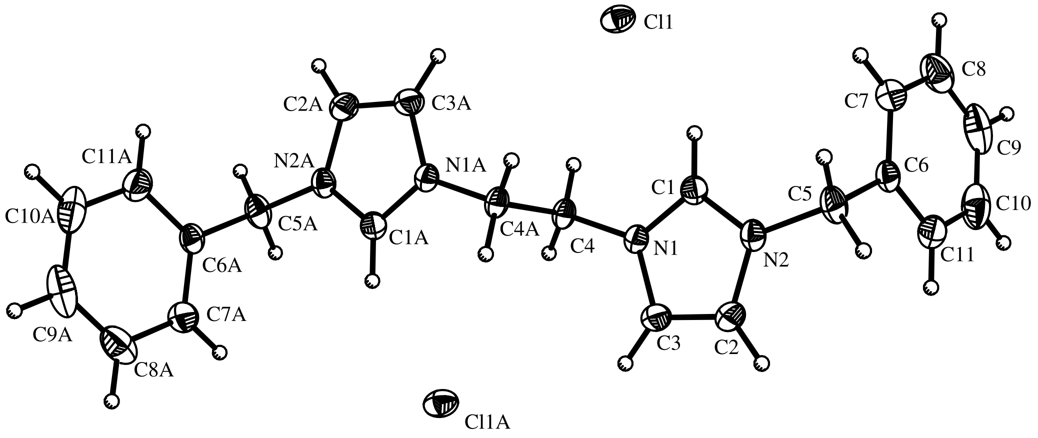


Figure 2. Molecular structure of **4d**.

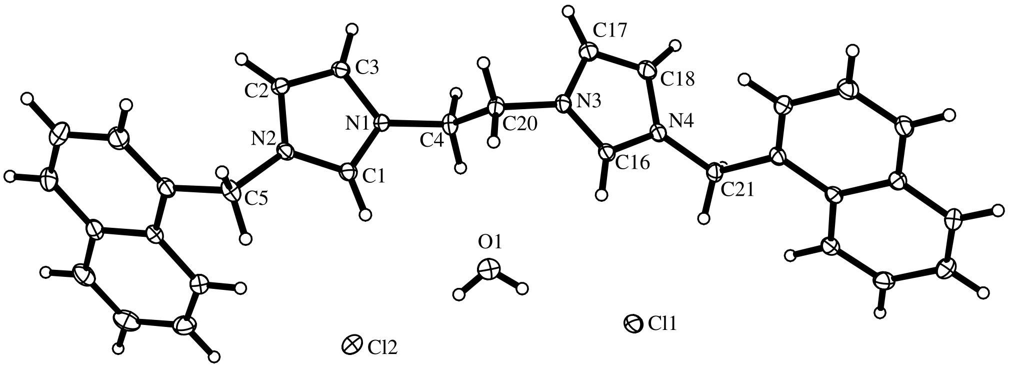


Figure 3. Molecular structure of **4e**·H_2O.

H$\cdots$Cl of the hydrogen atoms on C(1) and C(4) are 2.627 and 2.636 Å, respectively. The distance with hydrogen atom on C(2) of the second molecule and C(4) of the third molecules are 2.644 and 2.764 Å, respectively. All these distances are within the van der Waals approach of H$\cdots$Cl, i.e. <2.80–3.00 Å, and are therefore by definition hydrogen bonds (Table 2).[12]

The ethylene-bridged imidazolium chloride **4e** crystallizes in the triclinic space group $P\bar{1}$ with one ionic salt per

Table 2. Selected bond lengths (Å) and angles (°) for **2a**, **4d**, and **4e**

2a		**4d**		**4e**	
N(1)–C(9)	1.316(8)	N(1)–C(1)	1.3319(15)	N(1)–C(1)	1.334(3)
N(1)–C(11)	1.378(9)	N(1)–C(3)	1.3804(15)	N(1)–C(3)	1.378(3)
N(2)–C(9)	1.333(9)	N(1)–C(4)	1.4643(14)	N(1)–C(4)	1.464(3)
N(2)–C(10)	1.372(9)	N(2)–C(1)	1.3334(15)	N(2)–C(1)	1.327(3)
N(2)–C(12)	1.449(8)	N(2)–C(2)	1.3799(16)	N(2)–C(2)	1.380(3)
C(10)–C(11)	1.338(10)	C(2)–C(3)	1.3566(17)	N(3)–C(16)	1.327(3)
				N(3)–C(17)	1.385(3)
				N(3)–C(20)	1.467(3)
				N(4)–C(16)	1.328(3)
				N(4)–C(18)	1.380(3)
				C(2)–C(3)	1.351(3)
				C(17)–C(18)	1.345(3)
C(9)–N(1)–C(11)	109.4(7)	C(1)–N(1)–C(3)	109.31(10)	C(1)–N(1)–C(3)	108.74(18)
C(9)–N(2)–C(10)	108.2(6)	C(1)–N(2)–C(2)	109.04(10)	C(1)–N(2)–C(2)	109.06(18)
N(1)–C(9)–N(2)	108.2(7)	N(1)–C(1)–N(2)	107.98(10)	N(1)–C(1)–N(2)	108.24(19)
C(11)–C(10)–N(2)	107.9(2)	C(3)–C(2)–N(2)	107.03(10)	C(3)–C(2)–N(2)	106.8(2)
C(10)–C(11)–N(1)	106.3(7)	C(2)–C(3)–N(1)	106.64(10)	C(2)–C(3)–N(1)	107.13(19)
N(2A)–C(12)–N(2)	109.4(8)	N(1)–C(4)–C(4A)	109.12(11)	N(1)–C(4)–C(20)	110.03(18)
				C(16)–N(3)–C(17)	109.01(19)
				C(16)–N(4)–C(18)	108.28(19)
				N(3)–C(16)–N(4)	108.61(19)
				C(17)–C(18)–N(4)	107.8(2)
				C(18)–C(17)–N(3)	106.3(2)
				N(3)–C(20)–C(4)	108.76(18)

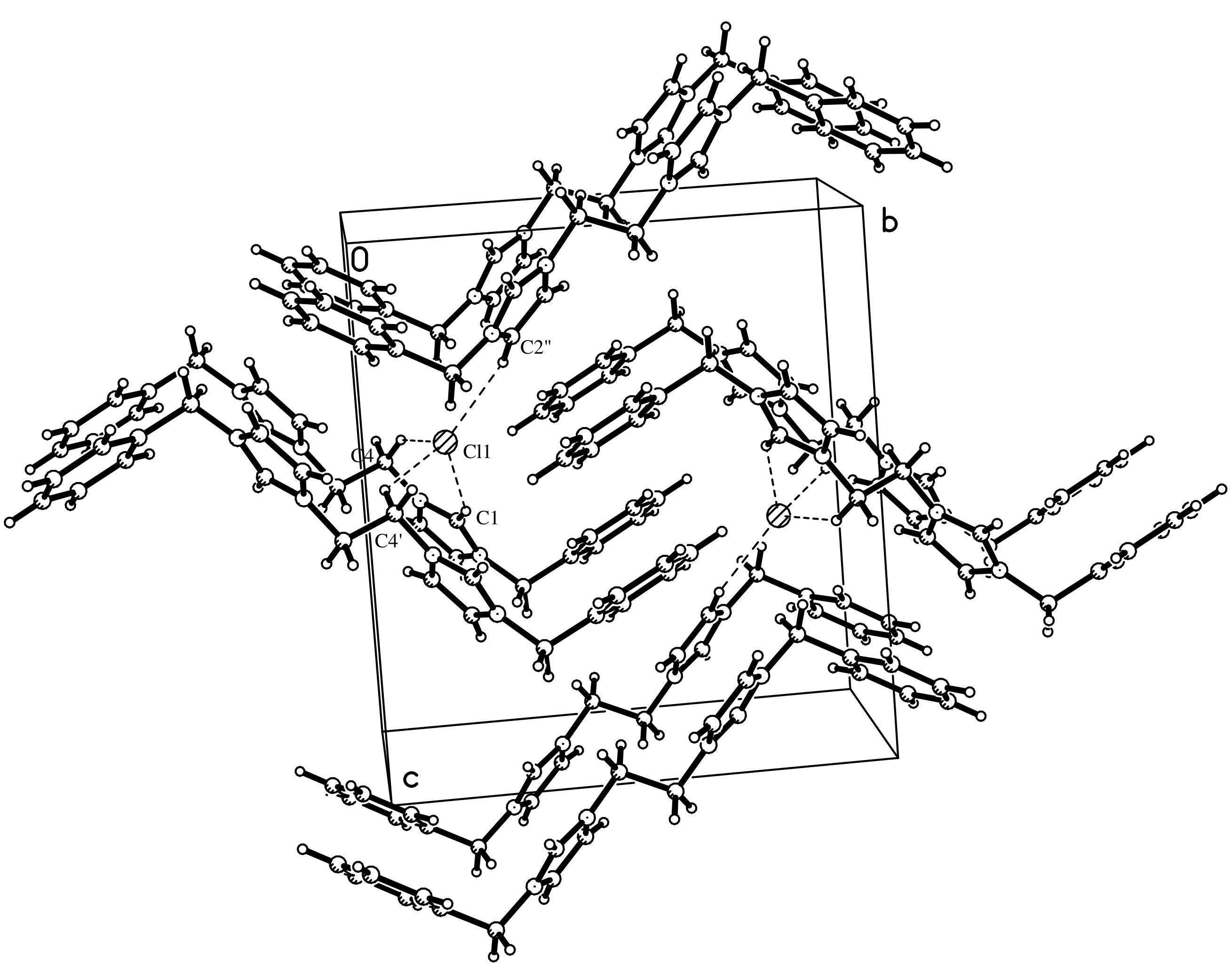


Figure 4. Packing diagram of **4d**. Dashed lines represent close contacts.

asymmetric unit. The striking differences between **4d** and **4e** are the *syn* relationship of the imidazole rings and the inclusion of a water molecule in the lattice. The water incorporated should come from the wet DMF solvent used. The separation between the two parallel imidazole planes (1.663 Å) is significantly bigger than that of **4d** (1.510 Å). The *syn* disposition may be attributed to the incorporated water molecule which forms extensive hydrogen contacts with the molecular cations and chloride anions. As shown in Figure 5, the two chloride ions form two hydrogen bonds with the hydrogen atoms on the water molecule (2.407 and 2.387 Å). The oxygen atom O(1) also interacts with the ethylene hydrogen atom on C(4) forming a H$\cdots$O contact distance of 2.372 Å. The chloride ions Cl(2) make three hydrogen contacts with the carbenic hydrogen on C(1), the naphthyl ring proton on C(14), and the imidazole ring proton on C(2) of a proximal molecular cation. The contact distances are 2.606, 2.729, and 2.576 Å respectively. The other chloride ion Cl(1) make four contacts with the carbenic hydrogen on C(16) (2.755 Å), the methylene proton on C(21) (2.684 Å), and the imidazole ring protons on C(3) (2.798 Å) and C(17) (2.834 Å) of the neighboring molecular cation. The naphthyl rings are π-π stacked along the *a*-axis with interplanar distances of 3.479 Å.

The methylene-bridged bis(imidazolium) bromide **2a** crystallizes in the monoclinic space group *C2/c* with one half of the molecular cation and a bromide anion per asymmetric unit. The second half and the other bromide are generated by the symmetry operation of a C_2 rotational axis passing through C(12) along the *b*-axis. Unlike **4d** and **4e**, **2a** contains two methylene-linked imidazole rings which can not be parallel but making an angle of 78.6° to each other. Interestingly, because of the *p*-OMe group on the phenyl ring, the cationic molecules are connected by, instead of $\pi-\pi$ stacking in **4d**, two intermolecular hydrogen bonds between O(1) and the hydrogen atom on C(1) of a proximal molecule, and the hydrogen atom on C(1) and O(1) of the proximal molecule, forming infinite chains along the *a*-axis (Fig. 6). Both of the two hydrogen bond distances are 2.689 Å. Similar to that in **4d**, a bromide anion also links up three cationic molecules through short hydrogen bonds. The H$\cdots$Br contact distances with the hydrogen atoms upon the carbenic carbon C(9) and the methylene carbon of the parent molecule C(12) are 2.767 and 2.868 Å, respectively. The short contacts on a second cationic molecule are with the hydrogen atom upon C(10) of imidazole ring and C(4) of the phenyl ring, while that on a third molecule is with the hydrogen atom upon C(11) of imidazole ring. The contact distances are 2.773, 2.985, and 2.734 Å, respectively.

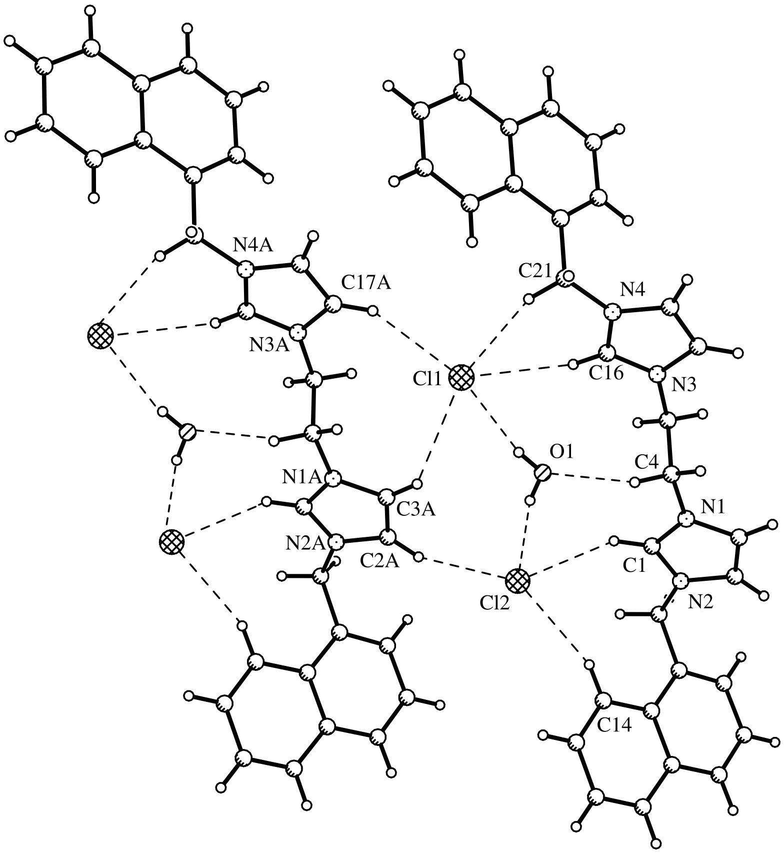


Figure 5. The hydrogen bonding interaction in **4e**. The hydrogen atoms of the water molecule were located in the difference map.

2.4. Molecular structures of palladium complexes of ethylene-bridged bis(carbene)

Single crystals of **6a**–**6e** can easily be grown from diffusion of diethyl ether into a DMF solution containing the palladium complexes. The molecular structures of **6a**–**6e** are shown in Figures 7–11. The crystallographic data are given in Table 3, and selected bond lengths and angles are listed in Tables 4–8. Each has fractional amounts of DMF incorporated as solvent of crystallization. For **6d**, there are two independent molecules in the asymmetric unit. In each of the structures, the palladium center adopts square planar coordination geometry. The sums of the angles at Pd(1) are 360.25° (**6a**), 359.83° (**6b**), 360.36° (**6c**), 360.54° (**6d**), and 360.04° (**6e**). Another common feature of the structures **6a**–**6e** is, rather unexpectedly, one of the benzyl/naphthylmethyl groups on the heterocyclic rings bends towards the palladium center. This is remarkably different from the

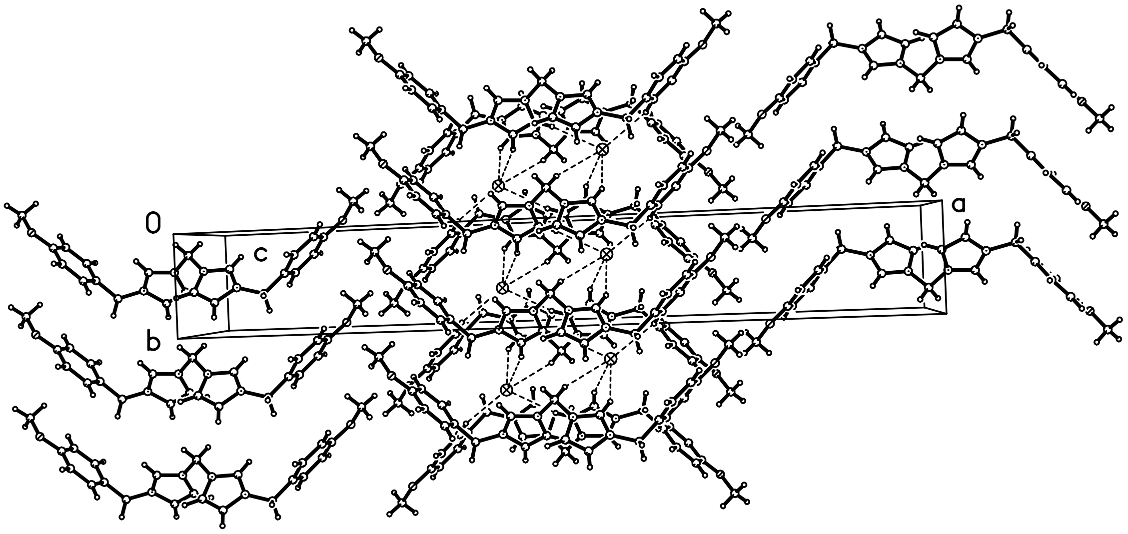


Figure 6. Packing diagram of **2a**. Dashed lines represent close contacts.

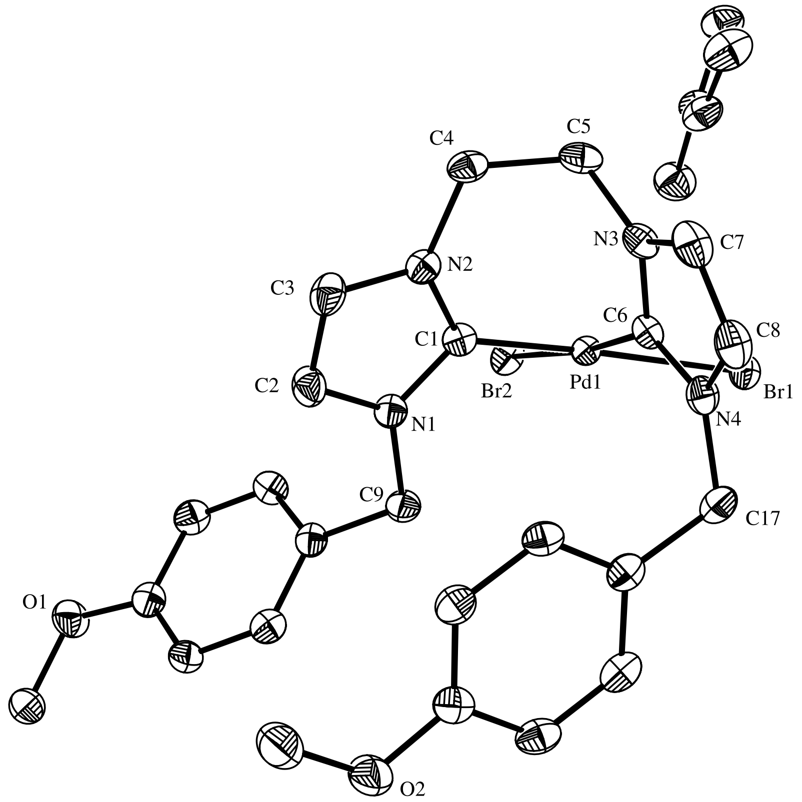


Figure 7. A drawing of the structure of **6a**·DMF. Hydrogen atoms are omitted for clarity.

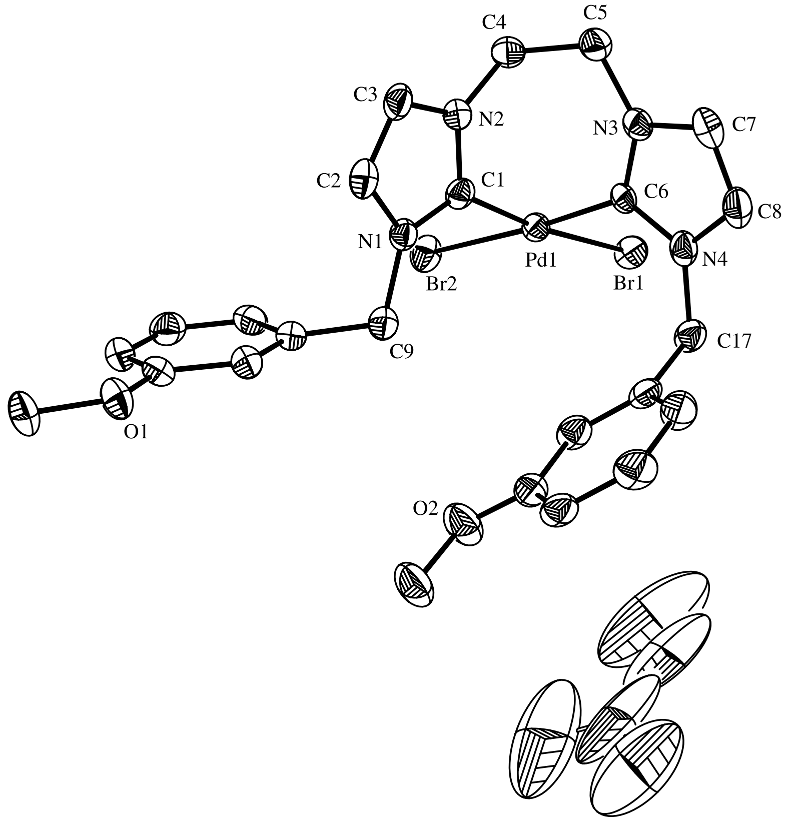


Figure 8. A drawing of the structure of **6b**·0.5DMF. Hydrogen atoms are omitted for clarity.

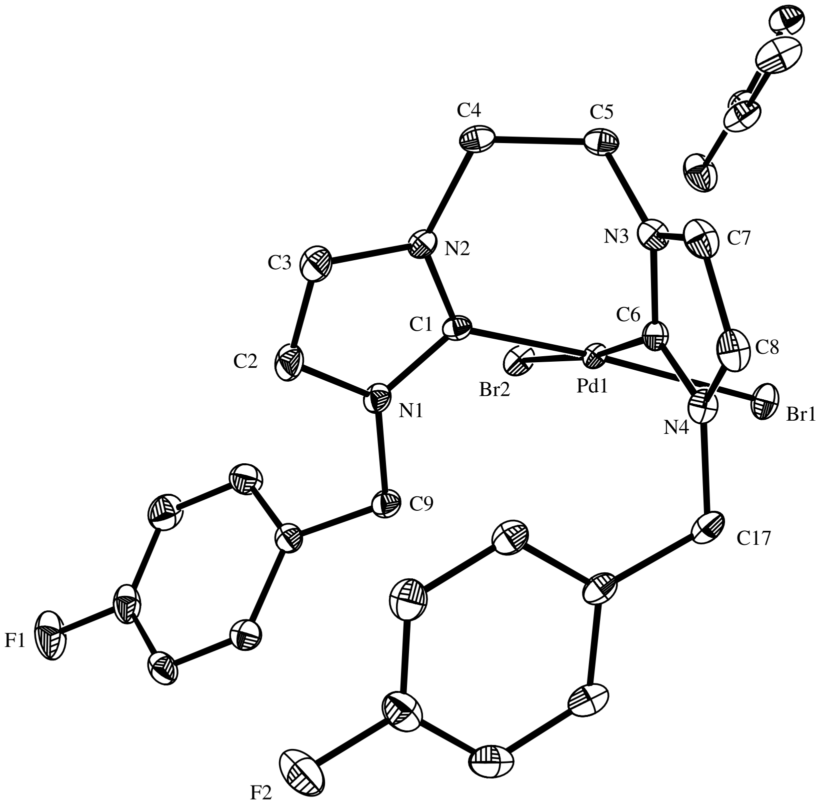


Figure 9. A drawing of the structure of **6c**·DMF. Hydrogen atoms are omitted for clarity.

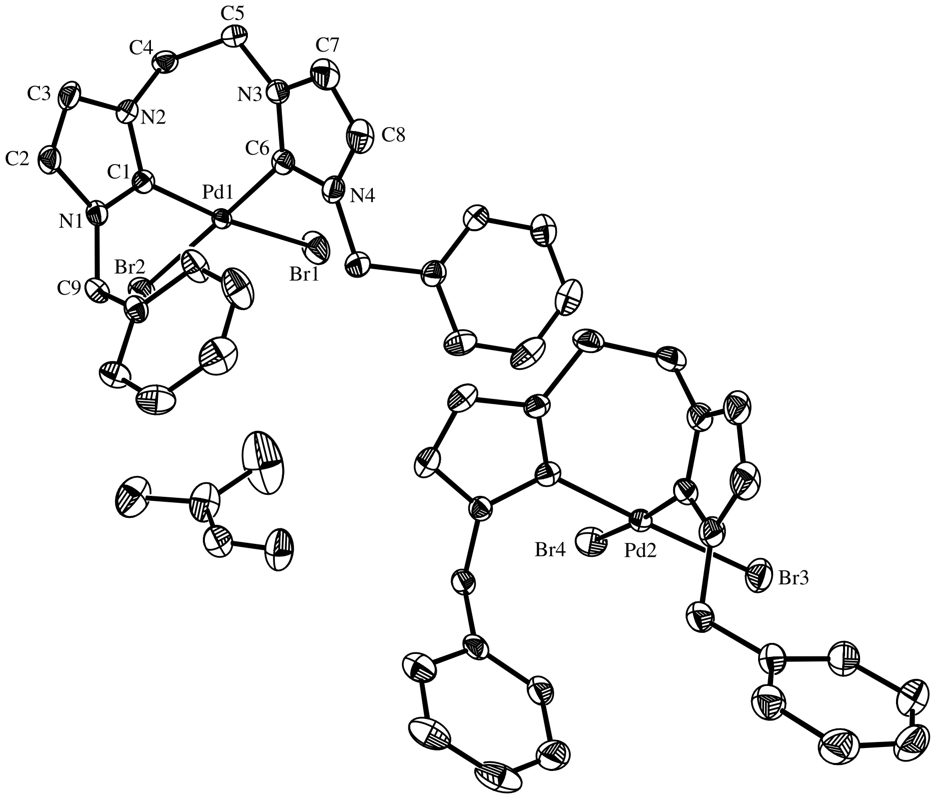


Figure 10. A drawing of the structure of **6d**·0.5DMF showing the two independent molecules and an incorporated DMF in the asymmetric unit. Hydrogen atoms are omitted for clarity.

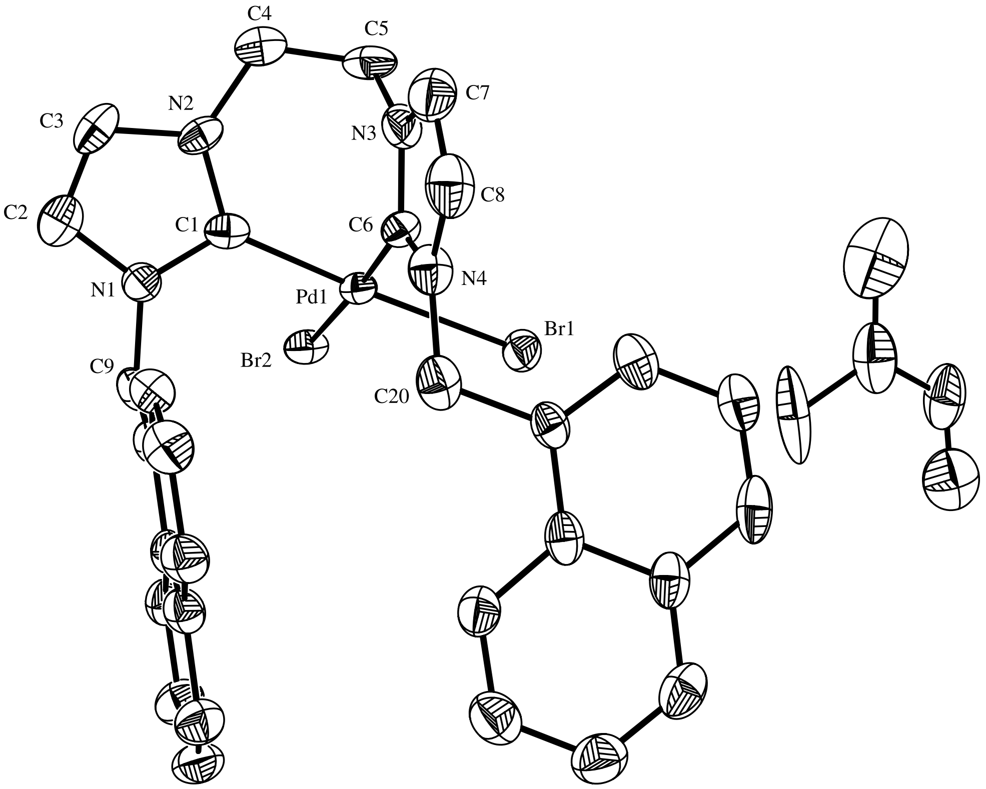


Figure 11. A drawing of the structure of **6e**·DMF. Hydrogen atoms are omitted for clarity.

solution structures by ^{1}H NMR which clearly shows the presence of mirror symmetry (vide supra). Previous to this paper, a similar palladium(II) methyl complex Pd(^{tbu}CC^{eth})Me$_2$ (^{tbu}CC^{eth}=1,2-ethylene-3,3′di-*tert*-butyl-diimidazol-2,2′-diylidene) (**8**),[13] nickel(II) complexes [Ni(^{tbu}CC^{eth})Cl(PMe$_3$)][BPh$_4$] (**9**)[11a] and Ni(^{tbu}CC^{eth})Me$_2$ (**10**)[11b] have been structurally characterized. Similar to these complexes, the seven-member palladacycles in **6a**–**6e**, also adopt boat-like conformations. However, the bite angles C(1)–Pd(1)–C(6) in **6a** (83.42°), **6b** (85.33°), **6c** (83.49°), **6d** (84.01°, 84.76° C(29)–Pd(2)–C(24)), and **6e** (84.56°) are significantly smaller than those in the three structures (88.1° in **8**; 88.38° in **9**; 88.93° in **10**), indicating the bigger steric bulkiness of the benzyl and naphthylmethyl groups. There is a wide distribution of the torsion angle of N(2)–C(4)–C(5)–N(3) in **6a** (50.81°), **6b** (44.20°), **6c** (48.85°), **6d** (42.25°, 54.30°), **6e** (50.66°) and the corresponding angles in **8** (50.76°), **9** (58.67°), and **10** (52.17°).

Table 3. Crystallographic data for **6a**–**6e**

	6a·DMF	**6b**·0.5DMF	**6c**·DMF	**6d**·0.5DMF	**6e**·DMF
Empirical formula	$C_{27}H_{33}Br_2N_5O_3Pd$	$C_{25.5}H_{29.5}Br_2N_{4.5}O_{2.5}Pd$	$C_{25}H_{27}Br_2F_2N_5OPd$	$C_{23.5}H_{25.5}Br_2N_{4.5}O_{0.5}Pd$	$C_{33}H_{33}Br_2N_5OPd$
Formula weight	741.80	705.26	717.74	1290.41	781.86
Color and Habit	Colorless prism	Colorless prism	Colorless prism	Colorless prism	Colorless parallelpipe
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	8.8637(6)	17.7146(18)	8.7820(19)	26.681(3)	10.4651(15)
b (Å)	8.8766(6)	8.3202(8)	8.792(2)	8.5241(7)	19.478(3)
c (Å)	18.7301(13)	19.639(2)	18.169(4)	20.0844(18)	15.232(2)
α (deg)	82.082(3)	90	83.475(11)	90	90
β (deg)	76.779(3)	109.703(6)	76.710(13)	99.247(7)	97.434(8)
γ (deg)	82.367(4)	90	83.582(11)	90	90
V (Å^3)	1413.07(17)	2725.0(5)	1351.1(5)	4846.4(7)	3078.8(8)
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Z	2	4	2	8	4
D_{calcd} (Mg/m^3)	1.743	1.719	1.764	1.769	1.687
μ (mm^{-1})	3.522	3.646	3.686	4.086	3.234
Range of transm. factor	0.65–0.16	0.78–0.30	0.56–0.19	0.74–0.14	0.61–0.01
No. of unique data	6226	6110	5900	11007	7026
No. of parameters refined	343	328	325	568	379
$R1[I>2\sigma I]$	0.0221	0.0384	0.0338	0.0441	0.0480
$wR2$ (all data)	0.0550	0.1012	0.0952	0.1305	0.1235
Residuals (eÅ^{-3})	0.441, −0.326	1.363, −1.022	1.483, −1.420	1.647, −1.929	0.891, −0.761

Table 4. Selected bond lengths (Å) and angles (°) for **6a**

Pd(1)–C(6)	1.971(2)	Pd(1)–Br(1)	2.5041(3)
Pd(1)–C(1)	1.993(2)	Pd(1)–Br(2)	2.5055(3)
C(2)–C(3)	1.345(3)	C(7)–C(8)	1.344(3)
N(1)–C(1)	1.348(3)	N(2)–C(1)	1.360(3)
N(3)–C(6)	1.351(3)	N(4)–C(6)	1.344(3)
C(6)–Pd(1)–C(1)	83.42(8)	C(6)–Pd(1)–Br(1)	91.48(6)
C(1)–Pd(1)–Br(1)	173.94(6)	C(6)–Pd(1)–Br(2)	173.99(6)
C(1)–Pd(1)–Br(2)	93.09(6)	Br(1)–Pd(1)–Br(2)	92.260(10)
C(1)–N(1)–C(2)	110.65(18)	C(1)–N(1)–C(9)	124.96(18)
C(1)–N(2)–C(4)	129.74(18)	C(3)–N(2)–C(4)	120.14(18)
C(6)–N(3)–C(7)	110.53(19)	C(6)–N(3)–C(5)	121.49(18)
C(7)–N(3)–C(5)	127.76(19)	C(6)–N(4)–C(8)	110.34(19)
N(1)–C(1)–N(2)	105.28(18)	N(1)–C(1)–Pd(1)	123.80(15)
N(2)–C(1)–Pd(1)	130.64(16)	N(2)–C(4)–C(5)	115.25(18)
N(3)–C(5)–C(4)	112.20(17)	N(4)–C(6)–N(3)	105.56(18)
N(4)–C(6)–Pd(1)	132.75(16)	N(3)–C(6)–Pd(1)	121.66(15)

Table 5. Selected bond lengths (Å) and angles (°) for **6b**

Pd(1)–C(6)	1.990(4)	Pd(1)–Br(1)	2.5036(6)
Pd(1)–C(1)	1.966(4)	Pd(1)–Br(2)	2.4741(6)
C(2)–C(3)	1.340(7)	C(7)–C(8)	1.338(7)
N(1)–C(1)	1.360(5)	N(2)–C(1)	1.345(6)
N(3)–C(6)	1.361(6)	N(4)–C(6)	1.354(5)
C(6)–Pd(1)–C(1)	85.33(17)	C(6)–Pd(1)–Br(1)	91.55(11)
C(1)–Pd(1)–Br(1)	173.71(13)	C(6)–Pd(1)–Br(2)	174.37(12)
C(1)–Pd(1)–Br(2)	89.23(12)	Br(1)–Pd(1)–Br(2)	92.72(2)
C(1)–N(1)–C(2)	109.6(4)	C(1)–N(1)–C(9)	125.8(4)
C(1)–N(2)–C(4)	121.3(4)	C(3)–N(2)–C(4)	127.1(4)
C(6)–N(3)–C(7)	110.6(7)	C(6)–N(3)–C(5)	129.5(4)
C(7)–N(3)–C(5)	119.8(4)	C(6)–N(4)–C(8)	111.4(4)
N(1)–C(1)–N(2)	105.1(4)	N(1)–C(1)–Pd(1)	133.8(3)
N(2)–C(1)–Pd(1)	121.1(3)	N(2)–C(4)–C(5)	113.7(4)
N(3)–C(5)–C(4)	115.5(4)	N(4)–C(6)–N(3)	104.2(4)
N(4)–C(6)–Pd(1)	127.3(3)	N(3)–C(6)–Pd(1)	128.4(3)

Table 6. Selected bond lengths (Å) and angles (°) for **6c**

Pd(1)–C(6)	1.973(3)	Pd(1)–Br(1)	2.4844(6)
Pd(1)–C(1)	1.987(3)	Pd(1)–Br(2)	2.4960(6)
C(2)–C(3)	1.345(3)	C(7)–C(8)	1.340(5)
N(1)–C(1)	1.342(5)	N(2)–C(1)	1.364(4)
N(3)–C(6)	1.353(4)	N(4)–C(6)	1.337(4)
C(6)–Pd(1)–C(1)	83.49(12)	C(6)–Pd(1)–Br(1)	91.55(9)
C(1)–Pd(1)–Br(1)	173.40(9)	C(6)–Pd(1)–Br(2)	173.68(9)
C(1)–Pd(1)–Br(2)	92.85(9)	Br(1)–Pd(1)–Br(2)	92.47(2)
C(1)–N(1)–C(2)	111.1(3)	C(1)–N(1)–C(9)	124.0(3)
C(1)–N(2)–C(4)	129.5(3)	C(3)–N(2)–C(4)	120.4(3)
C(6)–N(3)–C(7)	110.1(3)	C(6)–N(3)–C(5)	121.8(3)
C(7)–N(3)–C(5)	127.9(3)	C(6)–N(4)–C(8)	110.5(3)
N(1)–C(1)–N(2)	105.1(3)	N(1)–C(1)–Pd(1)	123.8(2)
N(2)–C(1)–Pd(1)	130.6(2)	N(2)–C(4)–C(5)	114.8(3)
N(3)–C(5)–C(4)	112.1(3)	N(4)–C(6)–N(3)	105.8(3)
N(4)–C(6)–Pd(1)	132.9(2)	N(3)–C(6)–Pd(1)	121.3(2)

Table 7. Selected bond lengths (Å) and angles (°) for **6d**[a]

Pd(1)–C(6)	1.988(5)	Pd(1)–Br(1)	2.4580(6)
Pd(1)–C(1)	1.978(5)	Pd(1)–Br(2)	2.4622(6)
C(2)–C(3)	1.335(7)	C(7)–C(8)	1.333(8)
N(1)–C(1)	1.342(6)	N(2)–C(1)	1.341(6)
N(3)–C(6)	1.356(6)	N(4)–C(6)	1.357(6)
C(6)–Pd(1)–C(1)	84.01(18)	C(6)–Pd(1)–Br(1)	93.06(13)
C(1)–Pd(1)–Br(1)	172.96(13)	C(6)–Pd(1)–Br(2)	172.47(13)
C(1)–Pd(1)–Br(2)	90.59(13)	Br(1)–Pd(1)–Br(2)	92.88(2)
C(1)–N(1)–C(2)	109.3(4)	C(1)–N(1)–C(9)	125.3(4)
C(1)–N(2)–C(4)	122.5(4)	C(3)–N(2)–C(4)	126.9(4)
C(6)–N(3)–C(7)	110.1(4)	C(6)–N(3)–C(5)	129.3(4)
C(7)–N(3)–C(5)	120.6(4)	C(6)–N(4)–C(8)	110.7(4)
N(1)–C(1)–N(2)	106.3(4)	N(1)–C(1)–Pd(1)	132.4(3)
N(2)–C(1)–Pd(1)	121.2(3)	N(2)–C(4)–C(5)	112.1(4)
N(3)–C(5)–C(4)	115.0(4)	N(4)–C(6)–N(3)	104.9(4)
N(4)–C(6)–Pd(1)	124.6(3)	N(3)–C(6)–Pd(1)	129.3(4)

[a] Only one independent molecule of **6d** is listed.

Table 8. Selected bond lengths (Å) and angles (°) for **6e**

Pd(1)–C(6)	1.959(6)	Pd(1)–Br(1)	2.4742(7)
Pd(1)–C(1)	1.993(6)	Pd(1)–Br(2)	2.5058(8)
C(2)–C(3)	1.315(9)	C(7)–C(8)	1.344(10)
N(1)–C(1)	1.351(7)	N(2)–C(1)	1.353(7)
N(3)–C(6)	1.348(7)	N(4)–C(6)	1.342(7)
C(6)–Pd(1)–C(1)	84.6(2)	C(6)–Pd(1)–Br(1)	89.85(16)
C(1)–Pd(1)–Br(1)	174.40(16)	C(6)–Pd(1)–Br(2)	176.62(16)
C(1)–Pd(1)–Br(2)	92.18(3)	Br(1)–Pd(1)–Br(2)	92.18(3)
C(1)–N(1)–C(2)	111.6(5)	C(1)–N(1)–C(9)	124.5(5)
C(1)–N(2)–C(4)	130.1(5)	C(3)–N(2)–C(4)	120.4(5)
C(6)–N(3)–C(7)	110.5(5)	C(6)–N(3)–C(5)	121.2(5)
C(7)–N(3)–C(5)	128.1(5)	C(6)–N(4)–C(8)	109.1(5)
N(1)–C(1)–N(2)	104.5(5)	N(1)–C(1)–Pd(1)	125.8(4)
N(2)–C(1)–Pd(1)	129.6(4)	N(2)–C(4)–C(5)	115.8(5)
N(3)–C(5)–C(4)	113.1(5)	N(4)–C(6)–N(3)	106.5(5)
N(4)–C(6)–Pd(1)	132.7(4)	N(3)–C(6)–Pd(1)	120.7(4)

The wide range of torsion angles and the fact that **6d** crystallizes with two independent molecules of quite extreme torsion angles indicate that the seven-member metallocycle with the ethylene-bridged bis(carbene) ligands are quite flexible and can adopt multiple conformations. The conformational flexibility of the metallocycles were also shown by the two imidazole planes making an angle of 91.4° in **6a**, 85.2° in **6b**, 88.8° in **6c**, 86.4° (85.4° of second molecule) in **6d**, and 88.1° in **6e**, which are significantly bigger than those of 74.6° in **9** and 84.1° in **10** but smaller than that of 102.6° in **8**. The average Pd–C distance in **6a**–**6e** is 1.98 Å, which is shorter than that of 2.08 Å in **8**, reflecting the stronger donating property of the methyl ligand.

2.5. Molecular structures of palladium complexes of methylene-bridged bis(carbene)

Single crystals of **5b**–**5d** can be grown from diffusion of diethyl ether into a DMF solution containing the palladium complexes. The molecular structures of **5b**–**5d** are shown in Figures 12–14. The crystallographic data are given in Table 9, and selected bond lengths and angles are listed in Table 10. Similar Pd(II) halide complexes with methylene-bridged bis(carbene) ligand, (1,1′-dimethyl-3,3′methylenediimidazoline-2,2′-diylidene)palladium(II) diiodide (**11**),[4a] (1,1′-di-*tert*-butyl-3,3′methylenedi-imidazoline-2,2′-diylidene)palladium(II) diiodide (**12**)[3a] and (1,1′-bis(2-hydroxyethyl)-3,3′-methylenedi-imidazolin-2,2′-diylidene)palladium(II) diiodide (**13**)[14] are known in the literature. Even though **5b**, **5c** and **5d** were grown under identical conditions, **5b** crystallizes without any solvent of crystallization. **5c** incorporates one half of a DMF

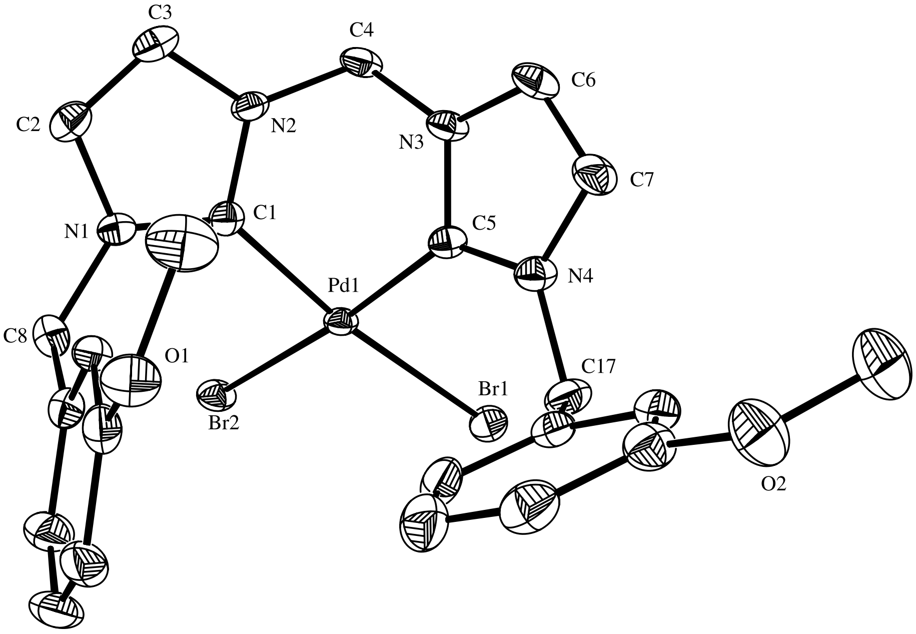


Figure 12. A drawing of the structure of **5b**. Hydrogen atoms are omitted for clarity.

molecule disordered at the center of inversion per asymmetric unit in the space group *C2/c*. **5d** crystallizes in the monoclinic space group of *P2₁/c* with two complex molecules per asymmetric unit. One of the benzyl groups in the second molecule is disordered with the major orientation of 74% site occupancy. Although, the bite angles, internal angles at the methylene carbon in **5a**–**5d**, **12**, and **13** are quite similar, indicating the rigidity of the six-member palladacycles, the relative orientation of the imidazole rings can have certain degree of flexibility as shown by the distribution of inter-planar angles in **5a** (61.3°), **5c** (59.0°), **5d** (56.1°), **12** (70.9°), and **13** (63.6°).

2.6. Suzuki coupling

The catalytic applicability of Pd(II) complexes with ethylene-bridged bis(carbene) and its comparison with methylene-bridged analogs towards Suzuki coupling of aryl bromides and phenylboronic acid was investigated (Table 11). As shown in the table, both series are effective in the activation of aryl bromides. For electron-deficient substrate, the ethylene-bridged bis(carbene) complexes are even more efficient than the methylene-bridged analogs (compare entries 1–7 with entries 8–13). With bromoanisole and bromobenzene, the two series give similar results. It is noteworthy that the catalytic activities of both

Table 9. Crystallographic data for **5b**, **5c**, and **5d**

	5b	**5c**·0.5DMF	**5d**·DMF
Empirical formula	$C_{23}H_{24}Br_2N_4O_2Pd$	$C_{22.5}H_{21.5}Br_2F_2N_{4.5}O_{0.5}Pd$	$C_{24}H_{27}Br_2N_5OPd$
Formula weight	654.68	667.16	667.73
Color and habit	Colorless prism	Colorless prism	Colorless parallelpipe
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*C2/c*	$P2_1/c$
a (Å)	8.032(4)	31.1566(6)	27.135(2)
b (Å)	9.673(5)	7.8468(14)	8.5617(5)
c (Å)	16.249(8)	22.966(5)	22.2462(15)
α (deg)	89.308(12)	90	90
β (deg)	76.010(10)	121.047(11)	101.300(6)
γ (deg)	77.729(17)	90	90
V (Å^3)	1036.3(8)	4810.2(16)	5068.2(6)
T (K)	150(2)	150(2)	150(2)
Z	2	8	8
D_{calcd} (Mg/m^3)	1.818	1.843	1.750
μ (mm^{-1})	4.144	4.131	3.912
Range of transm. factor	0.71–0.35	0.76–0.27	0.70–0.36
No. of unique data	5300	5473	11532
No. of parameters refined	289	317	596
$R1[I>2\sigma I]$	0.0376	0.0521	0.0439
$wR2$ (all data)	0.0924	0.1384	0.1163
Residuals (eÅ^{-3})	1.323, −1.052	1.416, −1.106	1.243, −0.635

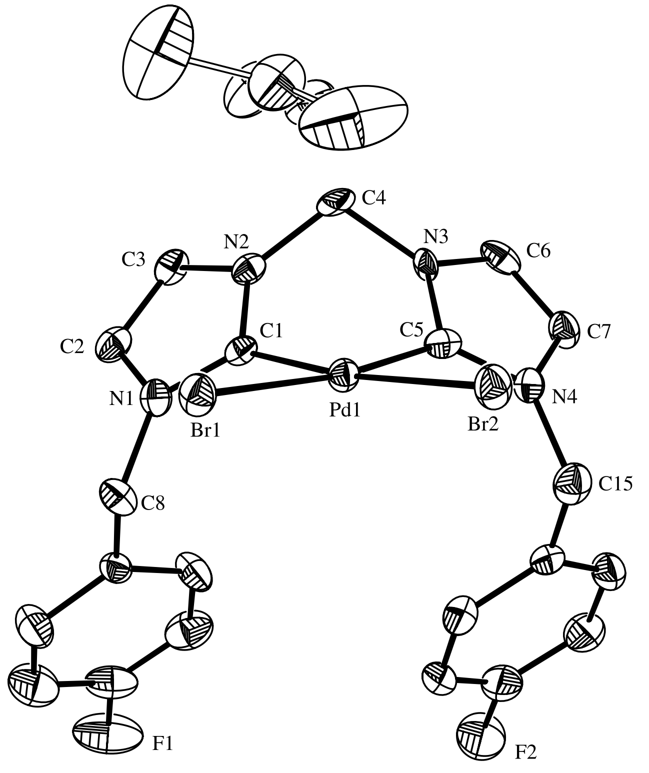


Figure 13. A drawing of the structure of **5c**·0.5DMF. Hydrogen atoms are omitted for clarity.

Table 10. Selected bond lengths (Å) and angles (°) for **5b**–**5d**[a]

	5b	**5c**	**5d**
Pd(1)–C(1)	1.975(4)	1.962(7)	1.962(7)
Pd(1)–C(5)	1.985(4)	1.986(7)	1.986(7)
Pd(1)–Br(1)	2.4767(10)	2.4830(9)	2.4888(9)
Pd(1)–Br(2)	2.4826(10)	2.4888(9)	2.4830(9)
N(1)–C(1)	1.336(6)	1.351(8)	1.351(8)
N(1)–C(2)	1.391(6)	1.400(8)	1.400(8)
N(2)–C(1)	1.357(6)	1.371(8)	1.371(8)
N(2)–C(3)	1.381(6)	1.380(8)	1.380(8)
N(2)–C(4)	1.455(6)	1.469(9)	1.469(9)
N(3)–C(5)	1.357(5)	1.363(8)	1.363(8)
N(3)–C(6)	1.369(5)	1.377(9)	1.377(9)
N(3)–C(4)	1.456(5)	1.464(8)	1.464(8)
N(4)–C(5)	1.330(5)	1.339(8)	1.339(8)
N(4)–C(7)	1.384(6)	1.399(8)	1.399(8)
C(2)–C(3)	1.332(7)	1.344(10)	1.344(10)
C(6)–C(7)	1.332(6)	1.335(10)	1.335(10)
C(1)–Pd(1)–C(5)	84.58(17)	84.2(3)	84.2(3)
C(1)–Pd(1)–Br(1)	173.13(13)	92.23(19)	92.23(19)
C(5)–Pd(1)–Br(1)	91.39(13)	172.87(19)	172.87(19)
C(1)–Pd(1)–Br(2)	92.77(12)	173.40(19)	173.40(19)
C(5)–Pd(1)–Br(2)	174.41(12)	92.4(2)	92.4(2)
Br(1)–Pd(1)–Br(2)	90.76(4)	90.55(3)	90.55(3)
C(1)–N(1)–C(2)	109.8(4)	110.9(6)	110.9(6)
C(1)–N(2)–C(3)	111.1(4)	111.2(6)	111.2(6)
C(1)–N(2)–C(4)	122.2(4)	121.4(5)	121.4(5)
C(3)–N(2)–C(4)	126.6(4)	127.2(5)	127.2(5)
C(5)–N(3)–C(6)	111.1(4)	110.5(6)	110.5(6)
C(5)–N(3)–C(4)	121.7(3)	122.3(5)	122.3(5)
C(5)–N(4)–C(7)	110.8(4)	109.8(6)	109.8(6)
C(6)–N(3)–C(4)	127.1(4)	127.2(5)	127.2(5)
N(1)–C(1)–N(2)	105.2(4)	104.2(5)	104.2(5)
N(1)–C(1)–Pd(1)	134.5(3)	134.4(5)	134.4(5)
N(2)–C(1)–Pd(1)	120.3(3)	121.4(5)	121.4(5)
C(3)–C(2)–N(1)	108.1(4)	106.7(6)	106.7(6)
C(2)–C(3)–N(2)	105.7(4)	106.9(6)	106.9(6)
N(2)–C(4)–N(3)	108.3(3)	107.9(5)	107.9(5)
N(4)–C(5)–N(3)	104.6(4)	105.5(6)	105.5(6)
N(4)–C(5)–Pd(1)	135.1(3)	134.0(5)	134.0(5)

[a] Only one independent molecule of **5d** is listed.

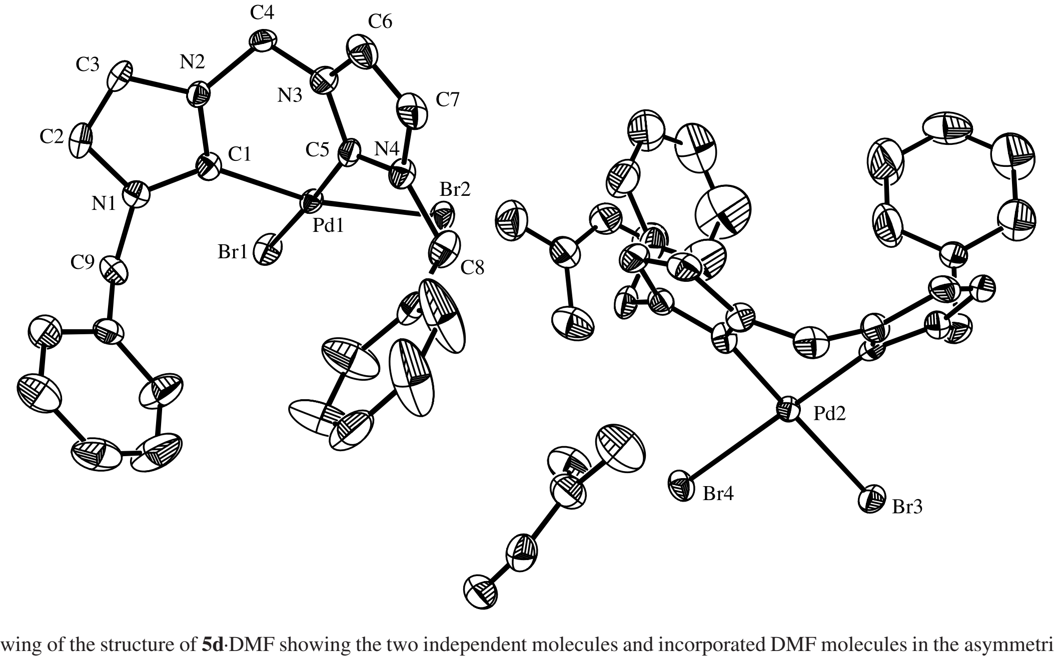
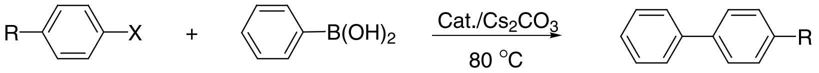


Figure 14. A drawing of the structure of **5d**·DMF showing the two independent molecules and incorporated DMF molecules in the asymmetric unit. Hydrogen atoms are omitted for clarity.

Table 11. Pd-catalyzed Suzuki coupling reaction between phenylboronic acid and aryl bromides[a]



Entry	Catalyst	X	R	Time (h)	Yield (%)
1	**5a**	Br	$COCH_3$	1	74^{b}
2	**5b**	Br	$COCH_3$	1	72^{b}
3	**5c**	Br	$COCH_3$	1	69^{b}
4	**5d**	Br	$COCH_3$	1	79^{b}
5	**5e**	Br	$COCH_3$	1	90^{b}
6	**5f**	Br	$COCH_3$	1	98^{b}
7	**5g**	Br	$COCH_3$	1	62^{b}
8	**6a**	Br	$COCH_3$	1	100^{b}
9	**6b**	Br	$COCH_3$	1	100^{b}
10	**6c**	Br	$COCH_3$	1	100^{b}
11	**6d**	Br	$COCH_3$	1	100^{b}
12	**6e**	Br	$COCH_3$	0.5	95^{b}
13	**6e**	Br	$COCH_3$	1	100^{b}
14	**3f**^{c}	Br	$COCH_3$	1	88^{b}
15	**3g**^{c}	Br	$COCH_3$	1	64^{b}
16	**5a**	Br	H	1	88^{d}
17	**5b**	Br	H	1	97^{d}
18	**5c**	Br	H	1	95^{d}
19	**5d**	Br	H	1	79^{d}
20	**5e**	Br	H	1	90^{d}
21	**5f**	Br	H	1	88^{d}
22	**5g**	Br	H	1	84^{d}
23	**6a**	Br	H	1	78^{d}
24	**6b**	Br	H	1	78^{d}
25	**6c**	Br	H	1	97^{d}
26	**6d**	Br	H	1	84^{d}
27	**6e**	Br	H	1	89^{d}
28	**3f**^{c}	Br	H	1	91^{d}
29	**3g**^{c}	Br	H	1	64^{d}
30	**5a**	Br	OMe	2	87^{d}
31	**5b**	Br	OMe	2	85^{d}
32	**5c**	Br	OMe	2	86^{d}
33	**5d**	Br	OMe	2	98^{d}
34	**5e**	Br	OMe	2	96^{d}
35	**5f**	Br	OMe	2	83^{d}
36	**5g**	Br	OMe	2	82^{d}
37	**6a**	Br	OMe	2	81^{d}
38	**6b**	Br	OMe	2	84^{d}
39	**6c**	Br	OMe	2	81^{d}
40	**6d**	Br	OMe	2	75^{d}
41	**6e**	Br	OMe	2	86^{d}
42	**3f**^{c}	Br	OMe	2	89^{d}
43	**3g**^{c}	Br	OMe	2	50^{d}

[a] Reaction condition: 1 mmol of aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol of Cs_2CO_3, 0.5 mol % of Pd catalyst, 3 mL of 1,4-dioxane.
[b] Determined by ^{1}H NMR.
[c] In situ catalyst of imidazolium salt/$Pd(OAc)_2$.
[d] Isolated yield.

series are rather insensitive towards different substitutions on the benzyl and naphthylmethyl groups (for example, entries 1–5, 8–13 and 37–41, etc). Although previous investigator, had shown that steric bulkiness on bis(imidazolium) salts are essential for high catalytic activity,[6] our results show that methylene-bridged bis(carbene) ligands with *N*-methyl or mesityl substitutions, with the exception of 4-bromoacetophenone as substrate (entries 6–7), essentially gave similar activities (entries 21–22 and 35–36). Interestingly, even though, we were not able to prepare Pd(II) complexes with **3f**, in situ catalyst employing $Pd(OAc)_2$/**3f** gave comparable activities relative to other preformed complexes (entries 14, 28 and 42), suggesting a mono-carbene complex with a pendant imidazolium arm might be involved.[3a] The combination of $Pd(OAc)_2$/**3g** gave the lowest activities (entries 15, 29 and 43).

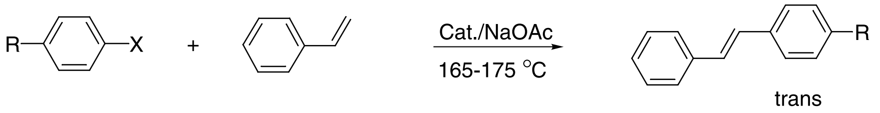
2.7. Heck coupling

The catalytic performance of the two series of Pd(II) complexes was also tested in the Heck coupling reaction of aryl bromides and styrene. As seen in Table 12, both complexes **5** and **6** are highly efficient. Entries 7, 14, 21, and 41 clearly shows that steric bulkiness on the nitrogen atoms are essential for high activities as the two bis(carbene) ligands with *N*-methyl groups gave the poorest results. Both complexes **5** and **6** were able to activate aryl chlorides but much longer reaction time and high catalysts loading were required (entries 42–45).

3. Conclusions

We have successfully prepared series of methylene and ethylene-bridged bis(imidazolium) halides employing substituted *N*-benzyl/naphthylmethyl imidazoles. The corresponding palladium(II) bis(*N*-heterocyclic carbene) complexes were also prepared by the $Pd(OAc)_2$ protocol. Crystallographic analysis of the palladium complexes with ethylene-bridged bis(carbene) shows that the seven-member palladacycles are conformationally more flexible compared with those of six-member analogs. The crystallographic determination on **4e** also reveals a possible conformational change induced by the presence of hydrogen bonding with the incorporated water molecule in the asymmetric unit. Even though Pd(II) bis(carbene) complexes are less reactive than those based on monodentate carbene ligands,[2] we demonstrated that the seven-member palladacycles are equally efficient with the six-member analogs in Suzuki and Heck coupling reactions. This finding indicates that the seven-member palladacycles can be a viable structural motif in the catalytic C–C coupling reactions and therefore opens up possibilities in the design of chelating ligands based on *N*-heterocyclic carbene.

Table 12. Pd-catalyzed Heck coupling reaction between styrene and aryl halides[a]



Entry	Catalyst	X	R	Time (h)	Yield (%)	Entry	Catalyst	X	R	Time (h)	Yield (%)
1	**5a**	Br	$COCH_3$	1	100[b]	28	**5a**	Br	OMe	4	89[b]
2	**5b**	Br	$COCH_3$	1	100[b]	29	**5b**	Br	OMe	4	87[b]
3	**5c**	Br	$COCH_3$	1	100[b]	30	**5c**	Br	OMe	4	86[b]
4	**5d**	Br	$COCH_3$	1	100[b]	31	**5d**	Br	OMe	4	91[b]
5	**5e**	Br	$COCH_3$	1	100[b]	32	**5e**	Br	OMe	4	92[b]
6	**5f**	Br	$COCH_3$	1	100[b]	33	**5f**	Br	OMe	4	86[b]
7	**5g**	Br	$COCH_3$	2	34[b]	34	**5g**	Br	OMe	4	43[b]
8	**6a**	Br	$COCH_3$	1	100[b]	35	**6a**	Br	OMe	4	88[b]
9	**6b**	Br	$COCH_3$	1	100[b]	36	**6b**	Br	OMe	2	62[b]
10	**6c**	Br	$COCH_3$	1	100[b]	37	**6c**	Br	OMe	2	79[b]
11	**6d**	Br	$COCH_3$	1	100[b]	38	**6d**	Br	OMe	4	90[b]
12	**6e**	Br	$COCH_3$	1	100[b]	39	**6e**	Br	OMe	4	90[b]
13	**3f**[c]	Br	$COCH_3$	1	100[b]	40	**3f**[c]	Br	OMe	4	57[b]
14	**3g**[c]	Br	$COCH_3$	1	59[b]	41	**3g**[c]	Br	OMe	4	9[b]
15	**5a**	Br	H	1	100[d]	42	**5e**[e]	Cl	Me	24	68[b]
16	**5b**	Br	H	1	100[d]	43	**6e**[e]	Cl	Me	24	72[b]
17	**5c**	Br	H	3	100[d]	44	**5e**[e]	Cl	$COCH_3$	24	81[b]
18	**5d**	Br	H	3	100[d]	45	**6e**[e]	Cl	$COCH_3$	24	96[b]
19	**5e**	Br	H	1	100[d]						
20	**5f**	Br	H	1	100[d]						
21	**5g**	Br	H	2	44[d]						
22	**6a**	Br	H	1	100[d]						
23	**6b**	Br	H	1	100[d]						
24	**6c**	Br	H	2	100[d]						
25	**6d**	Br	H	2	100[d]						
26	**6e**	Br	H	1	100[d]						
27	**3f**[c]	Br	H	1	100[d]						

[a] Reaction condition: 1 mmol of aryl halides, 1.4 mmol of styrene, 1.1 mmol of NaOAc, 0.5 mol% of Pd catalyst, 5 mL of DMA.
[b] Determined by ^{1}H NMR.
[c] In situ catalyst of imidazolium salt/Pd$(OAc)_2$.
[d] Isolated yield.
[e] 3 mol % of Pd catalyst.

4. Experimental

4.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk technique. Toluene and THF were dried by refluxing over sodium benzophenone ketyl. Dichloromethane and DMSO were dried by refluxing over calcium hydride. All solvents were distilled and stored in solvent reservoirs, which contained 4 Å molecular sieves, and purged with nitrogen. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AMX-300 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were recorded in ppm relative to residual proton of $CDCl_3$ (^{1}H: δ 7.24; ^{13}C: δ 77.0) and DMSO-d_6 (^{1}H: δ 2.50; ^{13}C: δ 39.5). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at Instrument Center, National Chung Hsing University, Taiwan. 1-Benzyl-1*H*-imidazole,[15] 1-(4-fluorobenzyl)-1*H*-imidazole,[16] 1-(4-methoxybenzyl)-1*H*-imidazole,[15] and 1-(3-methoxybenzyl)-1*H*-imidazole[9] were previously reported and synthesized with an improved procedure with higher yields.

4.2. Preparation of crystals

Crystals suitable for X-ray diffraction were obtained by the following procedure. A sample of compound (ca. 5 mg) was dissolved in minimum amount of DMF (ca. 1 mL). The solution was filtered and placed in a 2 mL vial. The vial was then loosely capped and placed inside a 20 mL scintillation vial containing ca. 5 mL of diethyl ether. Crystals formed after the system stood undisturbed for 1–2 d.

4.3. X-ray data collection

The crystal was removed from the vial with a small amount of mother liquor and immediately coated with silicon grease on a weighting paper. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker SMART CCD with graphite monochromated Mo K_α radiation (λ=0.71073 Å) at 150(2) K (**2a** was collected at 293(2) K). A full sphere of data was connected. No decay was observed in 50 duplicate frames at the end of the data collection.

4.4. Solution and structure refinements

Calculations for the structures were performed using SHELXS-97 and SHELXL-97. Tables of neutral atom scattering factors, f′ and f″, and absorption coefficient are from a standard source.[17] All atoms except hydrogen atoms were refined anisotropically. All hydrogen atoms were located in difference Fourier maps and included through the use of a riding model. Drawings of molecules were obtained using SHELXP-97 with 50% probability displacement ellipsoids for the non-hydrogen atoms. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 227255-227265. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax:+44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.4.1. 1-(3-Methoxybenzyl)-1*H*-imidazole (1b). A mixture of imidazole (3.26 g, 0.048 mol), *p*-methoxylbenzyl chloride (5.0 mL, 0.048 mol), and NaH (4.61 g, 0.19 mol) was stirred in 30 mL of THF under reflux overnight. The solvent was removed completely under vacuum. Water (30 mL) and dichloromethane (30 mL) were added. The organic layer was thoroughly washed with water two more times and then separated. The solvent was removed completely under vacuum to give an orange liquid, which can be used without further purification. Yield: 5.1 g, 56%. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 4.88 (s, 2H, C*H*$_2$), 6.49 (s, 1H, 2-C*H*), 6.56 (d, $^3J_{HH}$=7.5 Hz, 1H, 4-C*H*), 6.67 (dd, $^3J_{HH}$=8.2 Hz, $^4J_{HH}$=2.3 Hz, 1H, 6-C*H*), 6.90 (s, 1H, imi-*H*), 6.72 (s, 1H, imi-*H*), 7.08 (t, $^3J_{HH}$=8.0 Hz, 1H, 5-C*H*), 7.35 (s, 1H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 50.1 (Ar*C*H$_2$N), 54.8 (O*C*H$_3$), 112.7, 113.0, 119.1, 119.2, 129.2, 129.7, 137.1, 137.7, 159.7 (Ar-*C*, N*C*HN, imi-*C*).

4.4.2. 1-Naphthalen-1-ylmethyl-1*H*-imidazole (1e). The procedure follows that of **1b**. A brown viscous liquid was obtained. Yield: 99%. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 5.46 (s, 2H, C*H*$_2$), 6.89 (s, 1H, imi-*H*), 7.08 (s, 1H, imi-*H*), 7.13 (d, $^3J_{HH}$=7.1 Hz, 1H, Ar-*H*), 7.39–7.53 (m, 4H, NC*H*N, Ar-*H*), 7.82–7.88 (m, 3H, Ar-*H*). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 48.1 (Ar*C*H$_2$N), 119.3 (imi-*C*), 122.2 (imi-*C*), 125.8, 126.0, 126.7, 128.6, 128.8, 128.9, 129.3, 130.5, 131.4, 133.5 (Ar-*C*), 137.3 (N*C*HN).

4.5. A typical procedure for the preparation of compound 2

A mixture of **1a** (0.50 g, 2.7 mmol) in neat dibromomethane (1.9 mL) was stirred at 70–80 °C overnight. The white solid formed was filtered, washed with THF and dried under vacuum.

4.5.1. 1,1′-Di(4-methoxybenzyl)-3,3′-methylenediimidazolium dibromide (2a). Yield: 32%. Anal. calcd for $C_{23}H_{26}Br_2N_4O_2$: C, 50.20; H, 4.76; N, 10.18. Found: C, 50.34; H, 4.95; N, 10.45. Mp 249 °C. ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 3.77 (s, 6H, OC*H*$_3$), 5.41 (s, 4H, ArC*H*$_2$N), 6.65 (s, 2H, NC*H*$_2$N), 7.00 (d, $^3J_{HH}$=8.7 Hz, 4H, C*H*$_{meta}$), 7.44 (d, $^3J_{HH}$=8.7 Hz, 4H, C*H*$_{ortho}$), 7.88 (s, 2H, imi-*H*), 8.05 (s, 2H, imi-*H*), 9.56 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-*d*$_6$): δ 51.8 (Ar*C*H$_2$N), 55.2 (O*C*H$_3$), 58.2 (N*C*H$_2$N), 114.3 (*C*$_{meta}$), 122.4 (imi-*C*), 123.9 (imi-*C*), 125.8 (*C*$_{ipso}$), 130.4 (*C*$_{ortho}$), 137.3 (N*C*HN), 159.6 (*C*$_{para}$).

4.5.2. 1,1′-Di(3-methoxybenzyl)-3,3′-methylenediimidazolium dibromide (2b). Yield: 36%. Anal. calcd for $C_{23}H_{26}Br_2N_4O_2$: C, 50.20; H, 4.76; N, 10.18. Found: C, 50.03; H, 5.03; N, 9.98. Mp 238 °C. ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 3.77 (s, 6H, OC*H*$_3$), 5.48 (s, 4H, ArC*H*$_2$N), 6.72 (s, 2H, NC*H*$_2$N), 6.98–7.05 (m, 4H, 4-, 6-CH), 7.10 (s, 2H, 2-CH), 7.36 (virtual t, $^3J_{HH}$=7.8 Hz, 2H, 5-C*H*), 7.94 (s, 2H, imi-*H*), 8.12 (s, 2H, imi-*H*), 9.70 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-*d*$_6$): δ 51.7 (Ar*C*H$_2$N), 54.8 (O*C*H$_3$), 57.8 (N*C*H$_2$N), 113.7, 114.0 (2-, 6-*C*), 120.2 (4-*C*), 122.0 (imi-*C*), 122.7 (imi-*C*), 129.7 (5-*C*), 135.0 (1-*C*), 137.2 (N*C*HN), 159.1 (3-*C*).

4.5.3. 1,1′-Di(4-fluorobenzyl)-3,3′-methylenediimidazolium dibromide (2c). Yield: 43%. Mp 281 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 5.52 (s, 4H, ArC*H*$_2$N), 6.72 (s, 2H, NC*H*$_2$N), 7.30 (virtual t, $^3J_{HF}$=$^3J_{HH}$=8.6 Hz, 4H, C*H*$_{meta}$), 7.58 (dd, $^3J_{HH}$=8.4 Hz, $^4J_{HF}$=5.4 Hz, C*H*$_{ortho}$), 7.92 (s, 2H, imi-*H*), 8.12 (s, 2H, imi-*H*), 9.68 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-*d*$_6$): δ 51.4 (s, Ar*C*H$_2$N), 58.2 (s, N*C*H$_2$N), 115.8 (d, $^2J_{CF}$ = 21.7 Hz, *C*$_{meta}$), 122.5 (s, imi-*C*), 123.0 (s, imi-*C*), 130.3 (d, $^4J_{CF}$=2.9 Hz, *C*$_{ipso}$), 131.1 (d, $^3J_{CF}$=8.5 Hz, *C*$_{ortho}$), 137.6 (s, N*C*HN), 162.3 (d, $^1J_{CF}$=245.9 Hz, *C*F).

4.5.4. 1,1′-Dibenzyl-3,3′-methylenediimidazolium dibromide (2d). Yield: 81%. Anal. calcd for $C_{21}H_{22}Br_2N_4$: C, 51.45; H, 4.52; N, 11.43. Found: C, 51.25; H, 4.69; N, 11.25. Mp 278–280 °C. ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 5.54 (s, 4H, PhC*H*$_2$N), 6.76 (s, 2H, NC*H*$_2$N), 7.43–7.48 (m, 10H, Ph-*H*), 7.94 (s, 2H, imi-*H*), 8.16 (s, 2H, imi-*H*), 9.76 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-*d*$_6$): δ 52.3 (Ph*C*H$_2$N), 58.3 (N*C*H$_2$N), 122.5 (imi-*C*), 123.2 (imi-*C*), 128.7 (*C*$_{meta}$), 128.9 (*C*$_{para}$), 129.0 (*C*$_{ortho}$), 134.2 (*C*$_{ipso}$), 137.7 (N*C*HN).

4.5.5. 1,1′-Di(1-naphthalenemethyl)-3,3′-methylenediimidazolium dibromide (2e). Yield: 54%. Anal. calcd for $C_{29}H_{26}Br_2N_4$: C, 59.00; H, 4.44; N, 9.49. Found: C, 58.85; H, 4.71; N, 9.73. Mp 271–274 °C. ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 6.04 (s, 4H, ArC*H*$_2$N), 6.68 (s, 2H, NC*H*$_2$N), 6.60–7.66 (m, 8H, Ar-*H*), 7.96–8.18 (m, 10H, Ar-*H* and imi-*H*), 9.67 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-*d*$_6$): δ 50.3 (Ar*C*H$_2$N), 58.3 (N*C*H$_2$N), 122.4 (imi-*C*), 123.0 (imi-*C*), 123.5, 125.6, 126.5, 127.3, 128.2, 128.9, 129.4, 129.9, 130.5, 133.4 (Ar-*C*), 137.9 (N*C*HN).

4.6. A typical procedure for the preparation of compound 3

A mixture of **1a** (4.0 g, 21.3 mmol) and 1,2-dibromoethane (0.92 mL, 10.7 mmol) was stirred in THF (30 mL) at reflux for 2 d. The white solid formed was filtered, washed with THF and dried under vacuum.

4.6.1. 1,1′-Di(4-methoxybenzyl)-3,3′-ethylenediimidazolium dibromide (3a). Yield: 33%. Anal. calcd for $C_{24}H_{28}Br_2N_4O_2$: C, 51.08; H, 5.00; N, 9.93. Found: C, 51.02; H, 5.05; N, 9.84. Mp 241–242 °C. ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 3.73 (s, 6H, OC*H*$_3$), 4.74 (s, 4H, NC*H*$_2$), 5.33 (s, 4H, ArC*H*$_2$), 6.94 (d, $^3J_{HH}$=8.4 Hz, 4H, C*H*$_{meta}$), 7.35 (d, 4H, $^3J_{HH}$=8.4 Hz, C*H*$_{ortho}$), 7.68 (s, 2H, imi-*H*), 7.75 (s, 2H, imi-*H*), 9.33 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-*d*$_6$): δ 48.5 (N*C*H$_2$), 51.9 (Ar*C*H$_2$N), 55.5 (O*C*H$_3$), 114.6 (*C*$_{meta}$), 122.8 (imi-*C*), 123.0 (imi-*C*), 126.4 (*C*$_{ipso}$), 130.4 (*C*$_{ortho}$), 136.6 (N*C*HN), 159.8 (*C*$_{para}$).

4.6.2. 1,1′-Di(3-methoxybenzyl)-3,3′-ethylenediimidazolium dibromide (3b). Yield: 51%. Anal. calcd for $C_{24}H_{28}Br_2N_4O_2$: C, 51.08; H, 5.00; N, 9.93. Found: C, 51.11; H, 5.10; N, 9.90. Mp 205–207 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.77 (s, 6H, OCH_3), 4.81 (s, 4H, NCH_2), 5.43 (s, 4H, ArCH_2N), 6.96 (virtual t, $^3J_{HH}$=7.4 Hz, 4H, 4-, 6-C*H*), 7.08 (s, 2H, 2-C*H*), 7.33 (virtual t, $^3J_{HH}$=7.4 Hz, 2H, 5-C*H*), 7.80 (s, 2H, imi-*H*), 7.87 (s, 2H, imi-*H*), 9.48 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 48.3 (N*C*H$_2$), 51.9 (Ar*C*H$_2$N), 55.3 (O*C*H$_3$), 114.3, 114.3 (2-, 6-*C*), 120.4 (4-*C*), 122.7 (2×imi-*C*), 130.1 (5-*C*), 135.9 (1-*C*), 136.7 (N*C*HN), 159.5 (3-*C*).

4.6.3. 1,1′-Di(4-fluorobenzyl)-3,3′-ethylenediimidazolium dibromide (3c). Yield: 49%. Mp 288–289 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 4.78 (s, 4H, NCH_2), 5.47 (s, 4H, ArCH_2N), 7.26 (virtual t, $^3J_{HF}$=$^3J_{HH}$=8.3 Hz, 4H, CH_{meta}), 7.51 (virtual t, $^3J_{HH}$=$^4J_{HF}$=6.3 Hz, CH_{ortho}), 7.75 (s, 2H, imi-*H*), 7.85 (s, 2H, imi-*H*), 9.41 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 48.4 (s, N*C*H$_2$), 51.2 (s, Ar*C*H$_2$N), 115.8 (d, $^2J_{CF}$=21.9 Hz, C_{meta}), 122.7 (s, imi-*C*), 122.9 (s, imi-*C*), 130.9 (d, $^3J_{CF}$=8.3 Hz, C_{ortho}), 136.7 (s, N*C*HN), 162.2 (d, $^1J_{CF}$=245.3 Hz, *C*F), C_{ipso} not observed.

4.6.4. 1,1′-Dibenzyl-3,3′-ethylenediimidazolium dibromide (3d). Yield: 52%. Anal. calcd for $C_{22}H_{24}Br_2N_4$: C, 52.40; H, 4.80; N, 11.11. Found: C, 52.36; H, 4.82; N, 11.20. Mp 259–264 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 4.77 (s, 4H, NCH_2), 5.45 (s, 4H, PhCH_2N), 7.41 (s, 10H, Ph-*H*), 7.75 (s, 2H, imi-*H*), 7.84 (s, 2H, imi-*H*), 9.38 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 48.4 (N*C*H$_2$), 52.0 (Ph*C*H$_2$N), 122.8 (2×imi-*C*), 128.3 (C_{meta}), 128.7 (C_{para}), 128.9 (C_{ortho}), 134.5 (C_{ipso}), 136.7 (N*C*HN).

4.6.5. 1,1′-Di(1-naphthalenemethyl)-3,3′-ethylenediimidazolium dibromide (3e). Yield: 35%. Anal. calcd for $C_{30}H_{28}Br_2N_4$: C, 59.62; H, 4.67; N, 9.27. Found: C, 59.58; H, 4.70; N, 9.31. Mp 242–244 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 4.72 (s, 2H, NCH_2), 5.92 (s, 4H, ArCH_2N), 7.50–7.63 (m, 8H, Ar-*H*), 7.69 (s, 2H, imi-*H*), 7.78 (s, 2H, imi-*H*), 8.01–8.07 (m, 6H, Ar-*H*), 9.28 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 48.5 (N*C*H$_2$), 50.1 (Ar*C*H$_2$N), 122.7 (imi-*C* or Ar-*C*), 122.91 (imi-*C* or Ar-*C*), 122.99 (imi-*C* or Ar-*C*), 125.63, 126.44, 127.25, 127.85, 128.9, 129.7, 130.4, 130.4, 133.4 (Ar-*C*), 136.9 (N*C*HN).

4.6.6. 1,1′-Di(mesityl)-3,3′-ethylenediimidazolium dibromide (3f). Yield: 45%. Anal. calcd for $C_{26}H_{32}Br_2N_4$: C, 55.73; H, 5.76; N, 10.00. Found: C, 55.69; H, 5.72; N, 10.01. Mp >320 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 1.98 (s, 12H, *o*-CH_3), 2.33 (s, 6H, *p*-CH_3), 4.98 (s, 4H, CH_2), 7.14 (s, 4H, *m*-C*H*), 8.00 (s, 2H, imi-*H*), 8.06 (s, 2H, imi-*H*), 9.51 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 17.0(*o*-*C*H$_3$), 20.6 (*o*-*C*H$_3$), 48.7 (*C*H$_2$), 123.3 (imi-*C*), 124.4 (imi-*C*), 129.3 (C_{ortho}), 130.9 (C_{para}), 134.1 (C_{meta}), 138.0 (N*C*HN), 140.5 (C_{ipso}).

4.6.7. 1,1′-Di(methyl)-3,3′-ethylenediimidazolium dibromide (3g). Yield: 79%. Anal. calcd for $C_{10}H_{16}Br_2N_4$: C, 34.12; H, 4.58; N, 15.91. Found: C, 34.23; H, 4.60; N, 15.89. Mp 230–234 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.87 (s, 6H, CH_3), 4.78 (s, 4H, CH_2), 7.76 (s, 4H, imi-*H*), 9.28 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 33.6 (*C*H$_3$), 48.2 (*C*H$_2$), 122.3 (imi-*C*), 123.7 (imi-*C*), 137.1 (N*C*HN).

4.7. A typical procedure for the preparation of compound 4

A mixture of **1a** (3.2 g, 16.9 mmol) and 1,2-dichloroethane (0.67 mL, 0.84 mmol) was stirred in THF (30 mL) at reflux for 2 d. The solvent was removed completely under vacuum. Dichloromethane was added to the residue to give a white solid, which was filtered and dried under vacuum.

4.7.1. 1,1′-Di(4-methoxybenzyl)-3,3′-ethylenediimidazolium dichloride (4a). Yield: 17%. Anal. calcd for $C_{24}H_{28}Cl_2N_4O_2$: C, 60.63; H, 5.94; N, 11.78. Found: C, 60.61; H, 5.89; N, 11.68. Mp 265–268 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.75 (s, 3H, OCH_3), 4.77 (s, 4H, CH_2), 5.35 (s, 4H, CH_2), 6.96 (d, $^3J_{HH}$=8.6 Hz, 4H, CH_{meta}), 7.38 (d, $^3J_{HH}$=8.6 Hz, 4H, CH_{ortho}), 7.76 (s, 2H, imi-*H*), 7.79 (s, 2H, imi-*H*), 9.53 (s, 2H, NC*H*N).

4.7.2. 1,1′-Di(3-methoxybenzyl)-3,3′-ethylenediimidazolium dichloride (4b). Yield: 35%. Anal. calcd for $C_{24}H_{28}Cl_2N_4O_2$: C, 60.63; H, 5.94; N, 11.78. Found: C, 60.61; H, 5.90; N, 11.68. Mp 108–110 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.77 (s, 6H, OCH_3), 4.80 (s, 4H, NCH_2), 5.40 (s, 4H, ArCH_2N), 6.95 (d, $^3J_{HH}$=7.7 Hz, 4H, 4-, 6-C*H*), 7.06 (s, 2H, 2-C*H*), 7.33 (t, $^3J_{HH}$=7.7 Hz, 2H, 5-C*H*), 7.80 (s, 2H, imi-*H*), 7.82 (s, 2H, imi-*H*), 9.59 (s, 2H, NC*H*N).

4.7.3. 1,1′-Di(4-fluorobenzyl)-3,3′-ethylenediimidazolium dichloride (4c). Yield: 8%. Mp 263–265 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 4.79 (s, 4H, NCH_2), 5.45 (s, 4H, ArCH_2N), 7.25 (virtual t, $^3J_{HF}$=$^3J_{HH}$=8.9 Hz, 4H, CH_{meta}), 7.51 (virtual t, $^3J_{HH}$=$^4J_{HF}$=7.0 Hz, CH_{ortho}), 7.79 (s, 2H, imi-*H*), 7.83 (s, 2H, imi-*H*), 9.61 (s, 2H, NC*H*N).

4.7.4. 1,1′-Dibenzyl-3,3′-ethylenediimidazolium dichloride (4d). Yield: 34%. Anal. calcd for $C_{22}H_{24}Cl_2N_4$: C, 63.62; H, 5.82; N, 13.49. Found: C, 63.76; H, 6.03; N, 13.97. Mp 260 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 4.82 (s, 4H, NCH_2), 5.46 (s, 4H, PhCH_2N), 7.41 (s, 10H, Ph-*H*), 7.84 (s, 4H, imi-*H*), 9.65 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 48.3 (N*C*H$_2$), 52.0 (Ph*C*H$_2$N), 122.7 (imi-*C*), 122.9 (imi-*C*), 128.3 (C_{meta}), 128.7 (C_{para}), 128.9 (C_{ortho}), 134.6 (C_{ipso}), 137.0 (N*C*HN).

4.7.5. 1,1′-Di(1-naphthalenemethyl)-3,3′-ethylenediimidazolium dichloride (4e). Yield: 44%. Anal. calcd for $C_{30}H_{28}Cl_2N_4$: C, 69.90; H, 5.47; N, 10.87. Found: C, 69.65; H, 5.53; N, 10.61. Mp 248 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 4.72 (s, 2H, NCH_2), 5.91 (s, 4H, ArCH_2N), 7.48–7.62 (m, 8H, Ar-*H*), 7.70 (s, 2H, imi-*H*), 7.77 (s, 2H, imi-*H*), 8.01–8.07 (m, 6H, Ar-*H*), 9.37 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 48.4 (N*C*H$_2$), 50.0 (Ar*C*H$_2$N), 122.7, 122.9, 123.0 (imi-*C*, Ar-*C*), 125.6, 126.4, 127.2, 127.7, 128.9, 129.7, 129.7, 130.3, 133.4 (Ar-*C*), 137.0 (N*C*HN).

4.8. A typical procedure for the preparation of compound 5

A mixture of **2a** (0.5 g, 0.88 mmol) and $Pd(OAc)_2$ (0.20 g, 0.88 mmol) in ca. 5 mL of DMSO was heated at 50 °C for 2 h and then slowly to 110 °C for 3 h. The solvent was then removed completely under vacuum. The residue was added with dichloromethane to produce a white solid, which was filtered and dried under vacuum.

4.8.1. {1,1′-Di(4-methoxybenzyl)-3,3′-methylenediimidazolin-2,2′diylidene}palladium(II) dibromide (5a). Yield: 82%. Anal. calcd for $C_{23}H_{24}Br_2N_4O_2Pd$: C, 42.20; H, 3.69; N, 8.56. Found: C, 42.16; H, 3.82; N, 8.54. Mp 272 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.78 (s, 6H, OCH_3), 5.26 (d, $^2J_{HH}$=14.1 Hz, 2H, $ArCH_aH_bN$), 5.90–5.94 (br m, 2H, $ArCH_aH_bN$), 6.30–6.32 (m, 2H, NCH_2N), 6.85 (d, $^3J_{HH}$=8.4 Hz, 4H, CH_{meta}), 7.22 (s, 2H, imi-*H*), 7.29 (d, $^3J_{HH}$=8.4 Hz, 4H, CH_{ortho}), 7.56 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 52.9 ($ArCH_2N$), 54.9 (OCH_3), 62.5 (NCH_2N), 113.9 (C_{meta}), 121.6 (imi-*C*), 121.9 (imi-*C*), 128.3 (C_{ipso}), 129.6 (C_{ortho}), 158.3, (br, N*C*N), 158.9 (C_{para}).

4.8.2. {1,1′-Di(3-methoxybenzyl)-3,3′-methylenediimidazolin-2,2′diylidene}palladium(II) dibromide (5b). Yield: 82%. Anal. calcd for $C_{23}H_{24}Br_2N_4O_2Pd$: C, 42.20; H, 3.69; N, 8.56. Found: C, 41.97; H, 3.67; N, 8.46. Mp 291 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.71 (s, 6H, OCH_3), 5.36 (d, $^2J_{HH}$=14.4 Hz, 2H, $ArCH_aH_bN$), 5.84–5.89 (br m, 2H, $ArCH_aH_bN$), 6.34–6.36 (m, 2H, NCH_2N), 6.79–6.88 (m, 4H, 4-, 6-C*H*), 7.01 (s, 2H, 2-C*H*), 7.19 (virtual t, $^3J_{HH}$=8.0 Hz, 2H, 5-C*H*), 7.24 (s, 2H, imi-*H*), 7.59 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 52.8 ($ArCH_2N$), 54.5 (OCH_3), 62.2 (NCH_2N), 112.7, 113.7 (2-, 6-*C*), 119.5 (4-*C*), 121.4 (imi-*C*), 121.5 (imi-*C*), 129.2 (5-*C*), 137.3 (1-*C*), 158.8 (3-*C*), the carbene carbon was not observed.

4.8.3. {1,1′-Di(4-fluorobenzyl)-3,3′-methylenediimidazolin-2,2′diylidene}palladium(II) dibromide (5c). Yield: 85%. Mp 293 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 5.39 (d, $^2J_{HH}$=14.4 Hz, 2H, $PhCH_aH_bN$), 5.83–5.97 (br m, 2H, $PhCH_aH_bN$), 6.33–6.35 (m, 2H, NCH_2N), 7.12 (virtual t, $^3J_{HF}$=$^3J_{HH}$=8.7 Hz, 4H, CH_{meta}), 7.27 (s, 2H, imi-*H*), 7.37–7.39 (br m, 4H, CH_{ortho}), 7.60 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 52.9 (s, $ArCH_2N$), 63.1 (s, NCH_2N), 115.9 (d, $^2J_{CF}$=21.1 Hz, C_{meta}), 122.3 (s, imi-*C*), 123.6 (s, imi-*C*), 130.6 (d, $^3J_{CF}$=8.3 Hz, C_{ortho}), 133.2 (C_{ipso}), 157.1 (br, N*C*N), 161.9 (d, $^1J_{CF}$=243.8 Hz, *C*F).

4.8.4. {1,1′-Dibenzyl-3,3′-methylenediimidazolin-2,2′diylidene}palladium(II) dibromide (5d). Yield: 99%. Anal. calcd for $C_{21}H_{20}Br_2N_4Pd$: C, 42.42; H, 3.39; N, 9.42. Found: C, 42.40; H, 3.32; N, 9.50. Mp 282–284 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 5.35 (d, $^2J_{HH}$ = 14.7 Hz, 2H, $PhCH_aH_bN$), 5.94–5.98 (br m, 2H, $PhCH_aH_bN$), 6.34–6.36 (m, 2H, NCH_2N), 7.25 (s, 2H, imi-*H*), 7.31 (s, 10H, Ph-*H*), 7.61 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 53.5 ($PhCH_2N$), 62.6 (NCH_2N), 121.9 (imi-*C*), 122.1 (imi-*C*), 128.0 (C_{meta}), 128.7 (C_{ortho}), 136.5 (C_{ipso}), the C_{para} and carbene carbons were not observed.

4.8.5. {1,1′-Di(1-naphthalenemethyl)-3,3′-methylenediimidazolin-2,2′diylidene}palladium(II) dibromide (5e). Yield: 50%. Anal. calcd for $C_{29}H_{24}Br_2N_4Pd$: C, 50.14; H, 3.48; N, 8.06. Found: C, 50.05; H, 3.42; N, 8.11. Mp 292 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 5.97 (d, $^2J_{HH}$=14.7 Hz, 2H, $ArCH_aH_bN$), 6.35 (br m, 2H, $PhCH_aH_bN$), 6.31–6.35 (m, 2H, NCH_2N), 6.39–643 (d, $^2J_{HH}$=6.9 Hz, 2H, Ar-*H*), 7.15–7.20 (m, 4H, Ar-*H*, imi-*H*), 7.36–7.61 (m, 8H, Ar-*H*, imi-*H*), 7.87–7.96 (m, 4H, Ar-*H*), 8.23 (d, $^2J_{HH}$=7.8 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 52.0 ($ArCH_2$), 63.2 (NCH_2N), 123.4, 123.6, 125.9, 126.5, 127.1, 129.0, 130.9, 132.3, 133.7 (imi-*C*, Ar-*C*), 159.9 (br, N*C*N).

4.9. A typical procedure for the preparation of compound 6

A mixture of **3a** (0.50 g, 0.89 mmol) and $Pd(OAc)_2$ (0.20 g, 0.89 mmol) in 5 mL of DMSO was heated at 50 °C for 2 h and then slowly to 110 °C for 3 h. The solution was then filtered through a small column of Celite and the solvent was removed completely under vacuum. The residue was added with dichloromethane to produce a white solid, which was filtered and dried under vacuum.

4.9.1. {1,1′-Di(4-methoxybenzyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dibromide (6a). Yield: 30%. Anal. calcd for $C_{24}H_{26}Br_2N_4O_2Pd$: C, 43.11; H, 3.92; N, 8.38. Found: C, 43.09; H, 3.95; N, 8.31. Mp 295–296 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.72 (s, 6H, OCH_3), 4.53–4.55 (br m, 2H, NCH_aH_b), 4.94 (d, $^2J_{HH}$=14.6 Hz, 2H, $ArCH_aH_bN$), 5.28 (br m, 2H, NCH_aH_b), 5.20–5.35 (d, $^2J_{HH}$=14.6 Hz, 2H, $ArCH_aH_bN$), 6.89 (d, $^3J_{HH}$=8.4 Hz, 4H, CH_{meta}), 7.10 (s, 2H, imi-*H*), 7.16 (d, $^3J_{HH}$=8.4 Hz, 4H, CH_{ortho}), 7.40 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 46.9 (NCH_2), 52.6 ($ArCH_2N$), 55.1 (OCH_3), 114.0 (C_{meta}), 122.2 (imi-*C*), 123.0 (imi-*C*), 128.1 (C_{ipso}), 129.6 (C_{ortho}), 157.1, (br, N*C*N), 159.0 (C_{para}).

4.9.2. {1,1′-Di(3-methoxybenzyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dibromide (6b). Yield: 38%. Anal. calcd for $C_{24}H_{26}Br_2N_4O_2Pd$: C, 43.11; H, 3.92; N, 8.38. Found: C, 43.09; H, 3.91; N, 8.27. Mp 247 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 3.71 (s, 6H, OCH_3), 4.56–4.59 (br m, 2H, NCH_aH_b), 4.96 (d, $^2J_{HH}$=14.7 Hz, 2H, $ArCH_aH_bN$), 5.25–5.35 (br m, 2H, NCH_aH_b), 5.40 (d, $^2J_{HH}$=14.7 Hz, 2H, $ArCH_aH_bN$), 6.74 (d, $^3J_{HH}$=7.2 Hz, 2H, 4-C*H*), 6.82 (s, 2H, 2-C*H*), 6.90 (d, $^3J_{HH}$=7.2 Hz, 2H, 6-C*H*), 7.15 (s, 2H, imi-*H*), 7.26 (virtual t, $^3J_{HH}$=7.8 Hz, 2H, 5-C*H*), 7.43 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 46.9 (NCH_2), 52.9 ($ArCH_2N$), 55.1 (OCH_3), 112.2, 113.9 (2-, 6-*C*), 120.1 (4-*C*), 122.4 (imi-*C*), 123.2 (imi-*C*), 129.8 (5-*C*), 137.7 (1-*C*), 159.4 (3-*C*), the carbene carbon was not observed.

4.9.3. {1,1′-Di(4-fluorobenzyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dibromide (6c). Yield: 22%. Mp 268 °C (dec). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 4.55–4.58 (br m, 2H, NCH_aH_b), 5.10 (d, $^2J_{HH}$=14.7 Hz, 2H, $ArCH_aH_bN$), 5.27–5.29 (br m, 2H, NCH_aH_b), 5.41 (d, $^2J_{HH}$=14.7 Hz, 2H, $ArCH_aH_bN$), 7.15–7.18 (m, 4H, CH_{meta}), 7.21 (s, 2H, imi-*H*), 7.27–7.31 (m, 4H, CH_{ortho}), 7.43 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 47.0 (s, N*C*H_2), 52.4 (s, Ar*C*H_2N), 115.5 (d, $^2J_{CF}$=21.1 Hz, C_{meta}), 122.4 (s, imi-*C*), 123.4 (s, imi-*C*), 130.3 (d, $^3J_{CF}$=7.5 Hz, C_{ortho}), 132.5 (C_{ipso}), 157.2 (br, N*C*N), 161.9 (d, $^1J_{CF}$=243.8 Hz, *C*F).

4.9.4. {1,1′-Dibenzyl-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dibromide (6d). Yield: 50%. Anal. calcd for $C_{22}H_{22}Br_2N_4Pd$: C, 43.41; H, 3.65; N, 9.20. Found: C, 43.47; H, 3.69; N, 9.20. Mp 260–262 °C (dec). ^1H NMR (300.13 MHz, DMSO-d_6): δ 4.57–4.59 (br m, 2H, NCH_aH$_b$), 4.93 (d, $^2J_{HH}$=14.6 Hz, 2H, ArCH_aH$_b$N), 5.24–5.32 (br m, 2H, NCH$_a$$H_b$), 5.43 (d, $^2J_{HH}$=14.6 Hz, 2H, ArCH$_a$$H_b$N), 7.13–7.44 (m, 14H, imi-*H*, Ph-*C*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6):δ 47.3 (N*C*H_2), 53.4 (Ar*C*H_2N), 122.8 (imi-*C*), 123.9 (imi-*C*), 128.4 (C_{meta}), 129.1 (C_{ortho}), 136.7 (C_{ipso}), the C_{para} and carbene carbons were not observed.

4.9.5. {1,1′-Di(1-naphthalenemethyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dibromide (6e). Yield: 46%. Anal. calcd for $C_{30}H_{26}Br_2N_4Pd$: C, 50.84; H, 3.70; N, 7.90. Found: C, 50.86; H, 3.69; N, 7.88. Mp 282–284 °C (dec). ^1H NMR (300.13 MHz, DMSO-d_6): δ 4.65–4.67 (br m, 2H, NCH_aH$_b$), 5.30–5.38 (br m, 4H, ArCH_aH$_b$N, NCH$_a$$H_b$), 5.84 (d, $^2J_{HH}$=15.0 Hz, 2H, ArCH$_a$$H_b$N), 6.76 (d, $^2J_{HH}$=6.9 Hz, 2H, Ar-*H*), 7.04 (s, 2H, imi-*H*), 7.39–7.60 (m, 8H, Ar-*H*, imi-*H*), 7.85–8.01 (m, 6H, Ar-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 47.0 (N*C*H_2), 51.2 (Ar*C*H_2N), 122.6 (imi-*C*), 123.1 (Ar-*C* and imi-*C*), 125.4, 125.6, 126.2, 126.7, 128.5, 128.6, 130.4, 131.7, 133.2 (Ar-*C*), 157.9 (br, N*C*N).

4.10. A typical procedure for the preparation of compound 7

A mixture of **4a** (0.42 g, 0.89 mmol) and $Pd(OAc)_2$ (0.20 g, 0.89 mmol) in 3 mL of DMSO was heated at 50 °C for 2 h and then slowly to 110 °C for 2 h. The solution was then filtered through a small column of Celite and the solvent was removed completely under vacuum. The residue was added with THF to produce a white solid, which was filtered and dried under vacuum.

4.10.1. {1,1′-Di(4-methoxybenzyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dichloride (7a). Yield: 45%. Anal. calcd for $C_{24}H_{26}Cl_2N_4O_2Pd$: C, 49.72; H, 4.52; N, 9.66. Found: C, 49.88; H, 4.32; N, 9.77. Mp 242–246 °C (dec). ^1H NMR (300.13 MHz, DMSO-d_6): δ 3.63 (s, 6H, OCH_3), 4.37–4.39 (br m, 2H, NCH_aH$_b$), 4.93 (d, $^2J_{HH}$= 14.7 Hz, 2H, ArCH_aH$_b$N), 5.09–5.15 (br m, 2H, NCH$_a$$H_b$), 5.20 (d, $^2J_{HH}$=14.7 Hz, 2H, ArCH$_a$$H_b$N), 6.74 (d, $^3J_{HH}$= 8.4 Hz, 4H, CH_{meta}), 6.95 (s, 2H, imi-*H*), 7.06 (d, $^3J_{HH}$=8.4 Hz, 4H, CH_{ortho}), 7.22 (s, 2H, imi-*H*).

4.10.2. {1,1′-Di(3-methoxybenzyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dichloride (7b). Yield: 23%. Anal. calcd for $C_{24}H_{26}Cl_2N_4O_2Pd$: C, 49.72; H, 4.52; N, 9.66. Found: C, 49.69; H, 4.50; N, 9.62. Mp 242–246 °C (dec). ^1H NMR (300.13 MHz, DMSO-d_6): δ 3.71 (s, 6H, OCH_3), 4.54–4.57 (br m, 2H, NCH_aH$_b$), 5.10 (d, $^2J_{HH}$=14.7 Hz, 2H, ArCH_aH$_b$N), 5.26–5.29 (br m, 2H, NCH$_a$$H_b$), 5.42 (d, $^2J_{HH}$=14.7 Hz, 2H, ArCH$_a$$H_b$N), 6.72–6.92 (m, 6H, 4-C*H*, 2-C*H*, 6-C*H*), 7.15 (s, 2H, imi-*H*), 7.26 (virtual t, $^3J_{HH}$=7.8 Hz, 2H, 5-C*H*), 7.40 (s, 2H, imi-*H*).

4.10.3. {1,1′-Di(4-fluorobenzyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dichloride (7c). Yield: 37%. Mp 268 °C (dec). ^1H NMR (300.13 MHz, DMSO-d_6): δ 4.53–4.56 (br m, 2H, NCH_aH$_b$), 5.22 (d, $^2J_{HH}$= 14.6 Hz, 2H, ArCH_aH$_b$N), 5.28 (br s, 2H, NCH$_a$$H_b$), 5.41 (d, $^2J_{HH}$=14.6 Hz, 2H, ArCH$_a$$H_b$N), 7.15–7.21 (m, 6H, C$H_{meta}$, imi-*H*), 7.31–7.36 (m, 4H, CH_{ortho}), 7.42 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 47.0 (s, N*C*H_2), 52.0 (s, Ar*C*H_2N), 115.3 (d, $^2J_{CF}$=21.1 Hz, C_{meta}), 122.2 (s, imi-*C*), 123.1 (s, imi-*C*), 130.3 (d, $^3J_{CF}$=7.5 Hz, C_{ortho}), 132.6 (C_{ipso}), 155.6 (N*C*N), 161.7 (d, $^1J_{CF}$=243.8 Hz, *C*F).

4.10.4. {1,1′-Dibenzyl-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dichloride (7d). Yield: 15%. Anal. calcd for $C_{22}H_{22}Cl_2N_4Pd$: C, 50.84; H, 4.27; N, 10.78. Found: C, 50.85; H, 4.30; N, 10.72. Mp 304 °C (dec). ^1H NMR (300.13 MHz, DMSO-d_6): δ 4.54–4.57 (br m, 2H, NCH_aH$_b$), 5.07 (d, $^2J_{HH}$=15.0 Hz, 2H, ArCH_aH$_b$N), 5.24–5.30 (br m, 2H, NCH$_a$$H_b$), 5.43 (d, $^2J_{HH}$=15.0 Hz, 2H, ArCH$_a$$H_b$N), 7.13 (s, 2H, imi-*H*), 7.21–7.23 (m, 6H, Ph-*H*), 7.33–7.35 (m, 6H, Ph-*H*), 7.42 (s, 2H, imi-*H*).

4.10.5. {1,1′-Di(1-naphthalenemethyl)-3,3′-ethylenediimidazolin-2,2′diylidene}palladium(II) dichloride (7e). Yield: 52%. Anal. calcd for $C_{30}H_{26}Cl_2N_4Pd$: C, 58.13; H, 4.23; N, 9.04. Found: C, 58.32; H, 4.29; N, 8.82. Mp 282 °C (dec). ^1H NMR (300.13 MHz, DMSO-d_6): δ 4.62–4.65 (br m, 2H, NCH_aH$_b$), 5.34–5.38 (br m, 4H, ArCH_aH$_b$N, NCH$_a$$H_b$), 5.89 (d, $^2J_{HH}$=15.6 Hz, 2H, ArCH$_a$$H_b$N), 6.80 (d, $^2J_{HH}$=6.9 Hz, 2H, Ar-*H*), 7.01 (s, 2H, imi-*H*), 7.40–7.59 (m, 8H, Ar-*H*, imi-*H*), 7.94–8.01 (m, 6H, Ar-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ 46.6 (N*C*H_2), 50.3 (Ar*C*H_2N), 122.9, 122.4, 122.7 (imi-*C*, Ar-*C*), 124.9, 125.2, 125.7, 126.2, 128.1 (2×Ar-*C*), 130.0, 131.4, 132.7 (Ar-*C*), 156.1 (br, N*C*N).

4.11. General procedure for the Suzuki coupling reactions

In a typical run, a mixture of aryl bromides (1.0 mmol), phenylboronic acid (1.5 mmol), cesium carbonate (2.0 mmol) and 0.5 mol % of catalyst in 3 mL of 1,4-dioxane was stirred at 80 °C for 1–2 h under nitrogen. The solution was allowed to cool. A 1:1 mixture of diethyl ether/water (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL portion of diethyl ether, and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatiles were removed completely under high vacuum to give a crude product which either subject to column chromatography or analyzed by ^1H NMR.

4.12. General procedure for the Heck coupling reactions

In a typical run, a 50 mL two-neck flask equipped with a reflux condenser was charged with aryl halides (1.0 mmol), styrene (1.4 mmol), anhydrous sodium acetate (1.1 mmol) and 0.5 mol % of catalyst. The flask was thoroughly degassed, added with 5 mL of *N*,*N*-dimethylacetamide via a syringe, and then placed in a preheated oil bath at 165–175 °C. In the cases of bromobenzene as substrate, after fixed time 10 mL of diethyl ether was added to the reaction mixture and the organic layer was washed with five times of water and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatiles were removed completely under high vacuum to give the isolated product. With all the other substrates, aliquots (0.2 mL) were removed from the reaction after fixed time and added to dichloromethane (10 mL). The organic portion was washed with five times of water and dried with anhydrous $MgSO_4$. The solution was filtered and the solvent was removed completely under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR.

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References and notes

1. For recent reviews, see: (a) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69–82. (b) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309.
2. (a) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804–3805. (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *595*, 186–190. (c) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470–5472.
3. For examples, see: (a) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G. *Organometallics* **1999**, *18*, 4082–4809. (b) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239–247. (c) Clyne, D. S.; Jin, J.; Genest, E.; Callucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125–1128. (d) César, V.; Bellemin-Laponnaz, B.; Gade, L. H. *Organometallics* **2002**, *21*, 5204–5208. (e) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. *Chem. Commun.* **2002**, 32–33. (f) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596–3604.
4. (a) Hermann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93–96. (b) Zhang, C.; Trudell, M. L. *Tetrahedron Lett.* **2000**, *41*, 595–598.
5. Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617–618*, 546–560.
6. Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866–2873.
7. Drent, E.; Budzelaar, P. H. M. *J. Organomet. Chem.* **2000**, *593–594*, 211–225.
8. See for examples: (a) Bonnet, L. G.; Douthwaite, R. E. *Organometallics* **2003**, *22*, 4187–4189. (b) Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2003**, *22*, 1979–1982. (c) Danopoulos, A. A.; Winston, S.; Gelbrich, T.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun.* **2002**, 482–483. (d) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750–4758. (e) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511–1514.
9. Substituted *N*-benzylimidazoles were typically synthesized with inorganic bases such as K_2CO_3 in acetone or DMF. See: Baggaley, K. H.; Heald, M.; Hindley, R. M.; Morgan, B.; Tee, J. L.; Green, J. *J. Med. Chem.* **1975**, *18*, 833–836.
10. William, D. J.; Vanderveer, D.; Jones, R. L.; Menaldino, D. S. *Inorg. Chim. Acta.* **1989**, *165*, 173–178.
11. (a) Douthwaite, R. E.; Haüssinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Ana, M.; Martins, A. M.; Danopoulos, A. A. *Organometallics* **1999**, *18*, 4584–4590. (b) Douthwaite, R. E.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T. *Organometallics* **2001**, *20*, 2611–2615.
12. Sutton, L. E. *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Chemical Society Publications: UK, 1965.
13. Douthwaite, R. E.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T. *J. Chem. Soc., Dalton Trans.* **2002**, 1386–1390.
14. Schwarz, J.; Bohm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773–1780.
15. Milgrom, L. R.; Dempsey, P. J. F.; Yahioglu, G. *Tetrahedron* **1996**, *52*, 9877–9890.
16. Harper, J. L.; Smith, R. A. J.; Bedford, J. J.; Leader, J. P. *Tetrahedron* **1997**, *53*, 8211–8224.
17. Wilson, A. J. C. *International Tables for Crystallography*, Kluwer Academic: Dordrecht, 1992; Vol. C.