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Dinuclear *N*-heterocyclic carbene palladium(II) complexes as efficient catalysts for the Buchwald–Hartwig amination

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ABSTRACT

A series of dinuclear *N*-heterocyclic carbene (NHC) palladium complexes $[PdCl_2(NHC)]_2(\mu\text{-L})$ (**1**–**6**, L = diphosphine ligands) has been synthesized and fully characterized by ^1H NMR, ^{13}C NMR and ^{31}P NMR spectroscopies, elemental analysis, IR spectroscopy, and X-ray crystal structural study. The solid-state structures of **1**–**6** show dinuclear frameworks with two palladium(II) centres were held together by bridging diphosphine ligands. Each palladium centre was coordinated by an *N*-heterocyclic carbene ligand, a phosphorus atom and two chloro ions in a *trans*-arrangement. Further explorations of the catalytic potential of the dinuclear carbene palladium complexes as catalysts for Pd-mediated trans-formations have been examined under microwave irradiation conditions and the title complexes (**1**–**6**) displayed good catalytic activities in Buchwald–Hartwig aminations of aryl chlorides.

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Introduction

Since the first stable *N*-heterocyclic carbene (NHC) was isolated in 1991 by Arduengo, NHCs have been found to be powerful ligands for transition-metal-catalysed reactions [1]. In particular, *N*-heterocyclic carbene palladium(II) complexes have been widely investigated as potential catalysts for the C–C cross-coupling reactions, such as Suzuki–Miyaura, Mizoroki–Heck, Hiyama, and Kumada reactions as well as olefin polymerizations, Buchwald–Hartwig aminations, and the α-arylation of ketones [2]. Owing to their wide applications in C–C and C–N bond formations in organic synthesis, the chemistry of NHC–palladium complexes has become an area of great interest and has been extensively studied [3]. However, being strong σ-donors and generally weak π-acceptors, NHCs in general form strong bonds with the palladium centres and probably render the substrate activation at the metal centre during catalysis [4]. Since carbenes form strong M–C bonds, the presence of other donors that form weaker bonds with metal centres can make these carbene ligands potentially hemilabile. Toward this, various heteroatom donors (N, O, P, and S) have been involved in the coordination with the NHC–Pd complexes [5]. The geometry, stability, and catalytic property of the complexes can be greatly affected by the steric and electronic properties of the ancillary ligands. For example, Organ reported the Pd–PEPPSI complexes, which combined use of an σ-donating *N*-heterocyclic carbene (NHC) and a "throw-away" pyridyl ligand to promote C–C bond formation [6]. Recently, a similar family of complexes reported by Navarro, in which the pyridine fragment was substituted by triethylamine and diethylamine, showed higher activities for C–C bond and C–N bond formations [7]. Furthermore, Cazin described the application of a series of *N*-heterocyclic carbene (NHC)/PR_3 palladium(II) complexes as catalysts for Suzuki–Miyaura reactions [8]. Hahn reported a series of novel macrocyclic and multinuclear carbene complexes which were modified by the phosphine ligands [9]. The use of phosphine donors to support and activate the NHC–palladium complexes for catalysis is an emerging idea and has been extensively investigated. Mixed mononuclear NHC–phosphine complexes of palladium(II) derived from imidazole [10], imidazoline, [11] benzimidazole [12], benzothiazole [13], and even pyrazole [14] have been reported to be active catalyst precursors for C–C and C–N coupling reactions. In comprehensive reviews on Pd catalysed C–C and C–N coupling reactions they have been mentioned that, regardless of the catalyst used, a Pd(0)–Pd(II) cycle is involved in the coupling [15]. And the presence of both NHC ligands and phosphane ligands were found to be essential, which could leading to the formation of the [(NHC)–Pd(0)] or [(PR_3)-Pd(0)] active species that starts the catalytic cycle [16]. Furthermore, a synergic effect between these two families of ligands has been reported. Cazin and co-workers have

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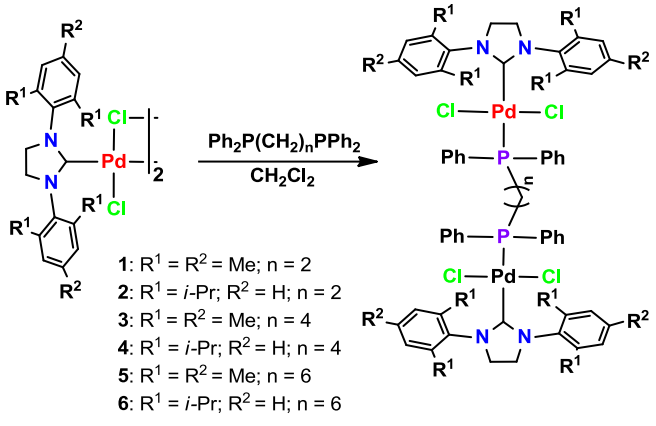
reported a family of mixed phosphite/*N*-Heterocyclic carbene complexes ((NHC)$PdCl_2P(OR)_3$). NMR studies to determine that the $P(OR)_3$ ligand, as a stronger σ-donor, remain attached to the [(NHC)–Pd(0)] after the reduction to Pd(0), which could stabilized the Pd(0) active species [8b]. In contrast to the widely study of mononuclear NHC–palladium(II) complexes, dinuclear NHC–palladium(II) complexes based on bridging ligands have been less well studied [17]. The design and synthesis of dinuclear *N*-heterocyclic carbene complexes are of considerable interest because the adjacent metals could function in a synergic manner in their interactions with substrate molecules [18]. In addition, the electronic and steric properties can be modified by the bidentate bridging ligand, which are important for their utilization as ligands in catalytic reactions [19]. Following our interest on the construction of functionalized complexes that can enter into an array of di- and multinuclear systems, herein, the cleavage of the saturated heterocyclic imidazolidin-2-ylidene dimeric compounds [Pd(μ-Cl)(Cl)(NHC)]$_2$ with the bridging diphosphine ligands to form the mixed phosphine-imidazolidin-2-ylidene palladium complexes were investigated (Scheme 1). Furthermore, the catalytic applications of the obtained complexes in Buchwald–Hartwig amination of a range of aryl chlorides with amines under microwave irradiation were studied.

Results and discussion

Synthesis

Following the synthetic route reported previously, the chloro-bridged dimeric carbene palladium complexes, [Pd(μ-Cl)(Cl)(SIMes)]$_2$ and [Pd(μ-Cl)(Cl)(SIPr)]$_2$ (SIMes = *N,N'*-bis-(2,4,6-trimethylphenyl)imidazolidin-2-ylidene and SIPr = *N,N'*-bis-(2,6-diisopropylphenyl)imidazolidin-2-ylidene) can be facilely synthesized [20], which are utilized in various reactions as reactants or catalysts. Dinuclear NHC–phosphine palladium complexes, [$PdCl_2$(SIMes)]$_2$(μ-dppe) (**1**), [$PdCl_2$(SIPr)]$_2$(μ-dppe) (**2**), [$PdCl_2$(SIMes)]$_2$(μ-dppb) (**3**), [$PdCl_2$(SIPr)]$_2$(μ-dppb) (**4**), [$PdCl_2$(SIMes)]$_2$(μ-dpph) (**5**), and [$PdCl_2$(SIPr)]$_2$(μ-dpph) (**6**) [dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,4-bis(diphenylphosphino) butane and dpph = 1,6-bis(diphenylphosphino)hexane] were synthesized by the bridge–cleavage reactions of the dimeric compounds, [Pd(μ-Cl)(Cl)(SIMes)]$_2$ or [Pd(μ-Cl)(Cl)(SIPr)]$_2$ with the bridging diphosphine ligands in CH_2Cl_2 at room temperature. The syntheses are straightforward, and all complexes have been isolated as yellow and air-stable solids.



Scheme 1. Overview the synthesis of the dinuclear *N*-heterocyclic carbene (NHC) palladium complexes **1**–**6**.

NMR characterization

All of these complexes were first characterized by ^1H, ^{13}C–{^1H}, and ^{31}P–{^1H} NMR spectroscopy and the selected NMR spectral data for complexes **1**–**6** were listed in Table 1. The ^1H NMR spectra of complexes **1**–**6** in $CDCl_3$ showed the distinctive stoichiometric proton signal resonances of the carbene ligands and the diphosphine ligands, which confirmed the formation of the dinuclear complexes. The single resonances at 3.95–4.08 ppm for the imidazoline ring of **1**–**6** are close to the values found for related mononuclear complex $PdCl_2$(SIMes)PPh_3 (4.00 ppm) [11c]. In addition, the formation of the metal complexes was evident from the distinctive metal-bound carbene peaks, which appeared as doublets at 198.3 ppm for **1**, 200.0 ppm for **2**, 198.2 ppm for **3**, 200.1 ppm for **4**, 198.2 ppm for **5**, 200.0 ppm for **6**, respectively. These values indicated that the electronic environment around the carbene carbon remains relatively constant in complexes **1**–**6** and were as expected close to the values found for the mononuclear complex $PdCl_2$(SIMes)PPh_3 (197.2 ppm) [11c]. However, these resonances were significantly downfield compared to that in the unsaturated carbene-phosphine palladium complex $PdCl_2$(IPr)PPh_3 (171.1 ppm, IPr = *N,N'*-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) [8a]. The large $^2J_{CP}$ coupling constants (198.2–200.1 Hz) are characteristic of the *trans* position of the phosphine ligands with respect to the NHC [10b]. The imidazoline backbone carbon atoms (NCH_2CH_2N), which appear as doublets (51.1–53.6 ppm, $^4J_{CP}$ = 5.8–6.6 Hz), remain largely unchanged upon the mononuclear complex (51.5 ppm for $PdCl_2$(SIMes)PPh_3). Furthermore, ^{31}P NMR spectra of all complexes showed sharp singlets (11.9–15.7 ppm) shifted downfield when compared to the mononuclear complexes $PdCl_2$(SIMes)PPh_3 (20.9 ppm) and $PdCl_2$(IPr)PPh_3 (20.4 ppm).

Solid-state characterization

The diphosphine ligands bridged dinuclear *N*-heterocyclic carbene palladium complexes were further characterized by X-ray crystallography (Fig. 1). Single crystals of **1**–**6** suitable for X-ray diffraction analysis were obtained from dichloromethane/*n*-hexane solutions of the corresponding complexes. Selected bond lengths, bond angles and dihedral angles were summarized in Table S1. Complexes **1** and **2** crystallize as CH_2Cl_2 solvates **1**·CH_2Cl_2 and **2**·$2CH_2Cl_2$, respectively. There are two independent molecules in a unit cell of the solvate **1**·CH_2Cl_2, only one molecule was shown in Fig. 1. The five-membered-ring topology of the saturated *N*-heterocyclic carbene ligands varies slightly for different complexes with the N–C–C–N dihedral angles are in a range of −5.56° to 16.04°. All of the complexes crystallized as *trans* configuration, in which each palladium centre is surrounded by a carbene, a phosphine donor from the bridging diphosphine ligands, and two chloro ions in a slightly distorted square planar fashion with angles

Table 1
Selected ^1H, ^{13}C–{^1H}, and ^{31}P–{^1H} NMR spectral data for complexes **1**–**6**.

NHC–Pd complex	^1H NMR[a]	^{13}C NMR[a]				^{31}P NMR[a]
	NCH_2CH_2N	Carbene		NCH_2CH_2N		$[(Ph_2P(CH_2)_n]$
	δ_H	δ_C	$^2J_{CP}$	δ_C	$^4J_{CP}$	δ_P
1	3.95	198.3	185.5	51.1	5.8	13.7
2	4.01	200.0	184.2	53.5	6.1	15.7
3	3.98	198.2	184.2	51.0	6.6	13.6
4	4.05	200.1	183.6	53.5	6.4	12.2
5	4.00	198.2	184.4	51.1	6.2	13.4
6	4.08	200.0	183.3	53.6	6.6	11.9

[a] ^1H, ^{13}C–{^1H} and ^{31}P–{^1H} NMR spectra were recorded in $CDCl_3$ at 298 K (δ in ppm, *J* in Hz).

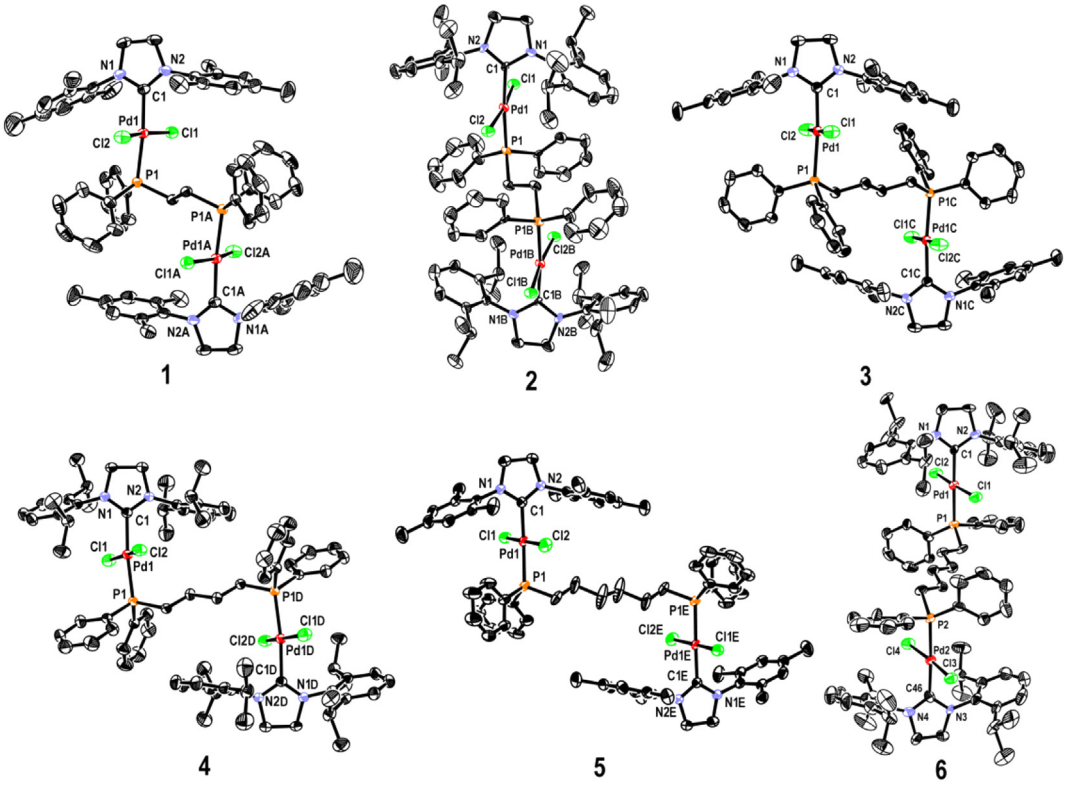


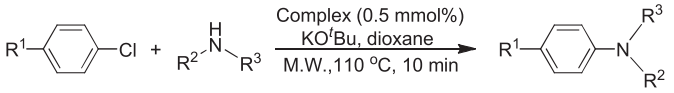
Fig. 1. ORTEP diagrams of complexes **1**–**6** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms and solvent molecules (CH_2Cl_2 for **1** and **2**) have been omitted for clarity. Symmetry codes: [A] $-x, 2-y, 1-z$; [B] $1.5-x, 0.5-y, 2-z$; [C] $1-x, -y, -z$; [D] $2-x, 1-y, -z$; [E] $0.5-x, 1.5-y, 2-z$.

between adjacent ligands ranging from 86.41(4)° to 95.17(9)°. The diphosphine ligands act as bridges, linking the palladium centres to form dinuclear NHC–palladium complexes with Pd···Pd separation from 6.70 Å to 11.13 Å. In complex **1**, the two *N*-heterocyclic carbene rings adopt a nearly coplanar orientation (with vertical separations of 0.064 and 0.416 Å), however, in complexes **2**–**5**, the two *N*-heterocyclic carbene rings adopt a parallel but non-coplanar orientation (with vertical separations of 2.041 Å for **2**, 3.775 Å for **3**, 3.104 Å for **4**, and 1.217 Å for **5**). In complex **6**, the two *N*-heterocyclic carbene rings are arranged in a slightly twisted orientation with a dihedral angle of 2.73°. In all complexes, the Pd–carbene bond lengths ranging from 2.005(11) Å to 2.046(4) Å and the Pd–P bond lengths ranging from 2.299(3) Å to 2.351(2) Å are similar to the related mononuclear NHC–phosphine palladium complex $PdCl_2(SMes)PPh_3$ [Pd–C: 2.028 (5) Å, Pd–P: 2.3137(6) Å] [11c]. The Pd–Cl bonds fall in a narrow range of 2.256(2)–2.3055(13) Å and are within the expected range, relative to the *N*-heterocyclic carbene–palladium complexes [8a,]. The carbene ring planes of all complexes are oriented almost perpendicularly to the square-planar Pd coordination plane ($PdCPCl_2$) with the dihedral angles varies from 71.28 to 84.86°, which are typical for NHC complexes to relieve steric congestion. On the other hand, the dihedral angles between the $PdCNCl_2$ coordination planes and the planes defined by the Pd1P1P1XPd1X in complexes **1**–**6** are significantly different, the values in complexes **1**, **3**, **4**, and **5** (87.26° and 83.47° for **1**, 70.66° for **3**, 60.41° for **4**, 70.99° for **5**) are significantly larger than that in **2** (34.23°) and **6** (dihedral angles of 35.98° and 36.73° between the $PdCNCl_2$ coordination planes and the Pd1P1P2Pd2 plane), which might be caused by the combination of the steric repulsion of *i*-Pr groups and the origination of carbene ring planes. The corresponding dihedral angles between the carbene ring planes and the Pd1P1P1XPd1X planes in the complexes **1**, **3**, **4**, and **5** are in a range of 7.25°–29.07°, which are significantly shorter than that in **2** (71.46°) and **6** (dihedral angles of 69.27 and 71.03° between the carbene ring planes and the Pd1P1P2Pd2 plane).

Catalytic studies

Palladium-catalysed Buchwald–Hartwig amination has become an important and widely employed method for the formation of C–N bonds [21]. Typically, electron-rich sterically hindered phosphine ligands have been commonly used for this reaction [22]. In addition to the widely used phosphine-based ligands, recent reports have shown that NHCs ligands are also efficient catalysts for the Buchwald–Hartwig amination with excellent activities [23]. As a derivative of the *N*-heterocyclic carbene palladium complexes, this kind of dinuclear NHC–Pd complexes would have potential uses in catalysis. In addition, microwave irradiation has gained popularity in the past decade as a powerful tool for efficient and rapid synthesis of a variety of compounds [24]. Herein, the catalytic activities of the dinuclear NHC–Pd complexes for the Buchwald–Hartwig amination under microwave irradiation were investigated. In order to test and compare the catalytic properties of the complexes, the coupling of chlorobenzene, 4-chlorotoluene and 4-chloroanisole with morpholine, *N*-methylaniline and aniline were chosen as model reactions. The results were listed in Table 2. In general, all the compounds gave rise to highly active catalysts for the aryl chloride substrates within 10 min at 110 °C under microwave irradiation conditions. For the activated substrate secondary amine morpholine, all of the complexes could give better coupling yields (92–97%) (Table 2, entries 1–6, 9–14 and 17–22) than *N*-methylaniline (83–91%) (Table 2, entries 23–31). For the less active primary amine aniline, the yields in these systems were slightly lower (81–87%) than the reaction of aryl chlorides with morpholine (Table 2, entries 32–40). For the substrates of aryl chloride, the electronic property of substituents on the aromatic rings had no

Table 2
Buchwald–Hartwig amination of aryl chlorides with amines.[a]



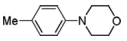
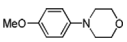
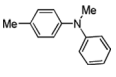
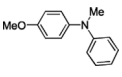
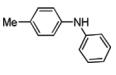
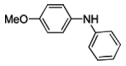
Entry	Halide	Amine	Product	Catalyst	Yield (%)[b]
1	R^1 = H			**1**	93
2				**2**	98
3				**3**	94
4				**4**	95
5				**5**	94
6				**6**	97
7				[Pd(μ-Cl)(Cl)(SIPr)]$_2$	91
8[c]				PdCl$_2$(SIPr)(PPh$_3$)	96
9	R^1 = CH_3			**1**	92
10				**2**	96
11				**3**	94
12				**4**	95
13				**5**	94
14				**6**	96
15				[Pd(μ-Cl)(Cl)(SIPr)]$_2$	92
16[c]				PdCl$_2$(SIPr)(PPh$_3$)	95
17	R^1 = OCH_3			**1**	93
18				**2**	97
19				**3**	94
20				**4**	96
21				**5**	93
22				**6**	95
23	R^1 = H			**1**	89
24				**2**	91
25				**3**	87
26	R^1 = CH_3			**4**	90
27				**5**	90
28				**6**	82
29	R^1 = OCH_3			**1**	87
30				**3**	83
31				**5**	86
32	R^1 = H			**1**	81
33				**2**	85
34				**3**	83
35	R^1 = CH_3			**4**	86
36				**5**	82

Table 2 (*continued*)

Entry	Halide	Amine	Product	Catalyst	Yield (%)[b]
37				**6**	85
38	R^1 = OCH_3			**2**	87
39				**4**	85
40				**6**	87

[a] Reaction conditions: aryl chloride (0.50 mmol), amine (0.60 mmol), KO^{t}Bu (0.75 mmol), complex (0.5 mmol%) in dry dioxane (1.0 mL) at 110 °C under microwave irradiation for 10 min.
[b] Isolated yield.
[c] Mononuclear NHC–Pd catalyst, 1.0 mol%.

significant impact on yields of the amination reactions. Generally, the results above-mentioned indicated that dinuclear NHC–palladium complexes exhibited moderate to good catalytic activities as precatalysts for Buchwald–Hartwig amination under microwave irradiation. The dinuclear palladium complexes demonstrated slightly higher catalytic activities than the chloro-bridged dimeric carbene palladium complex [Pd(μ-Cl)(Cl)(SIPr)]$_2$, but a similar level of catalytic activities compared with mononuclear analogue (Table 2, entries 7, 8, 15, and 16). The cooperative effect of the dinuclear catalysts in homogenous amination processes did not exhibited. Our further research will focus on the development of more efficient catalytic systems for this reaction.

Conclusions

In summary, a series of dinuclear NHC–palladium complexes **1**–**6** containing the imidazolidin-2-ylidene derivatives as the supporting ligands and the diphosphine ligands as linkers have been prepared by the reaction of dimeric compounds [Pd(μ-Cl)(Cl)(NHC)]$_2$ with the respective bridging diphosphine ligands. The new dinuclear NHC–palladium complexes were successfully examined in the catalytic Buchwald–Hartwig aminations of aryl chlorides with amines and exhibited good activities. As the derivatives of the *N*-heterocyclic carbene palladium complexes, this kind of dinuclear NHC–palladium would have potential uses in catalysis.

Experimental section

General considerations

The chemicals were purchased from commercial suppliers and were used without purification prior to use except where otherwise indicated. All ^{1}H, ^{13}C–{^{1}H} and ^{31}P–{^{1}H} NMR were performed in $CDCl_3$ and recorded on a Bruker Avance 400 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Bruker IFS 120HR spectrometer as KBr disks. Elemental analyses were performed on a Vario El III elementar. Flash column chromatography was carried out using 300–400 mesh silica gel.

*Synthesis of complexes **1**–**6***

A mixture of the dimeric complex [Pd(μ-Cl)(Cl)(NHC)]$_2$ (0.10 mmol) and the appropriate diphosphine ligand (0.10 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and stirred at ambient temperature overnight. The reaction mixture was filtered over Celite, the solvent was reduced under vacuum to about 1.0 mL and the yellow precipitate formed by careful addition of *n*-hexane (c.a. 10 mL). The yellow solid was then filtered off, washed with *n*-hexane, and dried under vacuum.

*[$PdCl_2$(SIMes)]$_2$(μ-dppe) (**1**)*

The procedure yielded 122 mg (90%) of the pure product **1** as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.13 (m, 16H), 6.91 (s, 8H), 3.95 (s, 8H, NCH_2CH_2N), 2.47 (s, 24H, *o*-CH_3), 2.25 (s, 12H, *p*-CH_3), 2.17 (br, 4H, PCH_2). ^{13}C–{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 198.3 (d, $^2J_{C,P}$ = 185.5 Hz, $C_{carbene}$), 137.6 (*o*-CH_3-*C* Ar), 137.1 (N–*C* Ar), 135.3 (*p*-CH_3-*C* Ar), 133.6 (d, $^3J_{C,P}$ = 10.6 Hz, *C*H Ph), 130.3 (d, $^1J_{C,P}$ = 42.1 Hz, *C* Ph), 129.4 (*C*H Ph), 129.1 (*C*H Ph), 127.5 (d, $^4J_{C,P}$ = 10.0 Hz, *C*H Ph), 51.1 (d, $^4J_{C,P}$ = 5.8 Hz, NCH$_2$CH$_2$N), 21.0 (*p*-CH_3), 19.1 (*o*-CH_3), 18.3 (PCH$_2$). ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 13.7. IR (KBr, cm^{-1}): 3441, 2961, 2918, 1488, 1454, 1435, 1300, 1267, 1178, 1103, 1028, 849, 721. Anal. Calc. for [$PdCl_2$(SIMes)]$_2$(μ-dppe) ($C_{68}H_{76}Cl_4N_4P_2Pd_2$): C, 59.79; H, 5.61; N, 4.10%. Found: C, 59.82; H, 5.31; N, 4.15%.

*[$PdCl_2$(SIPr)]$_2$(μ-dppe) (**2**)*

The procedure yielded 139 mg (91%) of the pure product **2** as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.29 (m, 4H), 7.25–7.24 (m, 4H), 7.18–7.12 (m, 24H), 4.01 (s, 8H, NCH_2CH_2N), 3.46 (sept, J = 6.8 Hz, 8H, CH(CH_3)$_2$), 1.92 (br, 4H, PCH_2), 1.24 (d, J = 6.4 Hz, 24H, CH(CH_3)$_2$), 1.17 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$). ^{13}C–{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.0 (d, $^2J_{C,P}$ = 184.2 Hz, $C_{carbene}$), 147.7 (*o*-CH_3-*C* Ar), 135.5 (N–*C* Ar), 133.9 (d, $^4J_{C,P}$ = 10.5 Hz, *p*-CH_3-*C* Ar), 130.1 (d, $^1J_{C,P}$ = 42.2 Hz, *C* Ph), 129.3 (*C*H Ph), 128.7 (*C*H Ph), 127.4 (d, $^4J_{C,P}$ = 9.8 Hz, *C*H Ph), 123.8 (*C*H Ph), 53.5 (d, $^4J_{C,P}$ = 6.1 Hz, NCH$_2$CH$_2$N), 28.5 (*C*H(CH_3)$_2$), 26.8 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 19.0 (PCH$_2$). ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 15.7. IR (KBr, cm^{-1}): 3051, 2962, 2867, 1477, 1447, 1435, 1327, 1269, 1243, 1106, 802, 755, 715. Anal. Calc. for [$PdCl_2$(SIPr)]$_2$(μ-dppe) ($C_{80}H_{100}Cl_4N_4P_2Pd_2$): C, 62.63; H, 6.57; N, 3.65%. Found: C, 62.49; H, 6.31; N, 3.43%.

*[$PdCl_2$(SIMes)]$_2$(μ-dppb) (**3**)*

The procedure yielded 121 mg (87%) of the pure product **3** as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.25 (m, 12H), 7.21–7.18 (m, 8H), 6.96 (s, 8H), 3.98 (s, 8H, NCH_2CH_2N), 2.51 (s, 24H, *o*-CH_3), 2.32 (s, 12H, *p*-CH_3), 1.88 (br, 4H, PCH_2CH$_2$), 1.17 (br, 4H, PCH$_2$CH_2). ^{13}C–{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 198.2 (d, $^2J_{C,P}$ = 184.2 Hz, $C_{carbene}$), 137.7 (*o*-CH_3-*C* Ar), 137.2 (N–*C* Ar), 135.3 (*p*-CH_3-*C* Ar), 133.5 (d, $^2J_{C,P}$ = 10.3 Hz, *C*H Ph), 130.7 (d, $^1J_{C,P}$ = 41.9 Hz, *C* Ph), 129.5 (d, $^3J_{C,P}$ = 2.4 Hz, *C*H Ph), 129.0 (*C*H Ph), 127.6 (d, $^4J_{C,P}$ = 9.9 Hz, *C*H Ph), 51.0 (d, $^4J_{C,P}$ = 6.6 Hz, NCH$_2$CH$_2$N), 29.0 (PCH$_2$CH$_2$), 21.0 (*p*-CH_3),19.1 (*o*-CH_3), 18.4 (PCH$_2$CH$_2$). ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 13.6. IR (KBr, cm^{-1}): 3051, 2918, 1488, 1452, 1435, 1298, 1267, 1182, 1102, 851, 740. Anal. Calc. for [$PdCl_2$(SIMes)]$_2$(μ-dppb) ($C_{70}H_{80}Cl_4N_4P_2Pd_2$): C, 61.52; H, 6.20; N, 3.83%. Found: C, 61.74; H, 6.48; N, 4.04%.

*[$PdCl_2$(SIPr)]$_2$(μ-dppb) (**4**)*

The procedure yielded 127 mg (81%) of the pure product **4** as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.24 (m, 10H), 7.22–7.15 (m, 22H), 4.05 (s, 8H, NCH_2CH_2N), 3.51 (sept, J = 6.8 Hz, 8H, CH(CH_3)$_2$), 1.88 (br, 4H, PCH_2CH$_2$), 1.31 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 1.20 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 0.91 (br, 4H, PCH$_2$CH_2). ^{13}C–{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.1 (d, $^2J_{C,P}$ = 183.6 Hz, $C_{carbene}$), 147.7 (*o*-CH_3-*C* Ar), 135.5 (N–*C* Ar), 133.5 (d, $^2J_{C,P}$ = 10.0 Hz, *C*H Ph), 130.8 (d, $^1J_{C,P}$ = 41.8 Hz, *C* Ph), 129.3 (d, $^3J_{C,P}$ = 2.2 Hz, *C*H Ph), 128.8 (*C*H Ph), 127.6 (d, $^4J_{C,P}$ = 9.8 Hz, *C*H Ph), 123.9 (*C*H Ph), 53.5 (d, $^4J_{C,P}$ = 6.4 Hz, NCH$_2$CH$_2$N), 31.5 (PCH$_2$CH$_2$), 28.5 (*C*H(CH_3)$_2$), 26.8 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$), 22.6 (PCH$_2$CH$_2$). ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 12.2. IR (KBr, cm^{-1}): 2962, 2925, 2864, 1476, 1453, 1436, 1382, 1324, 1269, 1244, 1180, 1100, 1058, 942, 800, 755, 736. Anal. Calc. for [$PdCl_2$(SIPr)]$_2$(μ-dppb) ($C_{82}H_{104}Cl_4N_4P_2Pd_2$): C, 61.75; H, 6.27; N, 3.79%. Found: C, 61.79; H, 6.41; N, 3.63%.

*[$PdCl_2$(SIMes)]$_2$(μ-dpph) (**5**)*

The procedure yielded 123 mg (86%) of the pure product **5** as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.28 (m, 12H), 7.22–7.19 (m, 8H), 7.00 (s, 8H), 4.00 (s, 8H, NCH_2CH_2N), 2.53 (s, 24H, *o*-CH_3), 2.38 (s, 12H, *p*-CH_3), 1.99 (br, 4H, PCH_2CH$_2$CH$_2$), 1.18 (br, 4H, PCH$_2$CH_2CH$_2$), 1.08 (br, 4H, PCH$_2$CH$_2$CH_2). ^{13}C–{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 198.2 (d, $^2J_{C,P}$ = 184.4 Hz, $C_{carbene}$), 137.7 (*o*-CH_3-*C* Ar), 137.2 (N–*C* Ar), 135.3 (*p*-CH_3-C Ar), 133.5 (d, $^2J_{C,P}$ = 10.1 Hz, *C*H Ph), 130.9 (d, $^1J_{C,P}$ = 41.8 Hz, *C* Ph), 129.5 (d, $^4J_{C,P}$ = 1.9 Hz, *C*H Ph), 129.0 (*C*H Ph), 127.6 (d, $^4J_{C,P}$ = 9.8 Hz, *C*H Ph), 51.1 (d, $^4J_{C,P}$ = 6.2 Hz, NCH$_2$CH$_2$N), 31.9 (PCH$_2$CH$_2$CH$_2$), 22.6 (PCH$_2$CH$_2$CH$_2$), 21.0 (*p*-CH_3), 19.1 (*o*-CH_3), 14.1 (PCH$_2$CH$_2$CH$_2$). ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 11.9. IR (KBr, cm^{-1}): 3442, 2919, 2856, 1488, 1452, 1435, 1294, 1267, 1180, 1102, 1027, 912, 851, 739. Anal. Calc. for [$PdCl_2$(SIMes)]$_2$(μ-dpph) ($C_{72}H_{84}Cl_4N_4P_2Pd_2$): C, 60.81; H, 5.95; N, 3.94%. Found: C, 60.63; H, 5.77; N, 4.02%.

*[$PdCl_2$(SIPr)]$_2$(μ-dpph) (**6**)*

The procedure yielded 132 mg (83%) of the pure product **6** as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 4H), 7.28–7.23 (m, 20H), 7.17–7.14 (m, 8H), 4.08 (s, 8H, NCH_2CH_2N), 3.55 (sept, J = 6.4 Hz, 8H, CH(CH_3)$_2$), 1.91 (br, 4H, PCH_2CH$_2$CH$_2$), 1.33 (d, J = 6.4 Hz, 24H, CH(CH_3)$_2$), 1.23 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 0.90 (br, 8H, PCH$_2$CH_2CH_2). ^{13}C–{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.0 (d, $^2J_{C,P}$ = 183.3 Hz, $C_{carbene}$), 147.7 (*o*-CH_3-*C* Ar), 135.5 (N–*C* Ar), 133.5 (d, $^2J_{C,P}$ = 9.9 Hz, *C*H Ph), 130.8 (d, $^1J_{C,P}$ = 41.8 Hz, *C* Ph), 129.3 (d, $^4J_{C,P}$ = 2.1 Hz, *C*H Ph), 128.8 (*C*H Ph), 127.4 (d, $^4J_{C,P}$ = 9.7 Hz, *C*H Ph), 123.9 (*C*H Ph), 53.6 (d, $^4J_{C,P}$ = 6.6 Hz, NCH$_2$CH$_2$N), 31.5 (PCH$_2$CH$_2$CH$_2$), 28.5 (CH(*C*H$_3$)$_2$), 26.8 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$), 22.6 (PCH$_2$CH$_2$CH$_2$), 14.1 (PCH$_2$CH$_2$CH$_2$). ^{31}P–{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 11.9. IR (KBr, cm^{-1}): 3057, 2960, 2927, 1477, 1453, 1435, 1383, 1327, 1268, 1243, 1179, 1102, 1056, 929, 802, 756, 738. Anal. Calc. for [$PdCl_2$(SIPr)]$_2$(μ-dpph) ($C_{84}H_{108}Cl_4N_4P_2Pd_2$): C, 63.44; H, 6.84; N, 3.52%. Found: C, 63.64; H, 6.52; N, 3.43%.

General procedure for the NHC–Pd catalysed Buchwald–Hartwig amination

The aryl chloride (0.50 mmol), amine (0.60 mmol), KO^{t}Bu (0.75 mmol), NHC–Pd complex (0.0025 mmol) and dry dioxane (1.0 mL) were added into oven-dried microwave vial. The reaction mixture was irradiated in a microwave apparatus at 110 °C for 10 min. After the reaction mixture was cooled to room temperature, the product was filtered over Celite and washed with ethyl acetate. Then the filtrate was concentrated with a rotary evaporator, and the residue was then subjected to purification via flash column chromatography (eluent: ethyl acetate/petroleum ether) to give the corresponding pure products.

X-ray crystallography

Data collection was performed on a Bruker-AXS SMART CCD area detector diffractometer at 296 K using ω rotation scans with a scan width of 0.3° and Mo-Kα radiation (λ = 0.71073 Å). Multi-scan corrections were applied using SADABS [25]. Structure solutions and refinements were performed with the SHELX-97 package [26]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. The hydrogen atoms to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of carbon atoms. Complex **2** crystallized in poor quality. The weak reflections cause a low observed/unique reflection ratio, which results in low completeness of the data set (0.918), and gives insufficient strong reflections to support full refinement of all non-hydrogen atoms. In complex **4**, the crystal lattice contains solvent accessible voids of 272 Å^3, however, the final difference

electron density map contained no chemically significant peaks, the highest peak being 0.83 e/Å^3 at a distance of 3.498 Å from the H(8) atom and no suitable model for any solvent could be found in difference Fourier syntheses. In complex **6**, the crystal lattice contains solvent accessible voids of 261 Å^3, however, the final difference electron density map contained no chemically significant peaks, the highest peak being 0.81 e/Å^3 at a distance of 1.47 Å from the Pd(2) atom and no suitable model for any solvent could be found in difference Fourier syntheses. A summary of the crystallographic data, data collection, and refinement parameters for complexes **1**–**6** were provided in Table S2.

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Appendix A. Supplementary material

CCDC 978965, 978966, 978967, 978968, 978969, and 978970 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.05.001.

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