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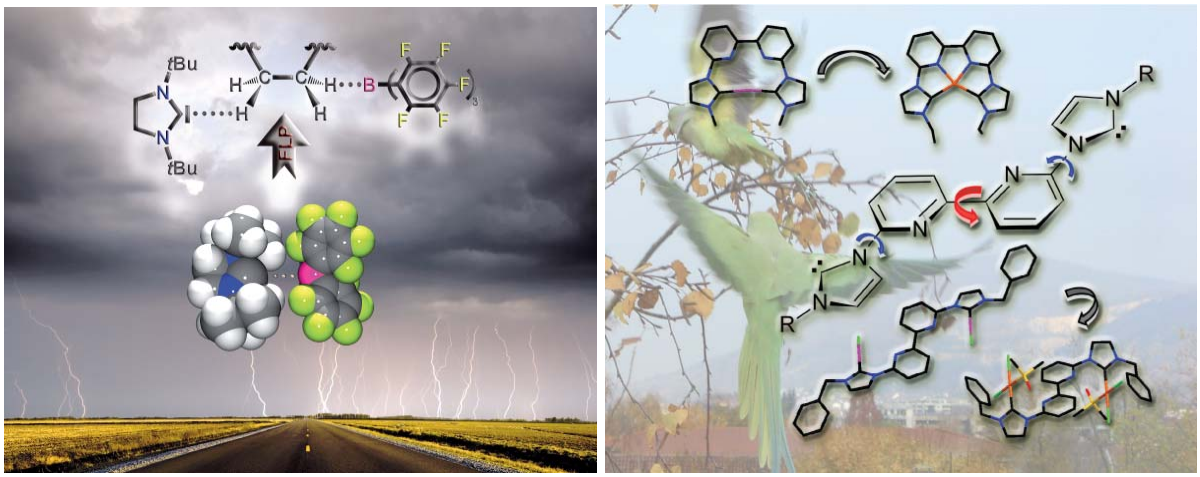

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Synthesis of tetra- and pentacoordinate palladium complexes of functionalized N-heterocyclic carbenes and a comparative study of their catalytic activities†

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Palladium complexes, [Pd(1-butyl-3-((7-methyl-1,8-naphthyridin-2-yl)methyl)imidazolylidene)$_2$](PF$_6$)$_2$ (**1**), [Pd(3-methyl-1-(pyrimidin-2-yl)imidazolylidene)$_2$(CH$_3$CN)](PF$_6$)$_2$ (**4**), [Pd(3-benzyl-1-(pyrimidin-2-yl)imidazolylidene)$_2$(CH$_3$CN)](PF$_6$)$_2$ (**5**), [Pd(3-ethyl-1-(pyrimidin-2-yl)imidazolylidene)$_2$Cl](PF$_6$) (**6**), and [Pd(3-benzyl-1-(pyrimidin-2-yl)imidazolylidene)Cl$_2$] (**7**), have been prepared *via* transmetallation of corresponding *in situ* generated silver-carbene complexes. These palladium complexes have been characterized by NMR spectroscopy and elemental analyses, and their structures were determined by X-ray single-crystal diffraction. Complexes **1** and **7** are tetracoordinate displaying square-planar geometry. Complexes **4–6** are pentacoordinate showing uncommon square-pyramidal geometry with acetonitrile or chloride at the equatorial position. The Suzuki and Hiyama coupling reactions of a wide range of aryl bromides and chlorides have been comparatively investigated by using tetracoordinate moncarbene, tetracoordinate dicarbene, and pentacoordinate dicarbene palladium complexes as catalysts. The tetracoordinate moncarbene palladium complex showed the highest catalytic activity for both coupling reactions.

Introduction

Transition metal complexes of N-heterocyclic carbenes (NHCs) have been attracting great interest because of their usefulness as ancillary ligands in metal-catalyzed reactions, primarily based on the analogy between NHCs and tertiary phosphines in the past decades.[1] A number of metal/NHC complexes have shown their enhanced catalytic activities in a wide range of organic transformations including C–C[2] and C–N[3] bond formation, olefin metathesis,[4] oligomerization and polymerization of alkenes.[5] It is generally accepted that the provision of monodentate or multidentate chelate functional groups to complement the strongly binding NHCs could promote a reversible coordination and dissociation mechanism which is highly desirable for catalytic applications.[6] In addition, the presence of sterically bulky groups bound to the N-atoms favors reductive elimination of the product from central metals.

The most successful application at present appears to be the use of palladium complexes of NHC ligands in C–C and C–heteroatom coupling reactions.[7] Among the known Pd-NHC complexes, most of them are tetracoordinate containing one or two chelate ligands in square planar geometry.[8] We have recently reported the synthesis and structures of a family of silver clusters,[9] palladium,[10] and nickel complexes[11] stabilized by pyridine-, pyrazole-, and naphthyridine-functionalized NHC ligands, and these palladium and nickel complexes were found to be good catalysts for C–C coupling reactions. The structural characterization and catalytic studies of non-square planar palladium complexes would provide useful information for the clarification of the reaction mechanism. Here in this paper, we report the synthesis and structural characterization of a few tetra- and pentacoordinate palladium complexes of functionalized NHC ligands, their catalytic behavior in Suzuki and Hiyama reactions of a range of aryl bromides and chlorides were comparatively studied.

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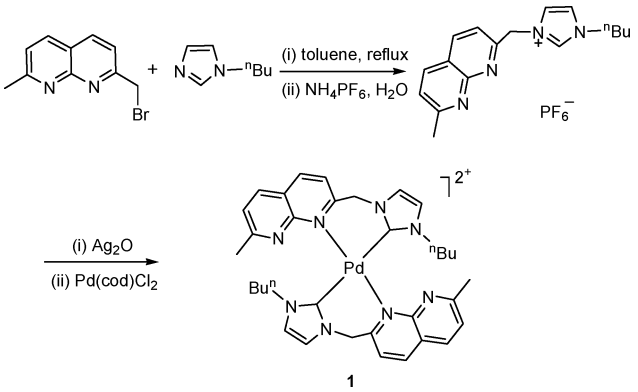
Results and discussion

Synthesis and characterization of tetracoordinate [Pd(L1)$_2$](PF$_6$)$_2$ (1).

The naphthyridine-functionlized imidazolium salt, HL1·PF$_6$, was prepared by refluxing 2-bromomethyl-7-methyl-1,8-naphthyridine and *N*-n-butylimidazole in toluene and subsequent anion exchange in water (Scheme 1). Deprotonation of the imidazolium salts with Ag$_2$O in CH$_3$CN proceeded smoothly at 50 °C, and subsequent addition of Pd(cod)Cl$_2$ to the colorless filtrate led to the isolation of **1** as a white powder in 73% yield. The formulation of **1** was determined by elemental analysis and further confirmed by NMR observations. ^{1}H NMR spectrum of **1** in DMSO-d_6 shows complete disappearance of the acidic NC*H*N signal which appears at 9.36 ppm in its precursor HL1·PF$_6$, and a downfield resonance of carbene carbon at 168.1 ppm was observed in its ^{13}C NMR spectrum. These strongly indicate that the two ligands are coordinated to the palladium center. These two ligands are magnetically equivalent and other chemical shifts are similar to its parent imidazolium salt, HL1·PF$_6$. Complex **1** is quite stable towards air and moisture. ESI-MS spectrum of **1** in acetonitrile displays peaks at 811.02, 665.27 and 386.15 amu which can be assigned to [Pd(L1)$_2$(PF$_6$)]$^+$ (calcd 811.20 amu), [Pd(L1)$_2$]$^+$ (calcd 666.24 amu), and [PdL1]$^+$ (calcd 386.07 amu), respectively.

The solid state structure of **1** was further confirmed by X-ray diffraction. The asymmetric unit of **1** contains two independent



Scheme 1 Synthesis of **1**.

molecules which are essentially the same, and thus only one is shown. As shown in Fig. 1, the palladium atom is bonded to two carbene carbons and two naphthyridyl nitrogen atoms adopting a square planar geometry. The two chelates adopt a *trans* arrangement around the palladium atom, such that there is a *C*i symmetry at the palladium center. Both *trans*-positioned NHC rings and naphthyridine rings are virtually coplanar. The imidazolylidene and naphthyridine rings are both bisected by the coordinated plane with dihedral angles of 47.24 and 51.49°, respectively. The Pd–C (2.009(6) Å) and Pd–N (2.039(5) Å) bond distances are quite normal as compared to many known tetracoordinate palladium(II)-NHC complexes.[8] It should be noted that NHC donors are usually *cis*-arranged in the previously reported dicarbene palladium complexes due to larger *trans* effect of carbenes.[8] So far only a few structurally characterized Pd-dicarbene complexes having a *trans*-conformation have already been reported.[12]

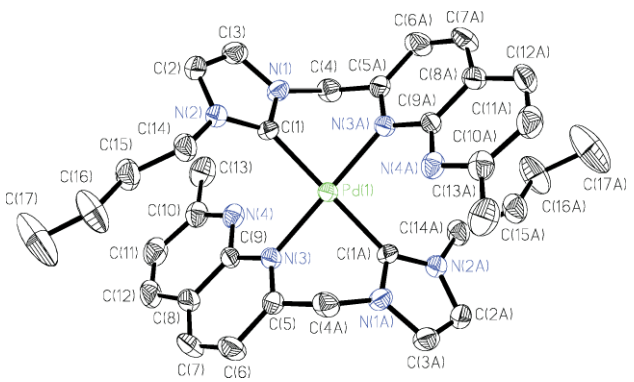


Fig. 1 ORTEP drawing of the cationic section of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Only one of the two independent molecules is shown. Selected bond distances (Å) and angles (°): Pd(1)–C(1) 2.008(7), Pd(1)–N(3) 2.037(6), C(1)–Pd(1)–C(1A) 180.0, C(1A)–Pd(1)–N(3) 84.7(3), C(1)–Pd(1)–N(3) 95.3(3), N(3)–Pd(1)–N(3A) 180.0. Symmetry code: #A $-x + 2, -y + 1, -z + 1$.

We have recently reported the structures of the naphthyridine and pyrimidine functionalized NHC palladium complexes **2**[10a] and **3**[10d] (Chart 1). These two complexes are also tetracoordinate adopting a square planar geometry, but the two ligands are *cis* arranged around the palladium center. We note that there is a methylene group between the NHC ring and the coordinated

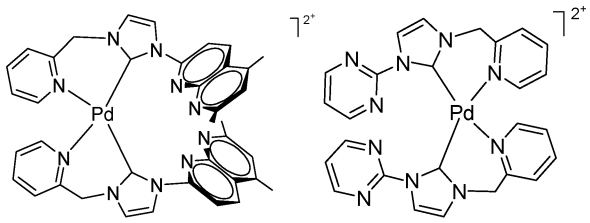
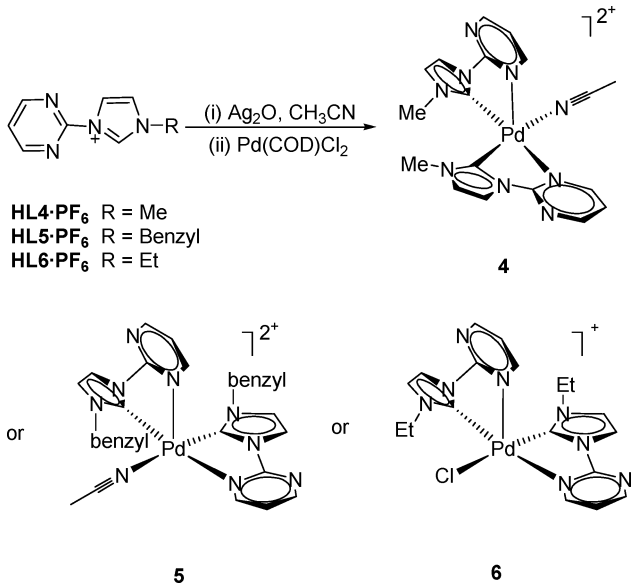


Chart 1

heteroarene group in all these three complexes. The flexibility of the ligand allows a palladium ion to be surrounded by two ligands forming six-membered rings in boat conformation, and thus usual square-planar complexes could be obtained. When the heteroarene is directly attached to the NHC ring, two rigid bidentate ligands are impossible to locate in a coordination plane due to steric repulsion. This steric effect can be clearly illustrated by the isolation and structural characterization of pentacoordinate complexes **4–6**.

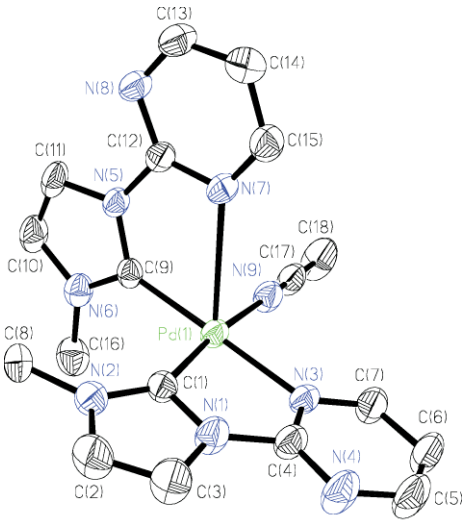
Synthesis and characterization of tetracoordinate $[Pd(L4)_2(CH_3CN)](PF_6)_2$ (4), $[Pd(L5)_2(CH_3CN)](PF_6)_2$ (5), and $[Pd(L6)_2Cl](PF_6)$ (6)

Imidazolium salts, 1-alkyl-3-pyrimidylimidazolium (R = Me, Bz, Et) were obtained by the condensation reaction of 2-chloropyrimidine and corresponding *N*-alkylimidazole. Treatment of these imidazolium salts with Ag_2O and then $Pd(COD)Cl_2$ afforded palladium(II)-NHC complexes **4**, **5**, and **6** in 53 to 76% yields (Scheme 2). Complexes **4** and **5** are pentacoordinate having the same formulation $[Pd(L)_2(CH_3CN)](PF_6)_2$. These complexes have been characterized by NMR spectroscopy and elemental analyses. The formation of the Pd-NHC complexes **4** and **5** was confirmed by the absence of the ^{1}H NMR resonance for the acidic NC*H*N protons at 10.13 and 10.4 ppm, where the resonance signals of $HL4{\cdot}PF_6$ and $HL5{\cdot}PF_6$ were found, respectively. In the ^{13}C NMR spectra of these two complexes, the resonances ascribed to the carbenic carbon atoms appear at 160.1 and 159.9 ppm,

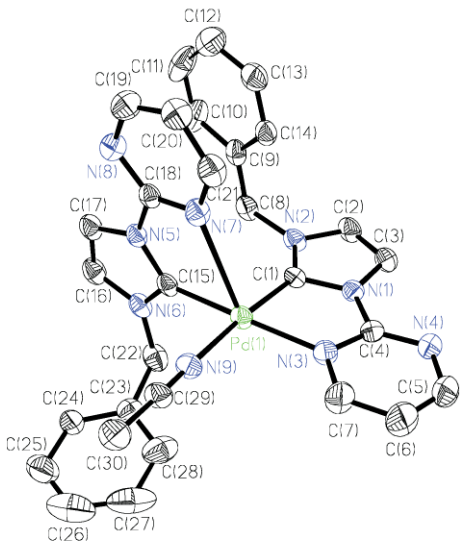


Scheme 2 Synthesis of **4–6**.

respectively, which fall in the range of 182.4–149.5 ppm for Pd-NHC complexes, depending upon the ancillary ligands.[13] Although the two pentacoordinate complexes contain two magnetically inequivalent 1-aryl-3-(2-pyrimidyl)imidazolylidene ligands in their solid state (see Fig. 2), their ^{1}H and ^{13}C NMR spectra show only one set of resonance signals assigned to the ligand. This result indicates that the two ligands are magnetically equivalent in solution due to dynamic behaviour. The ease of dissociation of the acetonitrile molecule allows facile exchange of two ligands. ESI-MS of complexes **4** and **5** in acetonitrile solution were studied. The most intense peaks at 465.17 and 617.20 amu corresponding to $[Pd(L4)_2(CH_3CN)]^+$ (calcd 467.07 amu) and $[Pd(L5)_2(CH_3CN)]^+$ (calcd 619.14 amu), respectively, are observed suggesting that these complexes are stable in solution, and the cationic cores supported by NHC ligands are maintained in the gas phase and solution.



(a)



(b)

Fig. 2 ORTEP drawing of the cationic section of **4** (a) and **5** (b). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for 4 (a): Pd(1)–C(9) 1.973(4), Pd(1)–C(1) 1.983(4), Pd(1)–N(9) 2.066(4), Pd(1)–N(3) 2.078(4), Pd(1)–N(7) 2.813(4), C(1)–Pd(1)–C(9) 95.45(17), C(1)–Pd(1)–N(9) 172.56(16), C(9)–Pd(1)–N(9) 89.55(15), C(1)–Pd(1)–N(3) 80.17(16), C(9)–Pd(1)–N(3) 174.94(15), N(9)–Pd(1)–N(3) 95.05(14), C(1)–Pd(1)–N(7) 96.46(15), C(9)–Pd(1)–N(7) 69.04(15), N(9)–Pd(1)–N(7) 90.47(14), N(3)–Pd(1)–N(7) 108.74(13). For 5 (b): Pd(1)–C(1) 1.974(4), Pd(1)–C(15) 1.996(4), Pd(1)–N(9) 2.062(4), Pd(1)–N(3) 2.075(4), Pd(1)–N(7) 2.834(4), C(1)–Pd(1)–C(15) 95.73(17), C(1)–Pd(1)–N(9) 174.66(16), C(15)–Pd(1)–N(9) 89.63(16), C(1)–Pd(1)–N(3) 79.85(16), C(15)–Pd(1)–N(3) 174.66(16), N(9)–Pd(1)–N(3) 94.79(15), C(1)–Pd(1)–N(7) 99.51(15), C(15)–Pd(1)–N(7) 68.42(16), N(9)–Pd(1)–N(7) 82.56(14), N(3)–Pd(1)–N(7) 115.08(14).

Complexes **4** and **5** have been further characterized by X-ray diffraction analyses. The molecular structures of the cationic section are depicted in Fig. 2. Both complexes are pentacoordinate with distorted square pyramidal geometry. The coordination geometry is completed by two *C,N*-chelate ligands and one acetonitrile molecule. The solvent molecules are located at the equatorial plane and arranged *trans* to NHC rings in **4** and **5**. The second carbene is *trans* to the pyrimidine group of a different ligand, and the apical position is occupied by another pyrimidine. The equatorial Pd–C (1.973–1.996 Å) and Pd–N (2.062–2.083 Å) bond distances are quite normal and comparable to the reported values in the Pd-NHC complexes,[8,13] whereas the two axial Pd–N bond distances are significantly longer (2.805(5), 2.834(4) Å) than normal Pd–N bonds. The long Pd–N bond distances in a Pd–NHC complex recently reported is 2.762(6) Å.[10d] The presence of the pentacoordinate sphere is suggested assuming the weak apical Pd–N interaction on the basis of the sum of van der Walls radii of two atoms is 3.18 Å. Pd(II) complexes tends to adopt square-planar coordination geometry. Pentacoordinate Pd(II) complexes are uncommon. So far only a few such complexes in distorted trigonal bipyramidal or square pyramidal environments supported by phenanthroline and polyphosphine ligands are known, and all of them show long apical Pd–N bonds ranging from 2.34 to 2.81 Å.[14]

Complex **6** was obtained by the carbene transfer reaction of $HL6{\cdot}PF_6$ and $Pd(COD)Cl_2$. Interestingly, complex **6** has a formulation of $[Pd(L6)_2Cl](PF_6)$ which is determined by elemental analysis and further confirmed by NMR observations. The absence of an acidic CH downfield proton resonance signal which appears at 10.19 ppm in its carbene precursor $HL6{\cdot}PF_6$ illustrates that the ligand is coordinated to palladium atom. In the ^{1}H NMR spectrum of **6**, two sets of signals assignable to L6 were observed revealing that two ligands around the palladium atom are magnetically inequivalent. ^{13}C NMR spectrum of **6** also exhibits two singlets at 161.8 and 160.7 ppm due to two NHC carbene carbon resonances *trans* to chloride and pyrimidine, respectively. The dynamically inert nature of the Pd–Cl bond inhibits the ligand exchange process as observed for **4** and **5**. The ESI-MS spectrum of **6** in acetonitrile also shows the most intense peak at 489.27 amu which can be ascribed to $[Pd(L6)_2(CH_3CN)]^+$ (calcd 489.05 amu).

The solid state structure of **6** determined by X-ray diffraction analysis is shown in Fig. 3. The palladium atom is pentacoordinate and has the same square pyramidal geometry as $[Pd(L)_2(CH_3CN)](PF_6)_2$ analogy. However, when much bulkier ligands having 2,6-diisopropylphenyl or 2,4,6-trimethylphenyl groups were employed, no NHC-Pd complex could be obtained. Probably the steric repulsion of ligands does not allow two ligands to coordinate to the same palladium ion. It should be noted that pentacoordinate palladium complexes are uncommon. To the best of our knowledge, only one example of a structurally characterized

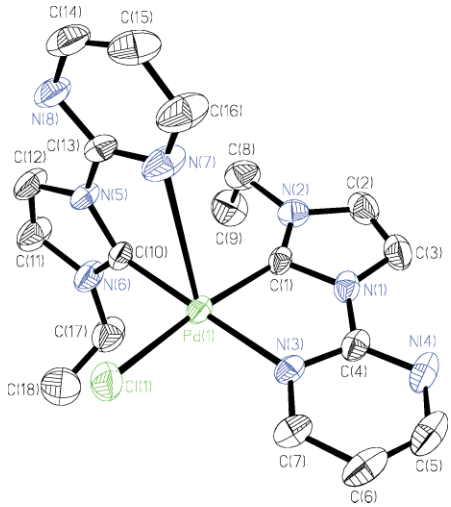
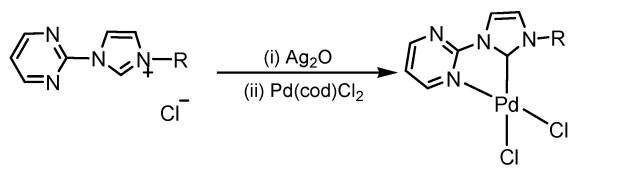


Fig. 3 ORTEP drawing of the cationic section of **6**. Thermal ellipsoids are shown at 30% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–C(10) 1.978(5), Pd(1)–C(1) 1.993(6), Pd(1)–N(3) 2.083(4), Pd(1)–Cl(1) 2.327(2), Pd(1)–N(7) 2.948(5), C(10)–Pd(1)–C(1) 98.2(2), C(10)–Pd(1)–N(3) 177.5(2), C(1)–Pd(1)–N(3) 79.86(19), C(10)–Pd(1)–Cl(1) 88.04(17), C(1)–Pd(1)–Cl(1) 173.66(15), N(3)–Pd(1)–Cl(1) 93.91(14), C(10)–Pd(1)–N(7) 66.36(19), C(1)–Pd(1)–N(7) 87.86(19), N(3)–Pd(1)–N(7) 114.89(15), Cl(1)–Pd(1)–N(7) 95.89(14).

palladium complex of NHC ligands has been recently reported by our group.[10d]

Synthesis and characterization of tetracoordinate [Pd(L5) Cl_2] (7)

Reactions of HL5·Cl with Ag_2O and subsequent Pd(cod)Cl_2 afforded **7** in 70% yield (Scheme 3). Because the chloride atom could coordinate to the central palladium atom, no matter what the R substituents were, palladium complexes with the same formulation of $PdLCl_2$ were obtained. The formulation of complex **7** was also confirmed by elemental analysis and NMR spectra. The ^{13}C resonance peak of the carbenic carbon appears at 156.9 ppm, which is consistent with those of known palladium-NHC complexes.[8,13] ESI-MS spectra of complexes **7** in acetonitrile show peaks at 378.49, 342.85, and 238.31 amu which can be ascribed to $[Pd(L7)Cl]^+$ (calcd 376.98 amu), $[Pd(L7)]^+$ (calcd 342.01 amu), and $[L7]^+$ (calcd 236.10 amu), respectively.



Scheme 3 Synthesis of **7**.

The structural determination shows that the geometry of complex **7** is square-planar. The asymmetric unit of **7** contains two independent molecules which are essentially the same, and thus only one is shown in Fig. 4. The Pd–C and Pd–Cl bond distances are normal and consistent with those of palladium(II) halide complexes containing NHC ligands. The bond distance of

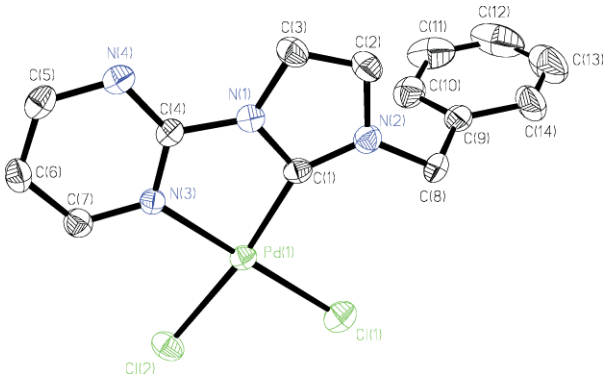
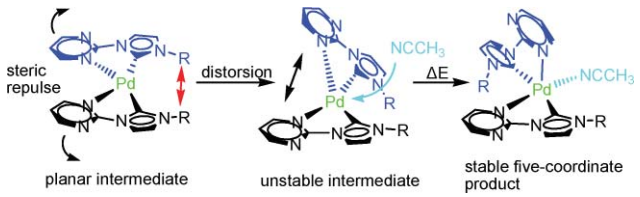


Fig. 4 ORTEP drawing of the molecule of **7** with thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Only one of the two independent molecules is shown. Selected bond distances (Å) and angles (°): Pd(1)–C(1) 1.971(6), Pd(1)–N(3) 2.056(5), Pd(1)–Cl(1) 2.287(2), Pd(1)–Cl(2) 2.353(2), C(1)–Pd(1)–N(3) 79.8(2), C(1)–Pd(1)–Cl(1) 98.60(19), N(3)–Pd(1)–Cl(1) 176.88(14), C(1)–Pd(1)–Cl(2) 172.25(19), N(3)–Pd(1)–Cl(2) 92.77(14), Cl(1)–Pd(1)–Cl(2) 88.90(7).

Pd–Cl *trans* to NHC ligand (2.353(2) Å) is longer than that of Pd–Cl *trans* to the pyrimidine group (2.287(2) Å) due to a larger *trans* effect of the carbene ligand. The benzyl ring plane is twisted out of the coordination plane, while the imidazolylidene ring and the pyrimidyl ring are essentially coplanar. The structure of **8** has been briefly described by our group recently.[11d]

Computational studies

We have recently shown that the rigidity and bulkiness of substituents play an important role in determining the structure of a nickel–carbene complex.[11f] Full molecular geometry optimizations have been carried out at the Becke3LYP (B3LYP) level of density functional theory (DFT) for the palladium complexes. We optimized their conformation on the assumption that the coordination sphere of these $[Pd(L)_2]^{2+}$ intermediates is square planar. We found that when the chelates form a rigid five-membered palladacycle, the steric repulsion between the substituent groups will force the coordination geometry distorted (Scheme 4). Actually the geometrically optimized structure is a distorted tetrahedron (Fig. 5(b)) in the case of pyrimidylimidazolylidene. However, the geometrically optimized structures of those complexes containing flexible six-membered palladacycle are in the case of (pyridylmethyl)imidazolylidene still square planar (compound **3**, Fig. 5(a)). The tetrahedral conformation of the 16e configuration is not energetically preferred and the space brought about due to steric repulsion would allow an additional donor, yielding more stable palladium complexes of higher coordination numbers (Scheme 4).



Scheme 4 Formation of pentacoordinate complexes.

Table 1 ΔE values (kcal mol^{-1}) in $[PdL_2S]^{2+}$ (S = CH_3CN)

$$[Pd(L)_2]^{2+} + S \xrightarrow{\Delta E} [Pd(L)_2S]^{2+}$$

Complexes	ΔE
$[Pd(L4)_2(CH_3CN)]^{2+}$	−20.5
$[Pd(L5)_2(CH_3CN)]^{2+}$	−19.0

The reaction energies for the formation of more stable $[Pd(L)_2S]^{2+}$ (ΔE) complexes from tetrahedron $[Pd(L)_2]^{2+}$ intermediates with a solvent molecule was calculated, and the results are given in Table 1. The theoretically calculated reaction energies ΔE are all negative, illustrating that the pentacoordinate palladium complexes are more stable than the distorted tetrahedral complexes.

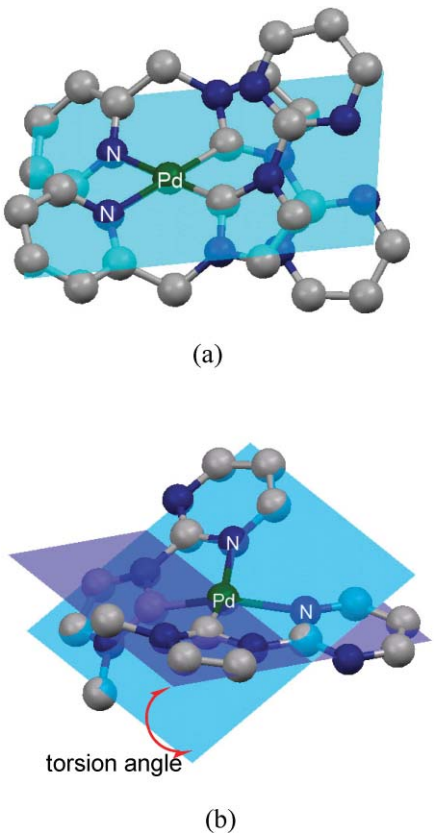


Fig. 5 Optimized structures of **3** (a) and $[Pd(L4)_2]^{2+}$ (b).

Catalytic studies

The catalytic activities of the tetra- and pentacoordinate palladium complexes were studied for C–C formation reactions. Suzuki coupling reactions have been the most versatile and important method for the synthesis of unsymmetrically substituted biaryl compounds.[15] The coupling reaction of 4-tolyl bromide with phenylboronic acid in a mixed solvent DMF/H_2O (10:1) with 1 mol% catalyst loading using Cs_2CO_3 as base at 80 °C was studied.[16] Complexes **1–8** are all active, and Fig. 6 demonstrates their differences under the same reaction conditions. The results show that the order of catalytic activity of these Pd–NHC

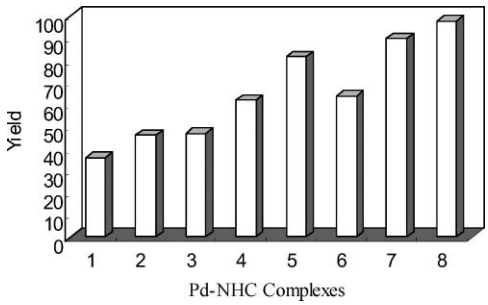
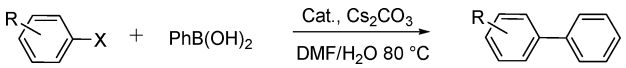


Fig. 6 Comparison of the catalytic activities of **1–8** for Suzuki reaction of 4-tolyl bromide with phenylboronic acid. Yields are determined by gas chromatography after 1 h.

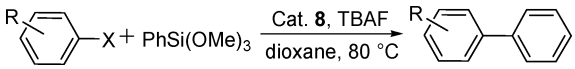
complexes based on the yields after 1 h follows: tetracoordinate monocarbene > pentacoordinate dicarbene > tetracoordinate dicarbene. The most active complexes **3**, **5**, and **8** are selected as the representatives of tetracoordinate dicarbene, pentacoordinate dicarbene, and tetracoordinate monocarbene palladium complexes, respectively. The Suzuki coupling reactions of a wide range of aryl bromides and chlorides with phenylboronic acid were further studied to compare the activities of complexes **3**, **5**, and **8** in detail and the results are listed in Table 2.

Table 2 Suzuki coupling reactions catalyzed by complexes **3**, **5**, and **8**[a]



Entry	R	X	Cat.	Time (h)	GC/Isolated Yield (%)
1	4-C(O)CH_3	Br	**3**	6	100/93
2	4-C(O)CH_3	Br	**5**	2	100/95
3	4-C(O)CH_3	Br	**8**	0.5	100/92
4	H	Br	**3**	6	93/87
5	H	Br	**5**	2	100/91
6	H	Br	**8**	0.5	100/97
7	4-Me	Br	**3**	12	71/63
8	4-Me	Br	**5**	3	99/92
9	4-Me	Br	**8**	0.5	99/95
10	4-MeO	Br	**3**	12	80/78
11	4-MeO	Br	**5**	6	98/90
12	4-MeO	Br	**8**	0.5	99/93
13	2-Me	Br	**3**	12	65/58
14	2-Me	Br	**5**	3	99/91
15	2-Me	Br	**8**	1	98/94
16	1-bromo naphthalene	Br	**3**	12	62/51
17	1-bromo naphthalene	Br	**5**	3	100/97
18	1-bromo naphthalene	Br	**8**	1	98/92
19	4-C(O)CH_3	Cl	**3**	12	64/60
20	4-C(O)CH_3	Cl	**5**	6	93/90
21	4-C(O)CH_3	Cl	**8**	2	95/90
22	4-CN	Cl	**3**	12	11
23	4-CN	Cl	**5**	6	95/91
24	4-CN	Cl	**8**	2	92/89
25	H	Cl	**8**	12	31
26[b]	H	Cl	**8**	6	87/82
27[b,c]	4-Me	Cl	**8**	6	53
28[b]	4-MeO	Cl	**8**	12	15

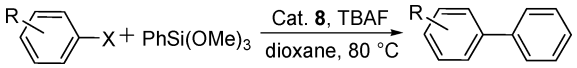
[a] Reaction conditions: aryl halide 1.0 mmol, phenylboronic acid 1.5 mmol, Pd 1 mol%, Cs_2CO_3 1.2 mmol, DMF/H_2O (3/0.3 mL), 80 °C. [b] 120 °C. [c] 4-Tolylboronic acid was used instead of phenylboronic acid.



All three catalysts are effective towards aryl bromides bearing either electron-withdrawing or electron-donating substituents, and activated aryl chlorides. The data clearly show that monocarbene complex **8** is more active than **3** and **5**, and the Suzuki coupling of aryl bromides and activated chlorides with phenylboronic acids by using 1 mol% of **8** could be completed within 0.5–2 h to give nearly quantitative yields (entries 3, 6, 9, 12, 21, and 24). The coupling of sterically hindered substrates, 2-bromotoluene and 1-bromonaphthalene, also gave excellent yields (entries 15 and 18). The dicarbene pentacoordinate complex **5** shows intermediate catalytic activities, and the yields of the target product are also excellent when the reaction time was prolonged to 2–6 h. The dicarbene tetracoordinate complex **3** is the least efficient. The coupling yields are relatively lower than in the cases of **5** and **8** even the reaction time was extended to 6–12 h. Complex **5** also shows good activities for electron deficient aryl chlorides such as 4-acetylphenyl chloride and 4-chlorobenzonitrile (entries 20 and 23). However, both complexes **3** and **5** are totally inefficient for the coupling of unactivated and deactivated aryl chlorides. When 1 mol% of **8** was employed, the coupling reaction of chlorobenzene with 4-tolylboronic acid could proceed affording only a 31% yield of 4-methylbiphenyl at 80 °C (entry 25). However, the yield could be improved to 87% when the reaction temperature was elevated to 120 °C (entry 26). The coupling of deactivated substrate, 2-chlorotoluene also gave a moderate yield of 53% (entry 27). Activation of C–Cl bond is still a challenging subject in organic chemistry. Complex **8** exhibits good catalytic activities towards a range of aryl chlorides. Taking account of its ease of preparation and robustness towards air and moisture, complex **8** would be expected to be practically applicable.

Recently, organosilanes have become a good choice for C–C cross-coupling reaction because they are environmentally benign and stable to various reaction conditions.[17] The so-called Hiyama coupling reactions have been widely applied for the preparation of biphenyl derivatives. However, Hiyama reactions promoted by metal–NHC complexes are relatively scarce.[18] The coupling reactions of aryl halides with trimethoxy(phenyl)silane were also tested by using complexes **3**, **5**, and **8** as catalysts in dioxane at 80 °C in the presence of TBAF which is a well known promoter for the Hiyama coupling reaction in organic solvents.[19] The results are summarized in Table 3. To our surprise, complexes **3** and **5** are totally inefficient even for the coupling reaction of activated 4-bromoacetophenone and trimethoxy(phenyl)silane. However, complex **8** is an excellent catalyst for Hiyama coupling of aryl bromides and activated aryl chlorides. These results again illustrate that the monocarbene complex is much more active than the dicarbene complexes for C–C formation reactions. When 1 mol% of **8** was employed, both electron-rich and electron-deficient aryl bromide substrates gave excellent yields of the corresponding biphenyl products within 6 h (entries 1–4). The complex also applies to steric hindered substrate such as 2-bromotoluene, but the yield of the corresponding product is a bit lower (entry 5). The coupling reaction of activated 4-chloroacetophenone and 4-chlorobenzonitrile also proceeded smoothly to give 95% and 83% yields (entries 6 and 7), respectively. For the less active chlorobenzene the yield dropped to 51%, and the reaction time had to be prolonged to 12 h (entry 8). Unfortunately, when deactivated substrates 4-chlorotoluene and 4-chloroanisole were involved, only trace amounts of products were observed.

Table 3 Hiyama reactions catalyzed by complex **8**[a]



Entry	R	X	Time (h)	GC/Isolated Yield (%)
1	4-C(O)CH_3	Br	2	100/95
2	H	Br	6	98/93
3	4-Me	Br	6	71/66
4	4-MeO	Br	6	88/81
5	2-Me	Br	6	68/62
6	4-C(O)CH_3	Cl	6	95/91
7	4-CN	Cl	6	83/80
8	H	Cl	12	51/47
9	4-Me	Cl	12	Trace
10	4-MeO	Cl	12	Trace

[a] Reaction conditions: aryl halide 1.0 mmol, trimethoxy(phenyl)silane 2.0 mmol, cat. 1 mol%, Cs_2CO_3 2.0 mmol, TBAF 2.0 mmol, dioxane 3 mL, 80 °C.

Conclusion

In summary, we have successfully prepared a series of tetra- and penta-coordinate Pd-NHC complexes bearing mono- and dicarbene ligands and their structures have been definitely determined by X-ray crystallography. The catalytic behaviour of tetracoordinate moncarbene, tetracoordinate dicarbene, and pentacoordinate dicarbene palladium complexes in Suzuki and Hiyama coupling reactions were comparatively studied. The tetracoordinate monocarbene complex was found to be the most efficient catalyst precursor for both coupling reactions of aryl bromides and chlorides. Dicarbene palladium complexes are much less active than the monocarbene palladium complex. It seems that the additional donor blocks one of the coordination sites at the metal inhibiting approach of substrate to metal center, thus reducing its catalytic activity.

Experimental

General procedures

All the chemicals were obtained from commercial suppliers and used without further purification. *N*-picolylimidazole,[20] and 2-(bromomethyl)-7-methyl-1,8-naphthyridine[21] were prepared according to the known procedures. The C, H, and N elemental analyses were carried out with a Vario EL III elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at $\delta = 0$ ppm and coupling constants (J) are expressed in Hz.

1-Butyl-3-((7-methyl-1,8-naphthyridin-2-yl)methyl)imidazolium hexafluorophosphate (HL1·PF_6)

2-(bromomethyl)-7-methyl-1,8-naphthyridine (2.36 g, 10 mmol) was added to a solution of *N*-*n*-butylimidazole (2.48 g, 20 mmol) in 100 mL of toluene. The mixture was refluxed for 48 h. The resulting

precipitate was isolated and washed with toluene (2 × 5 mL) and Et_2O (2 × 5 mL), which was then dissolved in water (20 mL). To the aqueous solution was added an excess of NH_4PF_6 (3.3 g, 20 mmol) resulting in an immediate light yellow precipitation. The yellow solid was collected and washed with water, Et_2O and dried under vacuum. Yield: 3.75 g (89%), light yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.36 (s, NC*H*N, 1H), 8.51, 8.37 (both d, $J = 8.8$, naphthyridine, each 1H), 7.88 (m, naphthyridine, 2H), 7.67, 7.55 (both d, $J = 8.0$, imidazolium, each 1H), 5.85 (s, CH_2, 2H), 4.29 (t, $J = 7.6$, CH_2, 2H), 2.69 (s, CH_3, 3H), 1.84, 1.33 (both m, CH_2, each 2H), 0.94 (t, $J = 7.6$, CH_3, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.5, 157.5, 154.9, 139.1, 137.7, 137.6, 124.1, 123.8, 122.7, 120.4, 120.3, 53.7, 49.1, 31.8, 25.4, 19.2, 13.7. Anal. Calcd (%) for $C_{17}H_{21}N_4F_6P$: C, 47.89; H, 4.96; N, 13.14. Found: C, 48.02; H, 4.98; N, 13.39.

[Pd(1-butyl-3-((7-methyl-1,8-naphthyridin-2-yl)methyl)imidazolylidene)$_2$](PF$_6$)$_2$ (1)

To a solution of HL1·PF_6 (213 mg, 0.5 mmol) in CH_3CN (10 mL) was added Ag_2O (64 mg, 0.275 mmol), and the mixture was stirred at room temperature for 5 h. To the filtrate was added Pd(cod)Cl_2 (73 mg, 0.25 mmol). After stirring overnight, the mixture was filtered through Celite®, and the filtrate was then concentrated to *ca.* 2 mL. Addition of Et_2O (20 mL) to the filtrate afforded a white precipitate immediately. The precipitate was collected and washed with Et_2O (20 mL) to afford a white powder. Yield: 164 mg (73%). X-ray quality crystals were obtained by slow diffusion of Et_2O into the CH_3CN solution of the complex. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.99, 8.60, 8.28, 7.75 (all d, $J = 8.0$, naphthyridine, each 2H), 7.60, 7.15 (both d, $J = 2.0$, imidazolylidene, each 2H), 6.54, 6.28 (both d, $J = 15.2$, CH_2, each 2H), 3.00 (t, $J = 8.0$, CH_2, 4H), 2.54 (s, CH_3, 6H), 1.18, 0.64, 0.45, 0.10 (all m, CH_2, each 2H), 0.46 (m, CH_3, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.1, 165.9, 161.4, 152.8, 143.7, 138.9, 126.0, 124.3, 122.7, 122.1, 121.5, 56.0, 48.7, 31.5, 25.6, 19.4, 13.6. Anal. Calcd (%) for $C_{34}H_{40}N_8F_{12}P_2Pd·H_2O$: C, 41.88; H, 4.34; N, 11.49. Found: C, 41.61; H, 4.52; N, 11.41.

3-Methyl-1-(pyrimidin-2-yl)imidazolium hexafluorophosphate (HL4·PF$_6$)

The compound was prepared following the procedure described for HL1·(PF_6) by starting from 2-chloropyrimidine (1.14 g, 10 mmol) and *N*-methylimidazole (1.64 g, 20 mmol). Yield: 2.75 g (90%), white powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.13 (s, NC*H*N, 1H), 9.04 (d, $J = 4.8$, pyrimidine, 2H), 8.46, 7.94 (both s, imidazolium, each 1H), 7.76 (t, $J = 4.8$, pyrimidine, 1H), 4.01 (s, CH_3, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 152.5, 136.8, 125.4, 122.7, 119.2, 36.8. Anal. Calcd (%) for $C_8H_9N_4F_6P$: C, 31.39; H, 2.96; N, 18.30. Found: C, 31.31; H, 3.04; N, 18.11.

[Pd(3-methyl-1-(pyrimidin-2-yl)imidazolylidene)$_2$(CH$_3$CN)](PF$_6$)$_2$ (4)

The compound was prepared according to the same procedure as for **1** starting from HL4·PF_6 (153 mg, 0.5 mmol), Ag_2O (64 mg, 0.275mmol), and Pd(cod)Cl_2 (73 mg, 0.25 mmol). Yield: 142 mg (76%), white powder. ^{1}H NMR (400 MHz, DMSO-d_6): 9.05 (d, $J = 4.8$, pyrimidine, 4H), 8.36 (d, $J = 2.0$, imidazolylidene, 2H), 7.79 (m, pyrimidine and imidazolylidene, 4H), 3.57 (s, CH_3, 6H), 2.07 (s, 2C*H*$_3$CN, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.1, 155.4, 155.3, 126.7, 121.6, 120.2, 118.5, 38.2, 1.5. Anal. Calcd for $C_{18}H_{19}N_9F_{12}P_2Pd·CH_3CN·H_2O$: C, 29.41; H, 2.96; N, 17.15. Found: C, 29.02; H, 2.99; N, 17.32.

3-Benzyl-1-(pyrimidin-2-yl)imidazolium hexafluorophosphate (HL5·PF$_6$)

The compound was prepared according to the same procedure as for HL1·(PF_6) starting from *N*-benzylimidazole (1.58 g, 10 mmol) and 2-chloropyrimidine (2.28 g, 20 mmol). Yield: 3.45 g (90%), white powder. ^{1}H NMR (400 MHz, DMSO-d_6): 10.4 (s, NC*H*N, 1H), 9.06 (d, $J = 4.8$, pyrimidine, 2H), 8.49, 8.02 (both s, imidazolium, each 1H), 7.76 (t, $J = 4.8$, pyrimidine, 1H), 7.54 (d, $J = 7.2$, phenyl, 1H), 7.43 (m, pyrimidine and phenyl, 3H), 5.59 (s, CH_2, 2H), ^{13}C NMR (100 MHz, DMSO-d_6): 160.4, 152.6, 136.6, 134.8, 129.5, 129.4, 128.9, 124.1, 122.9, 120.1, 53.1. Anal. Calcd for $C_{14}H_{13}N_4F_6P$: C, 43.99; H, 3.43; N, 14.66. Found: C, 44.21; H, 3.32; N, 14.93.

[Pd(3-benzyl-1-(pyrimidin-2-yl)imidazolylidene)$_2$(CH$_3$CN)](PF$_6$)$_2$ (5)

The compound was prepared according to the same procedure as for **1** starting from HL5·PF_6 (191 mg, 0.5 mmol), Ag_2O (64 mg, 0.275mmol) and Pd(cod)Cl_2 (73 mg, 0.25 mmol). Yield: 154 mg (68%), white powders. ^{1}H NMR (400 MHz, DMSO-d_6): 8.97 (d, $J = 5.6$, pyrimidine, 4H), 8.33, 7.86 (both d, $J = 1.6$, imidazolylidene, each 2H), 7.75 (t, $J = 5.2$, pyrimidine, 2H), 7.18, 7.01 (both m, benzyl, 10H), 5.11, 4.73 (both d, $J = 14.8$, CH_2, each 2H), 2.05 (s, 2C*H*$_3$CN, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 159.3, 155.3, 154.5, 134.5, 128.5, 128.1, 126.7, 125.5, 121.1, 120.3, 118.0, 53.8, 1.04. Anal. Calcd for $C_{30}H_{27}N_9F_{12}P_2Pd·CH_3CN·H_2O$: C, 39.66; H, 3.33; N, 14.45. Found: C, 39.28; H, 3.41; N, 14.42.

3-Ethyl-1-(pyrimidin-2-yl)imidazolium hexafluorophosphate (HL6·PF$_6$)

This compound was prepared following the procedure described for HL1·PF_6 by starting from 2-chloropyrimidine (1.14 g, 10 mmol) and *N*-ethylimidazole (1.92 g, 20 mmol). Yield: 2.78 g (87%), white powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.19 (s, NC*H*N, 1H), 9.06 (d, $J = 4.8$, pyrimidine, 2H), 8.49, 8.05 (both s, imidazolium, each 1H), 7.77 (t, $J = 4.8$, pyrimidine, 1H), 4.37 (m, CH_2, 2H), 1.52 (t, $J = 7.6$, CH_3, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 152.6, 135.3, 122.8, 122.1, 119.9, 53.9, 22.5. Anal. Calcd (%) for $C_9H_{11}N_4F_6P$: C, 33.76; H, 3.46; N, 17.50. Found: C, 33.91; H, 3.55; N, 17.82.

[Pd(3-ethyl-1-(pyrimidin-2-yl)-1-imidazolylidene)$_2$Cl](PF$_6$) (6)

The compound was prepared according to the same procedure as for **1** starting from HL6·(PF_6) (160 mg, 0.5 mmol), Ag_2O (64 mg, 0.275 mmol), and Pd(cod)Cl_2 (73 mg, 0.25 mmol). Yield: 84 mg (53%), white powder. ^{1}H NMR (400 MHz, CD_3CN): 9.35, 9.03 (m, pyrimidine, each 1H), 8.79 (d, $J = 4.8$, pyrimidine, 2H), 8.31, 7.94, 7.59, 7.27 (all d, $J = 2.0$, imidazolylidene, each 1H), 7.68, 7.49 (both t, $J = 4.8$, pyrimidine, each 1H), 4.62, 4.51, 3.39, 3.14 (all m, CH_2, each 1H), 1.57, 0.99 (both t, $J = 7.6$, CH_3, each 3H). ^{13}C NMR (100 MHz, CD_3CN): δ 161.8, 160.7, 159.1, 157.6,

156.9, 154.9, 123.4, 122.7, 121.7, 121.1, 120.4, 117.6, 47.9, 45.6, 14.8, 14.7. Anal. Calcd (%) for $C_{18}H_{20}N_8F_6PClPd{\cdot}2H_2O$: C, 32.21; H, 3.60; N, 16.69. Found: C, 32.30; H, 3.81; N, 17.03.

3-Benzyl-1-(pyrimidin-2-yl)-1*H*-imidazol-3-ium chloride (HL5·Cl)

2-Chloropyrimidine (2.28 g, 20 mmol) was added to a solution of *N*-benzylimidazole (1.58 g, 10 mmol) in 30 mL of toluene. The mixture was refluxed for 24 h. The resulting precipitate was isolated and washed with toluene (2 × 5 mL) and Et_2O (2 × 5 mL). Yield: 2.44 g (90%), light yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.58 (s, NC*H*N, 1H), 9.06 (d, $J = 5.2$, pyrimidine, 2H), 8.46, 8.16 (both s, imidazolium, each 1H), 7.78 (t, $J = 4.8$, pyrimidine, 1H), 7.60 (d, $J = 7.6$, benzyl, 2H), 7.60 (d, $J = 7.6$, benzyl, 2H), 7.49 (m, benzyl, 3H), 5.70 (s, CH_2, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 152.6, 136.5, 135.0, 129.3, 129.2, 129.0, 124.2, 122.8, 119.9, 52.7. Anal. Calcd (%) for $C_{14}H_{13}N_4Cl{\cdot}H_2O$: C, 57.83; H, 5.20; N, 19.27. Found: C, 57.61; H, 5.32; N, 19.30.

Pd(3-benzyl-1-(pyrimidin-2-yl)-1-imidazolylidene)Cl_2 (7)

A solution of HL7·Cl (136 mg, 0.5 mmol) in CH_3CN (10 ml) was treated with Ag_2O (64 mg, 0.275 mmol). The mixture was stirred at room temperature for 2 h with exclusion of light. Then the mixture was filtered and Pd(cod)Cl_2 (145 mg, 0.5 mmol) was added to the filtrate. The mixture was allowed to react for 2 h at room temperature. After filtration through a plug of Celite®, the solvent was removed *in vacuo* and the residue was washed with diethyl ether. Complex **7** was obtained as a yellow powder. Yield: 144 mg, 70%.^{1}H NMR (DMSO-d_6): 9.44, 9.07 (both br, pyrimidine, each 1H), 8.12, 7.63 (both d, $J = 2.0$, imidazolylidene, each 1H), 7.73 (t, $J = 4.8$, pyrimidine, 1H), 7.50 (d, $J = 8.0$, benzyl, 2H), 7.37 (m, benzyl, 3H), 6.02 (s, CH_2, 2H). ^{13}C NMR (DMSO-d_6): 156.9, 152.0, 136.7, 129.0, 128.5, 128.3, 125.1, 120.5, 118.2, 52.1. Anal. Calcd for $C_{14}H_{12}Cl_2N_4Pd{\cdot}H_2O$: C, 38.96; H, 3.27; N, 12.98. Found: C, 38.87; H, 3.35; N, 13.41. Crystals suitable for X-ray diffraction were grown by slow diffusion of Et_2O into its CH_3CN solution.

General procedure for Suzuki reactions with 8

4-Bromotoluene (170 mg, 1.0 mmol), phenylboronic acid (184 mg, 1.5 mmol), **8** (4 mg, 1 mmol%), Cs_2CO_3 (400 mg, 1.2 mmol), and DMF/H_2O (3/0.3 mL) were subsequently added to a Schlenk tube. The solution was heated to 80 °C under an atmosphere of N_2 for 0.5 h. The mixture was then allowed to cool to room temperature and added to 20 mL of water. The product was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to give the desired product.

General procedure for Hiyama reactions with 8

4-Bromoacetophenone (199 mg, 1.0 mmol), trimethoxy(phenyl)-silane (396 mg, 2.0 mmol), **8** (4 mg, 1 mmol%), Cs_2CO_3 2.0 mmol, TBAF (520 mg, 2.0 mmol), dioxane 3 mL were subsequently added to a Schlenk tube. The solution was heated to 80 °C under an atmosphere of N_2 for 2 h. The mixture was then allowed to cool to room temperature and added to 20 mL of water. The product was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to give the desired product.

X-Ray structural determination

Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart-*CCD* area-detector diffractometer with a Mo Kα radiation ($\lambda = 0.71073$ Å) by using an ω-2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the *SMART* and *SAINT* software.[22] The structures were solved

Table 4 Summary of X-ray crystallographic data for complexes **1** and **4–7**

	1	**4**	**5**	**6**	**7**
Formula	$C_{34}H_{40}F_{12}N_8P_2Pd$	$C_{20}H_{22}F_{12}N_{10}P_2Pd$	$C_{32}H_{30}F_{12}N_{10}P_2Pd$	$C_{18}H_{24}ClF_6N_8O_2PPd$	$C_{14}H_{12}Cl_2N_4Pd$
Fw	957.08	798.82	951.00	671.27	413.58
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	*P*-1	*P*-1	$P2_1/c$	$P2_1/c$
a, Å	17.283(2)	11.0400(10)	13.2820(13)	12.0874(14)	5.1207(14)
b, Å	11.3693(13)	12.9230(13)	13.3260(13)	7.4205(11)	24.454(3)
c, Å	22.236(3)	13.5160(16)	13.4030(15)	29.316(3)	23.766(3)
α, deg	90	111.148(2)	67.8290(10)	90	90
β, deg	109.000(2)	101.0820(10)	65.292(2)	90.932(2)	93.217(2)
γ, deg	90	107.4680(10)	72.3640(10)	90	90
V, Å^3	4131.2(8)	1614.7(3)	1965.8(3)	2629.2(6)	2971.3(9)
Z	4	2	2	4	8
D_{calc}, Mg m^{-3}	1.539	1.643	1.607	1.696	1.849
μ, mm^{-1}	0.617	0.773	0.649	0.943	1.605
F(000)	1936	792	952	1344	1632
θ range	1.93–25.01	1.72–25.01	1.71–25.01	1.39–25.01	1.67–25.01
Reflections collected	20274	8405	10131	12718	15239
Reflections Unique, R_{int}	7269, 0.0532	5582, 0.0179	6820, 0.0202	4614, 0.0335	5218, 0.0458
Goodness-of-fit on F^2	1.111	1.025	1.059	1.101	1.138
R, [$I > 2\sigma I$]	0.0572, 0.1234	0.0459, 0.1050	0.0500, 0.1297	0.0504, 0.1037	0.0509, 0.0916
R, (all data)	0.1276, 0.1700	0.0662, 0.1171	0.0658, 0.1486	0.0692, 0.1120	0.0677, 0.0971
Largest diff. Peak and hole, e Å^{-3}	0.751, –0.517	0.744, –0.314	0.869, –0.576	0.583, –0.749	0.702, –0.995

by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the *SHELXTXL* package.[23] Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C–H distances of 0.93–0.97 Å and $U_{iso}(H) = -1.2$–$1.5U_{eq}(C)$. For complex **1**, several restraints have been used to model the butyl groups, and the carbon atoms of butyl groups and fluorine atoms of the anions have been isotropically refined with occupancies of 1.0. For complex **4**, disordered acetonitrile molecules in its lattice could not be modelled successfully and were removed from the reflection data with SQUEEZE[24] with a solvent accessible void volume 305.2 Å^3. Further details of the structural analyses are summarized in Table 4.

Computational details

Full molecular geometry optimizations have been carried out at the Becke3LYP (B3LYP) level of density functional theory (DFT).[25] Frequency calculations at the same level of theory have also been performed. The effective core potentials (ECPs) of Hay and Wadt with double-f valence basis sets (LanL2DZ)[26] were used to describe Pd. Polarization functions were added for C ($\zeta(d) = 0.8$), H ($\zeta(d) = 0.11$).[27] The 6-31G basis set was used for all the atoms except Pd.[28] All the calculations were performed with the GAUSSIAN 98 software package.[29] In all the energy profiles, the calculated electronic energies were used to describe the energetic aspects. The computational method and the basis sets used in this work have been widely recognized in theoretically investigating structures, bonding and reaction mechanisms of organometallic systems.

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