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FULL PAPER

N-heterocyclic carbene–palladium complexes for Suzuki–Miyaura coupling reaction with benzyl chloride and aromatic boronic acid leading to diarylmethanes

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A family of N-heterocyclic carbene–palladium(II)–*N*,*N*-dimethylbenzylamine complexes ((NHC)LPdCl_2; L = *N*,*N*-dimethylbenzylamine) were synthesized as well as characterized using single-crystal X-ray diffraction and spectroscopic data. These complexes exhibited higher catalytic activities for the Suzuki reaction of benzyl chlorides to afford diarylmethanes under milder conditions than other efficient (NHC)LPdCl_2 complexes. Using the optimum conditions, the expected coupling products were obtained in moderate to high yields. All reactions were carried out in air and all starting materials were used as supplied without purification.

KEYWORDS
diarylmethane synthesis, homogeneous catalysis, N-donor, NHC–palladium complex, Suzuki–Miyaura reaction

1 | INTRODUCTION

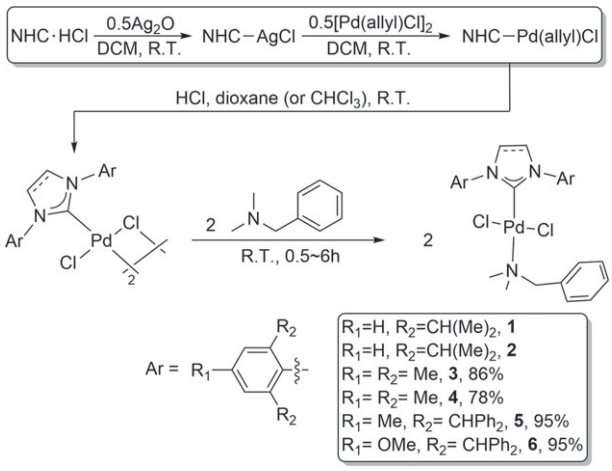
During the past decade, various palladium systems have been developed and applied successfully for the Suzuki–Miyaura cross-coupling reaction. The properties of the powerful and user-friendly conditions contribute to the formation of carbon–carbon bonds in diverse areas, like bioactive, conductive and fluorescent compounds, and many have been widely employed in pharmaceutical and materials sciences.[1] In recent research, more challenging electrophilic coupling reagents, aryl chlorides, have become most desirable and attractive because of their cost, availability and robustness, even though their reactivity is relatively low. Hence, to date for this purpose, numbers of auxiliary ligands have been developed, and most of them played important roles and showed excellent performances. In the literature several types of ligands have been reported, such as phosphine-based ligands, including biarylphosphines,[2] ferrocene-contained phosphines,[3] *N*-substituted heteroaryl phosphines,[4] and non-phosphine systems such as N-heterocyclic carbene (NHC) ligands.[5] Furthermore, the 'well-defined' complexes have been progressively developed and led as the guideline of catalyst design for cross-coupling reactions,[1d, 6] in place of the more classical *in situ* systems consisting of a metal salt and a ligand or ligand precursor.[7] The search for highly effective catalysts that can efficiently activate more challenging substrates in various coupling reactions, such as at low catalyst loadings, or under mild conditions, has become a leading research theme in this area.[7]

More recently, it was found that the use of well-defined NHC-bearing Pd complexes in cross-coupling reactions depends on the properties leading to much easier handling and better control of metal-to-ligand stoichiometry and significant improvements in activity.[5b] In most cases, these catalysts have more electron-rich and bulky ligands that promote not only the oxidative addition step, but also the reductive elimination step to afford the desired coupling product, then regenerate the catalytic active species in the catalytic cycle.[8] Successful

examples have been reported by the groups of Glorius,[9] Buchwald,[2] Nolan,[10] Organ,[11] Navarro,[12] etc. Relative to air-sensitive phosphine ligands, air-stable NHC–palladium complexes have become a good choice because of their good catalytic behaviors as good catalysts in coupling reactions.

Now, our research attention was focused on C—C bond formation, especially for the synthesis of diarylmethanes due to limited literature reports and systematic studies. Literature reviews of NHC systems in the synthesis of diarylmethanes yield the following. In 2014, Strassner and co-workers described a palladium-catalyzed C—C bond formation from benzyl chlorides and phenylboronic acid to achieve 60–90% yields at 60 °C under argon within 2 to 3 h.[13] Later on, two different solvent systems were developed: water containing dimethylformamide was used by the Wu group for the conversion of benzyl chlorides to diarylmethanes at 90 °C in 1 h; and the single solvent 'water' was used by the Reddy group at 100 °C in 3 h to afford products in moderate yields.[14] In addition, an analogous system containing Pd catalyzing the coupling of benzyl chlorides at 60 °C in 12 h in water under nitrogen was presented by the Lu group (Figure 1).[15]

Although these methods represent powerful synthetic tools, they still suffer from a relatively limited substrate scope or conditions needed to overcome, such as high temperature, long reaction time, under inert gas or lower catalytic activity. Recently, we have developed a new series of NHC–palladium complexes using *N*,*N*-benzyldimethylamine, instead of the commonly reported pyridine or 3-chloropyridine ligands, with the general formula (NHC)$NMe_2BzPdCl_2$ (complexes **1** and **2**; Scheme 1) which have proven to be very active pre-catalysts for cross-coupling reactions such as Suzuki–Miyaura even under very mild reaction conditions.[16] In the work reported in this paper, we aimed to extend their cross-coupling application in the presence of benzyl chlorides as substrates for the Suzuki–Miyaura reaction and therefore we synthesized four new complexes bearing mesityl or bulky *N*-substituents for a systematic investigation.



SCHEME 1 Synthesis of NHC palladium complexes

2 | EXPERIMENTAL

2.1 | Reagents and methods

Unless otherwise noted, all manipulations were performed in air. All solvents and reagents were used as received. The reagents were purchased from Sigma-Aldrich, Acros, Merck, TEDIA and Alfa-Aesar. The imidazolium salts IPr·HCl and SIPr·HCl and NHC–palladium complexes **1** and **2** were prepared by following literature procedures and their identity and purity were confirmed using ^{1}H NMR and ^{13}C NMR spectroscopy.[16,17]

All aryl halides and boronic acids were used as received. Technical-grade ethyl alcohol was used to carry out Suzuki–Miyaura cross-coupling reactions. All reactions were carried out in air at ambient temperature. Flash chromatography was performed on silica gel 60 (230–400 mesh) using mixtures of hexanes–ethyl acetate (10:1), unless otherwise noted.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded with Brucker-AV-400 (400 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed with a FLASH 2000 series nitrogen and carbon analyzer

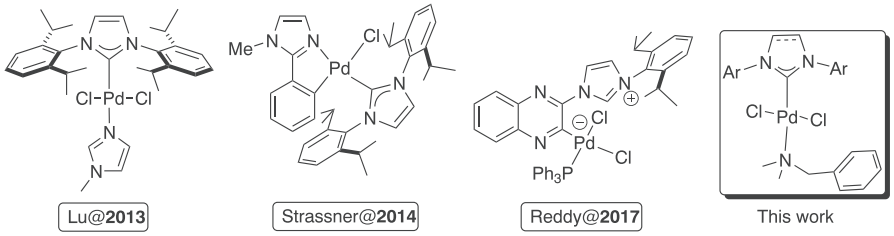
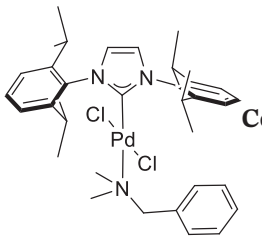


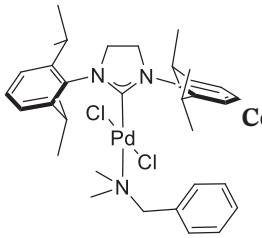
FIGURE 1 NHC–Pd complexes used for Suzuki–Miyaura reaction of benzyl chlorides

instrument (Thermo) or an Elementar vario EL CUBE (CHN-OS Rapid, Germany). The Suzuki–Miyaura cross-coupling reactions were analyzed using GC-MS with a Bruker SCION 436 SQ instrument equipped with a Bruker BR-5ms column. The MS detector was configured with an electronic impact ionization source.

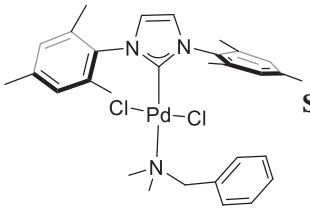
2.2 | Synthesis of complexes 1–6



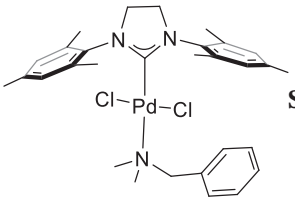
Complex 1. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 1.05 (d, J = 6.8 Hz, CH_3, 12H), 1.37 (d, J = 6 .8Hz, CH_3, 12H), 2.12 (s, N (CH_3)$_2$, 6H), 3.14 (septet, J = 6 .8Hz, CH, 4H), 3.60 (s, N (CH_2), 2H), 6.99 (t, J = 7 .6Hz, ArH, 2H), 7.07 (s, CH=CH, 2H), 7.12 (t, J = 7 .6Hz, ArH, 1H), 7.39 (t, J = 7 .2Hz, ArH, 6H), 7.54 (t, J = 7 .6Hz, ArH, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, δ, ppm): 22.9 (s, iPr), 26.4 (s, iPr), 28.6 (s, CHiPr), 49.6 (s, N (CH_3)$_2$), 65.0 (s, CH_2N(CH$_3$)$_2$), 124.0, 125, 127.3, 128.0, 130.0, 131.0 (s, CH aromatic), 134.9, 135.2, 147.0 (s, C aromatic), 153.6 (s, $C_{carbene}$).



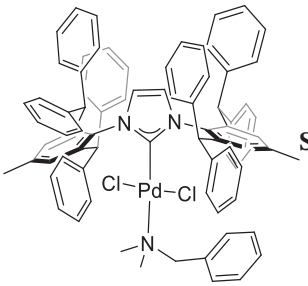
Complex 2. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 1.18 (d, J = 6.8 Hz, CH_3, 12H), 1.46 (d, J = 6.4 Hz, CH_3, 12H), 2.08 (s, N (CH_3)$_2$, 6H), 3.60 (septet, J = 7.3 Hz, CH, 4H), 4.05 (s, N (CH_2), 2H), 6.97 (t, J = 7.8 Hz, ArH, 2H), 7.12 (t, J = 7.4 Hz, ArH, 1H), 7.36 (m, ArH + CH_2CH_2, 8H), 7.49 (t, J = 7.8 Hz, ArH, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, δ, ppm): 23.9 (s, iPr), 27.0 (s, iPr), 28.7 (s, CHiPr), 49.3 (s, N (CH_3)$_2$), 53.6 (s, CH_2N(CH$_3$)$_2$), 64.9 (s, CH_2CH_2), 124.4, 127.2, 127.9, 130.9 (s, CH aromatic), 134.7, 135.4, 148.2 (s, C aromatic), 185.1 (s, $C_{carbene}$).



Synthesis of 3. A vial was charged with [Pd(μ-Cl)Cl (IMes)]$_2$ (0.68 g, 0.7 mmol) and *N*,*N*-dimethylbenzylamine (0.21 ml, 1.4 mmol) and dichloromethane (DCM; 2 ml) as solvent. The solution was stirred at room temperature for 0.5 h. The solution was filtered through a pad of Celite, and the filtrate was removed from the solvent to afford a pale yellow solid of the desired compound in 86% yield (0.74 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.18 (s, CH_3, 6H), 2.37 (s, CH_3, 12H), 2.43 (s, CH_3, 6H), 3.63 (s, NCH, 4H), 7.04 (s, NCH_2, 2H), 7.11 (s, ArH, 4H), 7.13 (d, J = 7 .6Hz, ArH, 2H), 7.19 (t, J = 7 .4Hz, ArH, 1H), 7.56 (d, J = 7 .2Hz, ArH, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ, ppm): 19.3 (s, CH$_3$), 21.2 (s, CH$_3$), 49.7 (s, CH$_3$), 65.1 (s, NCH_2), 124.2, 127.5, 127.9, 129.1, 130.7 (s, CH, aromatic), 135.3, 136.5, 139.0, 151.2, 147.0 (s, C aromatic), 153.6 (s, $C_{carbene}$). Anal. Calcd for $C_{30}H_{37}Cl_2N_3Pd$ (%): C, 58.40; H, 6.05; N, 6.81. Found (%): C, 58.49; H, 6.45; N, 6.75.

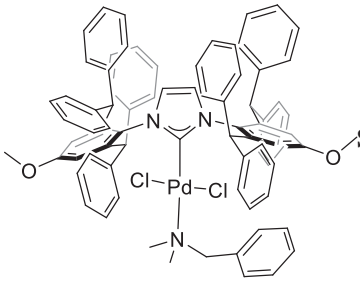


Synthesis of 4. The procedure for the preparation of **4** was similar to that used for **3** but with [Pd(μ-Cl)Cl (SIMes)]$_2$ (97 mg, 0.7 mmol) and *N*,*N*-dimethylbenzylamine (0.03 ml, 1.4 mmol), and 2 ml of DCM. A pale yellow solid was obtained in 78% yield (97 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.09 (s, CH_3, 6H), 2.37 (s, CH_3, 6H), 2.56 (s, CH_3, 12H), 3.99 (s, N (CH_2), 4H), 6.91 (s, ArH, 1H), 6.98 (s, ArH, 1H), 7.05 (s, ArH, 4H), 7.14 (t, J = 7 .3Hz, ArH, 1H), 7.41 (t, J = 10.9Hz, ArH, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ, ppm): 19.5 (s, CH$_3$), 21.1 (s, CH$_3$), 42.4 (s, CH$_3$), 49.5 (s, CH$_3$), 51.1 (s, CH$_2$), 64.9 (s, NCH_2), 127.4, 127.8, 129.4, 130.6, 131.2 (s, CH, aromatic), 135.1, 135.3, 137.4, 137.6, 138.2 (s, C aromatic), 183.1 (s, $C_{carbene}$). Anal. Calcd for $C_{30}H_{39}Cl_2N_3Pd$ (%): C, 58.21; H, 6.35; N, 6.79. Found (%): C, 58.55; H, 6.45; N, 6.80.



Synthesis of 5. The procedure for the preparation of **5** was similar to that used for **3** but with [Pd(μ-Cl)Cl (IPr*)]$_2$ (1 g, 0.46 mmol) and *N*,*N*-dimethylbenzylamine (124 mg, 0.92 mmol), and 2 ml chloroform and reaction time of 6 h. A pale yellow solid was obtained in 95% yield (1.07 g). ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.18 (s, CH_3, 6H), 2.40 (s, N (CH_3)$_2$, 6H), 4.00 (s, NCH, 2H), 4.55 (s, CH_2, 2H), 6.14 (s, CH (CH$_3$)$_2$, 4H), 6.74 (s, ArH, 8H), 7.0–7.15 (m, ArH, 15H), 7.17–7.42 (m, ArH, 15H), 7.38–7.62 (q, J = 7.3 Hz, ArH, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, δ, ppm): 45.3 (s,

CH_3), 49.1 (s, CH_3), 50.8 (s, *C*H), 65.0 (s, CH_2), 123.5, 125.9, 126.0, 127.1, 127.7, 127.8, 128.0, 128.1, 128.3, 129.2, 129.4, 130.1 (s, *C*H aromatic), 130.9, 131.3, 134.0, 138.4, 142.5, 143.9, 145.0 (s, *C* aromatic), 151.1 (s, $C_{carbene}$). Anal. Calcd for $C_{78}H_{69}Cl_2N_3Pd$ (%): C, 76.43; H, 5.67; N, 3.43. Found (%): C, 76.95; H, 5.53; N, 3.34.



Synthesis of 6. The procedure for the preparation of **6** was similar to that used for **3** but with [Pd(μ-Cl)Cl (IPr*^{OMe})]$_2$ (1 g, 0.46 mmol) and *N*,*N*-dimethylbenzylamine (124 mg, 0.92 mmol), and 2 ml of chloroform and reaction time of 6 h. A pale yellow solid was obtained in 95% yield (1.10 g). ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.56 (s, OCH_3, 6H), 2.40 (s, N (CH_3)$_2$, 6H), 4.00 (s, NC*H*, 2H), 4.55 (s, CH_2, 2H), 6.14 (s, C*H* (CH_3)$_2$, 4H), 6.74 (s, Ar*H*, 8H), 7.0–7.15 (m, Ar*H*, 15H), 7.17–7.42 (m, Ar*H*, 19H), 7.38–7.62 (m, Ar*H*, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, δ, ppm): 49.2 (s, CH_3), 51.0 (s, CH_3), 55.0 (s, *C*H), 114.8, 123.6, 126.0, 126.2, 127.9, 128.0, 128.1, 129.3, 130.8, 131.3 (s, *C*H aromatic), 143.7, 144.6, 144.8 (s, *C* aromatic), 159.0 (s, $C_{carbene}$). Anal. Calcd for $C_{78}H_{69}Cl_2N_3O_2Pd$ (%): C, 74.49; H, 5.53; N, 3.34. Found (%): C, 74.28; H, 5.77; N, 3.54.

2.3 | X-ray data collection and structure refinement

Crystals of **3–6** were grown from concentrated DCM solution and isolated by filtration. Data were collected using a Bruker AXS SMART 1000 diffractometer mounted with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Absorption correction was applied using SADABS.[18] The structure was solved by direct methods using the SHELXTL package.[19] All non-hydrogen atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms, and fixed isotropic parameters were used for hydrogen atoms. Some details of the data collection and refinement are given in Table S1.

CCDC 1823931, 1823932, 1887333, 1887334 are contained in the supporting information for this paper. These detailed crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4 | Procedure of Suzuki–Miyaura cross-coupling reaction

Complex (1 mol %) and base (1 equiv.) were added in turn to a vial equipped with a magnetic bar and sealed with a screw cap. Technical-grade solvent (1 ml) was injected into the vial, and the mixture stirred on a stirring plate at room temperature. All reactions were carried out in air and all starting materials were used as supplied without purification. Benzyl chloride (0 .5mmol) and arylboronic acid (0.6 mmol) were then injected and the mixture was heated at 50°C. The reaction was monitored by GC-MS. When finished, the mixture was quenched with 0.1 N HCl, and the crude product was collected and purified using flash chromatography. The amount of product shown is the average of two runs. The crude material was purified by flash chromatography on silica gel using a mixture of hexane and ethyl acetate (1–10%) as the eluent.

3 | RESULTS AND DISCUSSION

According to literature procedures,[20] both IPr*·HCl and IPr*^{OMe}·HCl ligand precursors were synthesized. The new complexes **3–6** were prepared under air and at room temperature and silver(I) oxide was used as the carbene transfer reagent to afford NHC–palladium dimer complexes.[12a, 16] Complexes **3** and **4** were synthesized straightforwardly and were achieved by the treatment of [(NHC)$PdCl_2$]$_2$ dimers with 2 equiv. of *N*,*N*-dimethylbenzylamine in DCM at room temperature within 0.5 h reaction time. Because of the mediocre solubility of complex precursor dimers [(IPr*)(μ-Cl)$PdCl$]$_2$ and [(IPr*^{OMe})(μ-Cl)$PdCl$]$_2$ in DCM, it was necessary to change the solvent to $CHCl_3$ and prolong the reaction time to 6 h. Synthetic details are summarized in Scheme 1. The target complexes were isolated in good yields for complexes **3–6** at 86% for **3**, 78% for **4** and 95% for **5** and **6** by evaporating the solvent. All complexes are stable in air and moisture and were fully characterized using elemental analysis and ^{1}H NMR and ^{13}C NMR spectroscopy.

Suitable crystals of **3–6** for single-crystal X-ray diffraction were obtained from a slow recrystallization in a DCM–hexane solution. As expected, the molecular structure of **3** (Figure 2) shows a distorted square planar geometry and the Pd center with the chloride ligands perpendicular to the plane of NHC and *N*,*N*-dimethylbenzylamine ligands *trans* to each other. Complexes **4–6** adopted a similar coordination behavior shown in Figures 3–5. Compared with general NHC-bearing complexes, the Pd—$C_{carbene}$ distance is in the range of a single bond (2.009(5) Å for **3**, 1.965(3) Å for

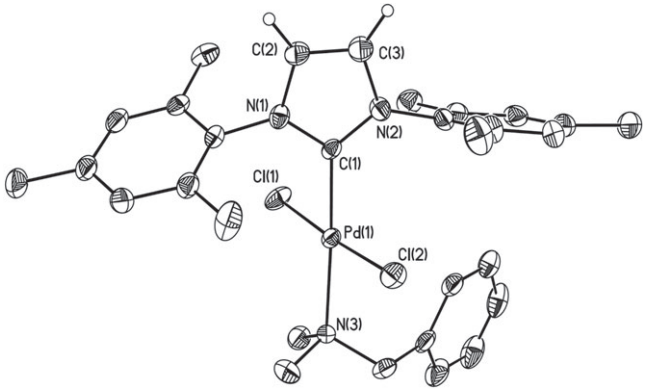


FIGURE 2 Crystal structure of **3** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

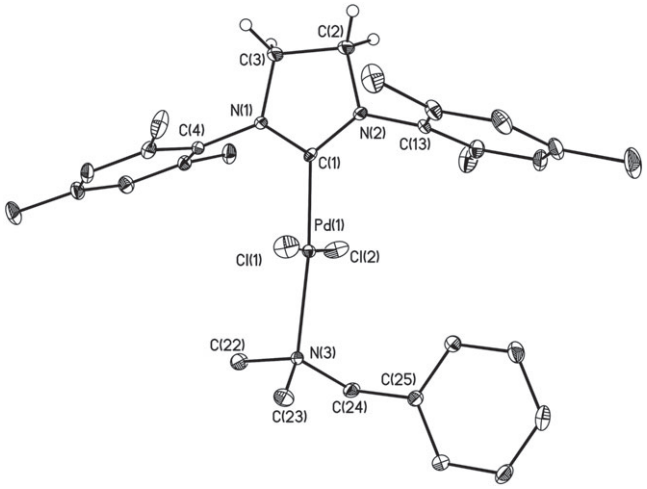


FIGURE 3 Crystal structure of **4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

4, 1.971(2) Å for **5** and 1.974(2) Å for **6**), close to that of the same N donor group with $^{i\text{Pr}}$NHC **1** or S$^{i\text{Pr}}$NHC **2** (1.957(6) Å for **1** and 1.963(3) Å for **2**) also the $^{i\text{Pr}}$Ar and S$^{i\text{Pr}}$Ar parent dimer complexes. Both the Pd—Cl bond distances of complexes **3**–**6** fall between the values found for the Pd—(μ-Cl) and Pd—Cl bond distances of the dimer [($^{i\text{Pr}}$Ar)(μ-Cl)PdCl]$_2$, [(S$^{i\text{Pr}}$Ar)(μ-Cl)PdCl]$_2$: ($^{i\text{Pr}}$Ar)Pd—(μ-Cl) 2.4029(9); (S$^{i\text{Pr}}$Ar)Pd—(μ-Cl) 2.4029(9), Pd—Cl: 2.2936(14), 2.3037(15) for **3**; 2.3016(8), 2.3021(8) for **4**; 2.3005(6), 2.3062(6) for **5** and 2.3086(6) for **6**. Compared with flexible bulky ligands such as IPent,[21] IPr*[10a] or IPr*$^{\text{OMe}}$[10b] but supported by different donor group, the bond length of Pd—C for complexes **3**–**6** was located between 1.9710 and 2.038 Å and the bond length of Pd—Cl was located between 2.281 and 2.3455 Å. Selected bond distances for complexes **3**–**6** and ^{13}C signals of C_{carbene} are listed in Table 1.

Now with the isolation of complexes **3**–**6** achieved, the question of the activity of these systems towards catalysis

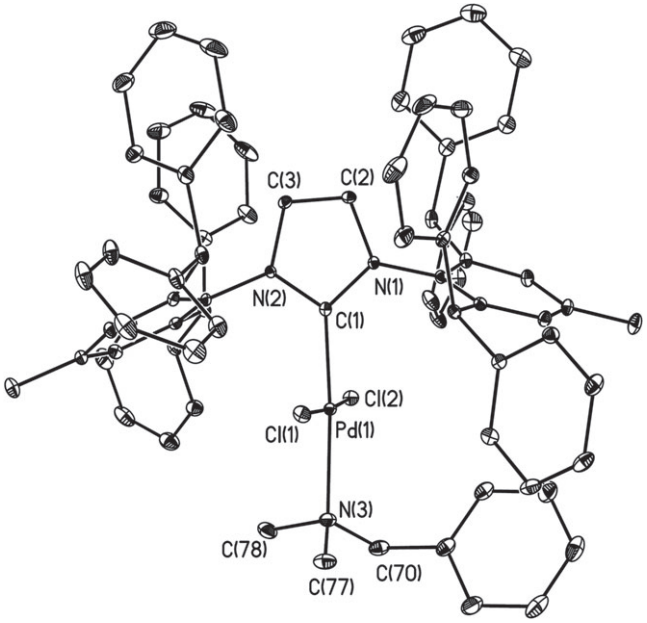


FIGURE 4 Crystal structure of **5** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

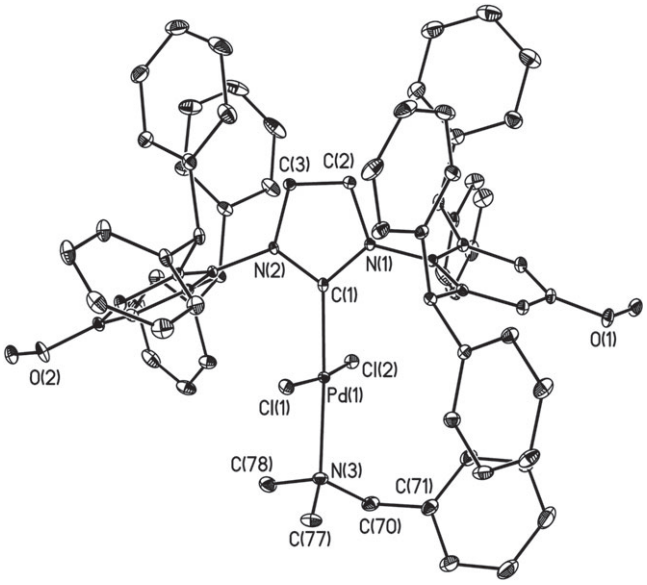


FIGURE 5 Crystal structure of **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

was examined. Herein, the Suzuki–Miyaura reaction of benzyl chloride and phenylboronic acid was selected as the model and investigated under air atmosphere. For initial studies, we chose complex **3** to explore and determine the optimum conditions. Representative results are listed in Table 1. After the optimum solvent/base combinations, the optimum results were found to be ethanol at 30°C after several trials on running reaction with six bases (NaOH, NaO^{t}Bu, KO^{t}Bu, K_3PO_4, Na_2CO_3, K_2CO_3) and five solvents (IPA, EtOH, toluene, THF, DME) using **3** as the model catalyst. A comparison of the performance

TABLE 1 Comparison of Pd—$C_{carbene}$ bond distances and δ $C_{carbene}$

Complex	Pd—$C_{carbene}$ (Å)	Pd—Cl (Å)	Pd—N (Å)	δ $C_{carbene}$ (ppm)
1[a]	1.957(6)	2.2995(17), 2.2965(18)	2.194(5)	153.6
2[a]	1.963(3)	2.2964(8), 2.2953(8)	2.2083(19)	185.1
3	2.009(5)	2.2931(14), 2.3037(15)	2.205(5)	153.6
4	1.965(3)	2.3016(8), 2.3021(8)	2.187(2)	183.1
5	1.971(2)	2.3005(6), 2.3062(6)	2.1910(19)	151.1
6	1.974(2)	2.3086(6), 2.3086(6)	2.194(2)	159.0

[a]Chen and Kao.16

of five family complexes and other active (NHC)$LPdCl_2$ complexes was conducted. The screened complexes comprising our previous Suzuki reaction studies exhibited good activities for complexes **1** and **2**,[16] and effective catalytic species: (^{iPr}Ar)(allyl)PdCl (**7**),[22] (^{iPr}Ar)(cinnamyl)PdCl (**8**),[23] (^{iPr}Ar)PEPPSIPdCl_2 (**9**)[24] and (^{iPr}Ar)TEAPdCl_2 (**10**)[25]. For the investigation of coupling conditions, benzyl chloride and phenylboronic acid were employed, and the screened catalyst structures are presented in Figure 6.

Following this preliminary optimum conditions study, utilizing **3** as the catalyst to screen the best combined performance of base/solvent, NaO^{t}Bu/EtOH gave higher yield (70%) than others when using benzyl chloride and phenylboronic acid as starting materials (Table 2, entry 5). Other base/solvent combinations such as NaO^{t}Bu/toluene and KO^{t}Bu/DME did not work, affording 0% conversion (entries 2 and 11), and secondary alcoholic solvents, such as IPA, afforded less than 50% conversion (entries 13 and 14). When obtaining the optimum conditions to screen the family of complexes **1**–**6**, the temperature was raised to 50°C, and the six complexes showed close activities to afford more than 80% conversion within 1 h with the same starting materials, only complexes **4** and **6** showing inferior conversion (for **4**: 71%; for **6**: 43%). Hence, the phenylboronic acid was changed to 2,6-xyleneboronic acid to examine the activities of other complexes for a prolonged reaction time of 7 h. The results are collected in Table 1 (entries 15–22). Comparing the activities of the family of complexes, only complex

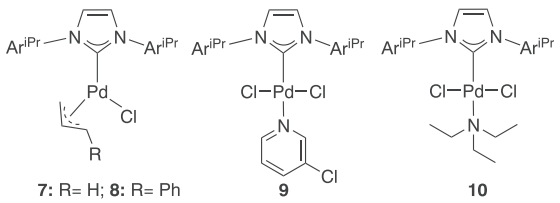
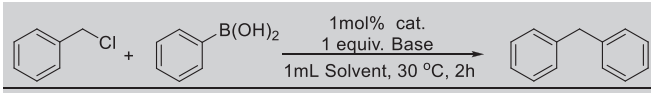


FIGURE 6 Efficient (NHC)$LPdCl_2$ complexes, the activities of which were compared in this study

TABLE 2 Optimum conditions of Suzuki–Miyaura reaction of benzyl chloride with phenylboronic acid[a]



Entry	Catalyst	Base	Solvent	Conversion (%)[b]
1	**3**	NaOH	Toluene	43
2	**3**	NaO^{t}Bu	Toluene	0
3	**3**	K_3PO_4	Toluene	56
4	**3**	NaOH	EtOH	68
5	**3**	**NaO^{t}Bu**	**EtOH**	**70**
6	**3**	KO^{t}Bu	EtOH	55
7	**3**	K_3PO_4	EtOH	47
8	**3**	Na_2CO_3	EtOH	14
9	**3**	K_2CO_3	EtOH	45
10	**3**	NaOH	DME	29
11	**3**	KO^{t}Bu	DME	0
12	**3**	K_3PO_4	THF	3
13	**3**	KO^{t}Bu	IPA	2
14	**3**	K_3PO_4	IPA	47
15	**3**	NaO^{t}Bu	EtOH	42
16[c]	**1**	NaO^{t}Bu	EtOH	75
17[c]	**2**	NaO^{t}Bu	EtOH	50
18[c]	**5**	NaO^{t}Bu	EtOH	32
19[c]	**7**	NaO^{t}Bu	EtOH	5
20[c]	**8**	NaO^{t}Bu	EtOH	54
21[c]	**9**	NaO^{t}Bu	EtOH	43
22[c]	**10**	NaO^{t}Bu	EtOH	39
23[d]	—	NaO^{t}Bu	EtOH	0

[a]Reaction conditions: 0.5 mmol benzyl chloride, 0.6 mmol phenylboronic acid, 1equiv. base, 1 mol% catalyst and 1 ml solvent, 30°C, 2 h.

[b]Determined by GC-MS, average of two runs.

[c]Reaction conditions: T = 50°C, 2,6-xyleneboronic acid used as reagent, reaction time: 7 h.

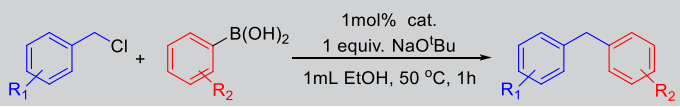
[d]Reaction conditions: 50°C, reaction time: 24 h.

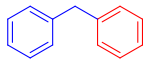
1 allowed the coupling to proceed in high yield (75%; entry 16). Based on the same conditions, **7** achieved 5% yield, **8** 54%, **9** 43% and **10** 39% (entries 19–22). After screening these catalysts, complex **1** showed greater activity for the Suzuki–Miyaura reaction of benzyl chloride than other high-efficiency (NHC)LPdCl$_2$ complexes shown in Figure 6.

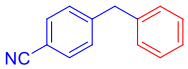
The coupling between a range of substituted benzyl chlorides and functionalized arylboronic acids was examined systematically (Table 2). All Suzuki–Miyaura reactions of benzyl chlorides with arylboronic acids were carried out using 1:1.2 stoichiometric ratio of benzyl chlorides and arylboronic acids and 1 equiv. of NaO^{t}Bu in ethanol under anhydrous and air-free conditions at 50°C with loading of 1 mol% complex **1** as pre-catalyst (Table 3).

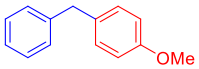
The reactions between benzyl chlorides and arylboronic acids were found to proceed smoothly to afford corresponding coupled products. All reactions were carried out in air operation process. These conditions allowed the coupling of activated and inactivated benzyl chlorides with phenylboronic acid (**10b–e**), cross-coupling combinations between the neutral, activated, inactivated benzyl chloride and mono-*ortho*-substituent and di-*ortho*-substituted arylboronic acids (other case studies presented in Table 3), for a reaction time of 1 h to afford more than 70–96% yields. Only the arylboronic acids having di-*ortho*-substituted functional groups needed a longer time of 7 h to achieve 75% isolated yield (**11d**). This should be attributable to the bulky substrate coordination behaviors inhibiting the palladium activity. In order to determine the catalytic activity of complex **1** in water, three

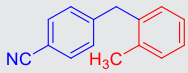
TABLE 3 Scope of benzyl chlorides and phenylboronic acids[a]

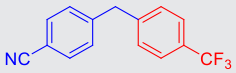


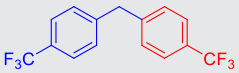

10a, 89% (88%)

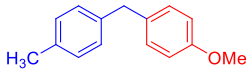

10b, 93% (90%)

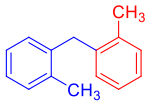

10c, 92%, (90%)

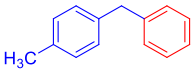

10d, 99% (98%)

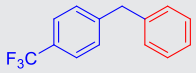

10e, 96% (93%)

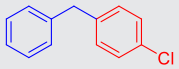

11a, 92% (91%)

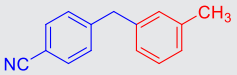

11b, 92% (90%)

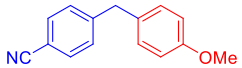

11c, 79% (75%)

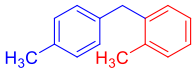

11d, 7 h, 75% (71%)

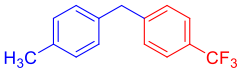

12a, 80% (77%)

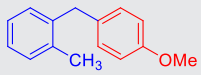

12b, 83% (79%)

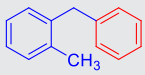

12c, 80% (77%)

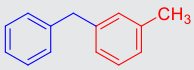

12d, 93% (92%)

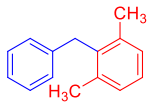

12e, 99% (97%)

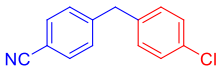

13a, 97% (92%)

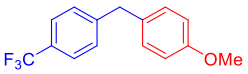

13b, 91% (90%)

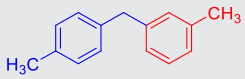

14a, 91% (89%)

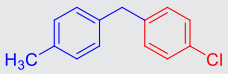

14b, 82% (80%)

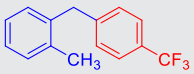

14c, 82% (80%)


14d, 94% (92%)


14e, 75% (70%)


15a, 89%, (88%)


15b, 90%, (87%)


15c, 85%, (82%)

[a]Reaction conditions: 0.5 mmol benzyl chloride, 0.6 mmol arylboronic acid, 1 equiv. NaO^{t}Bu, 1 mol% **1** and 1 ml EtOH.

[b]Determined by GC-MS, average of two runs; values in parentheses refer to isolated yield after column chromatography.

bases (NaO^tBu, KOH, K_2CO_3) were employed to afford 90% yield of product at 50°C (reaction time: for NaO^tBu, 2 h; KOH, 5 h; K_2CO_3, 7 h; see supporting information, Table S2). All experimental results are evidence of the good activity for coupling reactions.

4 | CONCLUSIONS

A series of NHC–palladium(II)–*N*,*N*-dimethylbenzylamine complexes have been prepared and characterized. Newly synthesized complexes **3**–**6** showed moderate activity and complex **1** showed higher catalytic activity in the Suzuki–Miyaura reaction of benzyl chlorides and arylboronic acids than other efficient $(NHC)LPdCl_2$ complexes. This meant fine-tuning the design of complex **1** combining both 2,6-diisopropyl-substituted group on NHC and *N*,*N*-dimethylbenzylamine as the N-donor supported on Pd center leading to high performance in the reaction. Under optimum conditions, complex **1** exhibited good activities for coupling successfully with inactivated benzyl chlorides, mono-*ortho*-substituted benzyl chlorides or both mono-*ortho*-substituted and di-*ortho*-substituted arylboronic acids. Also, this protocol represents a general, practical and user-friendly approach for the preparation of diarylmethanes.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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