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FULL PAPER

Heteroleptic (N-heterocyclic carbene)–Pd–pyrazole (indazole) complexes: Synthesis, characterization and catalytic activities towards C–C and C–N cross-coupling reactions

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Eight heteroleptic palladium complexes containing both N-heterocyclic carbenes and NH-heterocycle azoles (pyrazole and indazole) were synthesized and characterized, and their structures were unambiguously confirmed using single-crystal X-ray diffraction. Further investigation of the complexes as catalysts in the Suzuki–Miyaura reaction and Buchwald–Hartwig amination revealed good reactivities for aryl chlorides.

KEYWORDS

Buchwald–Hartwig amination, N-heterocyclic carbene, NH-heterocycle azoles, palladium complexes, Suzuki–Miyaura reaction

1 | INTRODUCTION

Since the first stable N-heterocyclic carbene (NHC) was isolated in 1991 by Arduengo et al.,[1] NHCs have attracted extensive interest as ligands in coordination catalysis due to the strong σ-donating ability and unique steric demand.[2] Design and synthesis of well-defined NHC complexes have been of continuous interest in organometallic chemistry. Within this realm, the major development has been devoted to NHC–Pd and NHC–Ru complexes due to their high catalytic activities.[3,4] However, mixing of imidazolium salts with Pd catalysts *in situ* sometimes gives different results compared to preformed NHC–Pd complexes.[5] It is necessary to prepare well-defined NHC complexes, which is also important for understanding their catalytic reactivities. Recently, the focus of NHC–Pd complexes has been mainly on the development of more efficient and stable catalysts.[6] In a typical NHC–Pd-catalyzed C─C coupling reaction, the π-electron donating ability of NHC assists the initial reduction and oxidative addition, the steric bulkiness increases the rate of reductive elimination and the σ-donation character facilitates oxidative addition of aryl halides.[7] However, a bulky NHC might also hinder the coordination of incoming substrates to the metal center, decreasing the catalytic activity. In order to improve the activity of an NHC–Pd complex, an external hemilabile donor can be incorporated into the complex. Especially, the external donor allows efficient stabilization of the NHC–Pd, while in the catalytic process the complex could lose the external donor, thus releasing a free coordination site for incoming substrates. In this connection, a series of heteroleptic NHC–Pd complexes with nitrogen donors have been reported and have shown promising catalytic activity in organic transformations.[8] The landmark work involved (NHC)$PdCl_2$(3-chloropyridine) complexes (Pd-PEPPSI-(NHC); PEPPSI = pyridine, enhanced, precatalyst, preparation, stabilization and initiation), which was developed by Organ's group.[8] Although the activity of the NHC–Pd catalyst is mainly dependent on the properties of NHC, the external donor also affects the catalytic activity to some extent. Organ and co-workers reported that (NHC)$PdCl_2$(pyridine) was more active than its 3-chloropyridine analogue.[8] Navarro and co-workers found that (NHC)$PdCl_2$(triethylamine) exhibited a higher catalytic activity at lower temperature, as compared to Pd-PEPPSI-(NHC).[8]

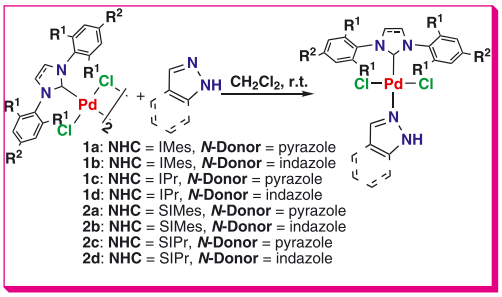
Previous research of N-containing ancillary ligands has mainly focused on the coordination of the nitrogen atom and steric hindrance of the ligands. To the best of our knowledge, N-containing ligands with an active NH group have not been reported up to now, except for morpholine.[8] It is well known that pyrazole and indazole are commercially available and weakly basic NH-heterocycle azoles. However, mixed

carbene/azole complexes are rare in the literature.[9] Herein, we report a facile synthesis of eight (NHC)$PdCl_2$(azole) complexes (azole = pyrazole and indazole) (Scheme 1). In addition, their catalytic activities towards C—C and C—N coupling reactions were preliminarily examined.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and Characterization of (NHC) $PdCl_2$(azole) Complexes

The (NHC)$PdCl_2$(azole) complexes (**1a**–**1d** and **2a**–**2d**) were synthesized by direct cleavage of dimeric compounds [Pd(μ-Cl)(Cl)(NHC)]$_2$ with pyrazole or indazole and a range of expected heteroleptic complexes was achieve: $PdCl_2$(IMes)(pyrazole) (**1a**), $PdCl_2$(IMes)(indazole) (**1b**), $PdCl_2$(IPr)(pyrazole) (**1c**), $PdCl_2$(IPr)(indazole) (**1d**), $PdCl_2$(SIMes)(pyrazole) (**2a**), $PdCl_2$(SIMes)(indazole) (**2b**), $PdCl_2$(SIPr)(pyrazole) (**2c**) and $PdCl_2$(SIPr)(indazole) (**2d**) (IMes = *N*,*N*′-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene; IPr = *N*,*N*′-bis-(2,6-di(isopropyl)phenyl)imidazol-2-ylidene; SIMes = *N*,*N*′-bis-(2,4,6-trimethylphenyl)imidazolidin-2-ylidene; SIPr = *N*,*N*′-bis-(2,6-di(isopropyl)phenyl)imidazolidin-2-ylidene).



SCHEME 1 Synthetic route of the [(NHC)$PdCl_2$(azole)] complexes

Although the frameworks of **1a**–**1d** and **2a**–**2d** are similar to each other, the solubility is significantly different. When the complexes are crystallized from CH_2Cl_2, the solids of the complexes with pyrazole are slightly soluble in common solvents, such as CH_2Cl_2, $CHCl_3$, dimethylformamide, dimethylsulfoxide (DMSO), etc. However, the complexes with indazole could be dissolved in common chlorinated solvents. Based on this, the NMR spectrum of complex **1a** was recorded in CD_2Cl_2, the NMR spectra of **1c** and **2a** were measured in a mixed solvent of CD_2Cl_2–DMSO-d_6 (3:1 *v*/v) and the NMR spectra of **1b**, **1d**, **2b**, **2c** and **2d** were obtained in $CDCl_3$.

The formation of heteroleptic complexes is evident according to the distinctive stoichiometric proton signal resonances of the NHCs and azoles in ^{1}H NMR spectra, especially the appearance of diagnostic NH single peaks (11.51–11.65 ppm) of pyrazole and indazole. In the ^{13}C NMR spectra, the diagnostic peaks of carbene carbons for **1a**–**1d** are in the range 150.6–153.8 ppm, which indicate identical electronic environments around carbene carbons. For the saturated NHC–Pd complexes (**2a**–**2d**), the ^{13}C NMR signals for carbene carbons appear in the range 191.7–194.2 ppm, at lower field relative to their unsaturated counterparts **1a**–**1d**.

2.2 | Crystal Structures

The solid-state structures of the complexes were further characterized using X-ray crystallography. As shown in Figure 1, all complexes are mononuclear structures with each

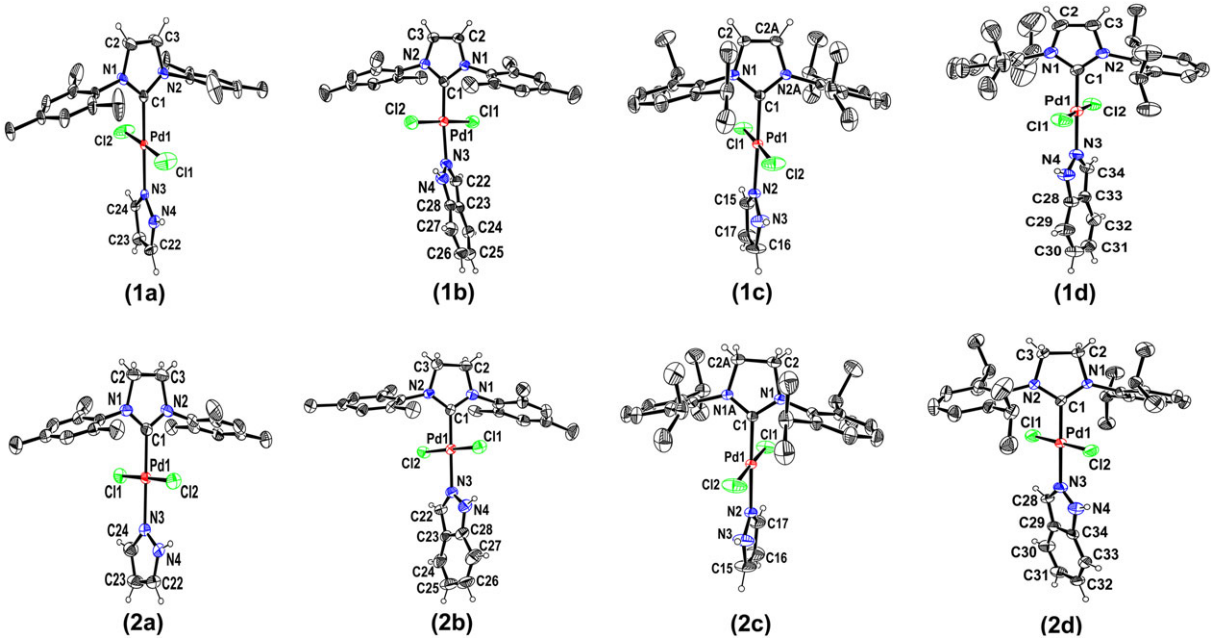


FIGURE 1 ORTEP diagrams of **1a**–**1d** and **2a**–**2d** with thermal displacement parameters drawn at 30% probability. Parts of the hydrogen atoms and solvent molecules have been omitted for clarity. There are two and four independent molecules in a unit cell of the solvates (**1b**)$_2$·CH_2Cl_2 and (**2b**)$_4$·CH_2Cl_2, respectively; only one molecule is shown. Symmetry codes: [A] *x*, 1.5 − *y*, *z*

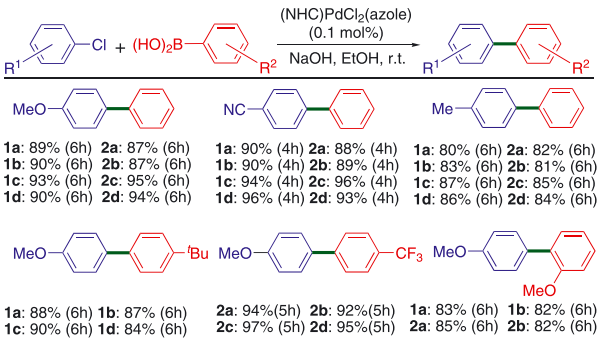
palladium center coordinated by an NHC, an azole ligand and two chlorides in a *trans* arrangement. The carbene ring planes are twisted out of the {$PdCNCl_2$} coordination planes with dihedral angles ranging from 69.76° to 90.00° in order to avoid intra-ligand repulsion. As usual in NHC-bearing complexes, Pd─$C_{carbene}$ distances fall in the range of single bonds (1.949(4)–1.979(7) Å). The azoles are coordinated to Pd centers and tilted by 0–27.24° relative to the {$PdCNCl_2$} coordination planes, while carbene ring planes are oriented approximately perpendicularly to the azoles with dihedral angles in the range 67.38–90.00°. The Pd─N bond distances are in the range 2.069(3)–2.115(3) Å, similar to the related distances in NHC–$PdCl_2$–(N-donor) complexes.

2.3 | Catalytic Investigation

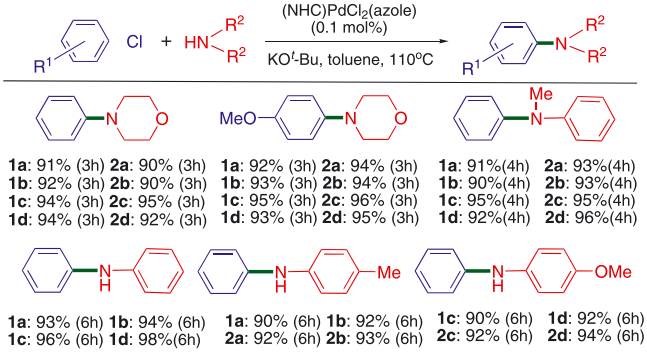
With the obtained (NHC)$PdCl_2$(azole) complexes, their catalytic activities in the Suzuki–Miyaura reaction were firstly investigated. The coupling of 4-chloroanisole with phenylboronic acid was chosen as a model reaction to optimize the reaction conditions. The initial assessment of (NHC)$PdCl_2$(azole) was conducted at a loading of 0.50 mol% with NaOH as the base in ethanol at room temperature, all catalysts showed good catalytic activities. The catalytic properties of the Pd catalysts at lower loading were further investigated. With a catalyst loading of 0.10 mol%, all complexes also displayed high catalytic activities. However, when the catalyst loading was reduced to 0.05 mol%, a significant decrease in catalytic activities was observed. Therefore, 0.10 mol% of (NHC)$PdCl_2$(azole) was found to be the best catalyst loading and was selected for further investigation. Furthermore, the reaction time was also examined. The reaction could be finished in 4–6 h. The catalysts degenerated after 6 h which was consistent with the observation of palladium black deposition. To examine the versatility of this protocol, the (NHC)$PdCl_2$(azole)-catalyzed Suzuki–Miyaura reactions of arylboronic acids with a variety of aryl chlorides were investigated. Under the reaction conditions without further optimization, all (NHC)$PdCl_2$(azole) complexes exhibit good catalytic activities towards both electron-poor and electron-rich aryl chlorides, such as 4-chloroanisole, 4-chlorobenzonitrile and 4-chlorotoluene, providing good yields in most cases (Scheme 2). For the activated substrates, complexes with IPr or SIPr give slightly better catalytic activities than their IMes or SIMes analogues, due to the sterically bulky isopropyl substituent. Moreover, arylboronic acids bearing 4-^{t}Bu and 4-CF_3 substituents could also react with 4-chloroanisole effectively and a highest yield of 97% was achieved. Furthermore, the use of sterically hindered (2-methoxyphenyl) boronic acid allows us to compare the activities of the catalysts towards more resistive coupling. Under the given conditions, (2-methoxyphenyl)boronic acid can be effectively coupled with 4-chloroanisole and the highest yield of 85% was achieved with complex **2a**.

The catalytic activities of (NHC)$PdCl_2$(azole) in Buchwald–Hartwig amination were then examined. According to the general reaction conditions, amination reaction was directly performed in toluene in the presence of KO^{t}Bu at 110 °C. In initial experiments, chlorobenzene and morpholine were used as the coupling partners. All reactions proceeded smoothly and afforded the desired products in good yields and a comparable reactivity in catalytic performance between **1a**–**1d** and **2a**–**2d** was observed (Scheme 3). The reaction time was also screened, and the experimental data indicated that most of the reaction was complete within 3–6 h when 0.1 mol% loading of complexes was used. In order to further examine the catalytic property of the complexes, the coupling reactions of chlorobenzene with aromatic amines, such as *N*-methylaniline, aniline, 4-methylaniline and 4-methoxyaniline, were investigated. The results indicated that (NHC)$PdCl_2$(azole) exhibited good catalytic activities for Buchwald–Hartwig aminations of chlorobenzene with aromatic amines.

In order to investigate the nature of the catalytically active species in the reactions, poisoning experiments were performed. Through addition of Hg (1000 equiv., based upon the catalyst loading) at the start of the reactions, no conversion to products was observed. Poisoning occurred with all



SCHEME 2 Suzuki–Miyaura coupling catalyzed by **1a**–**1d** and **2a**–**2d**. Reaction conditions: aryl chloride (0.50 mmol), arylboronic acid (0.60 mmol), (NHC)$PdCl_2$(azole) (0.0005 mmol), NaOH (1.0 mmol) in EtOH (2.0 ml) at room temperature for 4–6 h. Isolated yields are shown



SCHEME 3 Buchwald–Hartwig amination catalyzed by **1a**–**1d** and **2a**–**2d**. Reaction conditions: aryl chloride (0.50 mmol), amine (0.60 mmol), (NHC)$PdCl_2$(azole) (0.0005 mmol), KO^{t}Bu (0.75 mmol) in toluene (2.0 ml) at 110 °C for 3–6 h. Isolated yields are shown

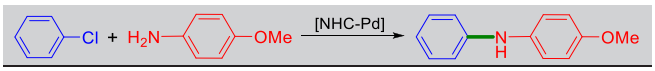
catalysts. Moreover, in order to obtain more information about the heterogeneity of the active species, in a second experiment, Hg was added 1 h after the coupling reaction was started. The reaction was then stirred for an additional 5 h. No further conversion to the desired products took place after the addition of Hg. These results further indicate the heterogeneous character (Pd nanoparticles) of the catalytically active species. Furthermore, the recyclability of the catalysts was investigated. After carrying out the reaction, the catalysts were separated by centrifugation and washed with ethanol. The recovered catalysts were used in the next run; unfortunately, only trace amount of product was observed, indicating palladium black deposition in the reactions.

Finally, a comparison of the catalytic activities between some well-defined IPr–Pd complexes and **1c** and **1d** was conducted. The coupling of chlorobenzene with 4-methoxyaniline was chosen as a model reaction. As evident from Table 1, complexes **1c** and **1d** show a similar level of catalytic activity compared with (IPr)$PdCl_2$(3-chloropyridine), but a slightly higher activity in comparison with the dimer [Pd(μ-Cl)(Cl)(IPr)]$_2$. However, there is no advantage in catalyst amount and reaction activity compared to the recently reported NHC–Pd complexes with 1-methylindazole and 1-methylpyrazole.[9] As ancillary ligands, the pyrazole and indazole indeed alter the σ-donation property of the NHC. However, there seems to be little difference in catalytic activities between the two kinds of complexes due to the same coordination abilities of pyrazole and indazole to the palladium center. Moreover, the NH groups in the azoles do not facilitate the catalytic activities of the complexes as precatalysts for the reactions. The real role of the nitrogen donors in the catalytic process needs to be further investigated.

3 | CONCLUSIONS

In summary, we have prepared eight (NHC)$PdCl_2$(azole) complexes via incorporating pyrazole and indazole as ancillary ligands. The obtained complexes exhibited good catalytic activities in the Suzuki–Miyaura reaction and Buchwald–Hartwig amination for aryl chlorides. As analogues of Pd-PEPPSI-(NHC) catalysts, these kinds of (NHC)$PdCl_2$(azole) complexes would have potential applications in organic synthesis which are currently under investigation in our laboratory.

TABLE 1 Buchwald–Hartwig amination catalyzed by selected NHC–Pd catalysts[a]



Entry	Catalyst	Yield (%)[b]
1	**1c**	90
2	**1d**	92
3	(IPr)$PdCl_2$(3-chloropyridine)	88
4	(IPr)$PdCl_2$(1-methylindazole)	95
5	(IPr)$PdCl_2$(1-methylpyrazole)	95
6[c]	[Pd(μ-Cl)(Cl)(IPr)]$_2$	82

[a]Reaction conditions: aryl chloride (0.50 mmol), amine (0.60 mmol), NHC–Pd (0.0005 mmol), KO^{t}Bu (0.75 mmol) in toluene (2.0 ml) at 110 °C for 6 h.

[b]Isolated yield.

[c]Amount of catalyst was 0.05 mol%.

4 | EXPERIMENTAL

4.1 | General Remarks

Chemicals were purchased from commercial suppliers and were used without further purification. NMR spectra were recorded at 400 MHz (for ^{1}H NMR) and 100 MHz (for ^{13}C NMR) with a Bruker Avance 400 NMR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained with samples in CD_2Cl_2, $CDCl_3$ or CD_2Cl_2–DMSO-d_6 with tetramethylsilane as an internal standard. Infrared (IR) spectra were recorded with a Bruker IFS 120HR spectrometer using KBr discs. C, H and N analyses were performed with a Vario El III Elementar. Flash column chromatography was carried out using 300–400 mesh silica gel. The dimeric compounds [Pd(μ-Cl)(Cl)(NHC)]$_2$ were prepared according to a report in the literature.[10]

4.2 | Synthesis of Complexes 1a–1d and 2a–2d

A mixture of dimeric complex [Pd(μ-Cl)(Cl)(NHC)]$_2$ (0.10 mmol) and the appropriate pyrazole or indazole ligand (0.20 mmol) was dissolved in CH_2Cl_2 (5.0 ml). After stirring for 12 h at room temperature, the solvent was reduced under vacuum and the resulting residue was washed with ether to give a yellow solid. Single crystals of the complexes for X-ray diffraction analysis were obtained from evaporation of their *n*-hexane–CH_2Cl_2 solutions.

4.2.1 | [(IMes)$PdCl_2$(pyrazole)] (1a)

The procedure yielded 94 mg (85%) of pure **1a** as a yellow powder. ^{1}H NMR (CD_2Cl_2, 400 MHz, δ, ppm): 11.65 (s, 1H, NH), 7.88 (s, 1H), 7.41 (s, 1H), 7.14 (s, 2H), 7.09 (s, 4H), 6.22 (s, 1H), 2.40 (s, 6H, *p*-CH_3), 2.39 (s, 12H, *o*-CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz, δ, ppm): 150.8 ($C_{carbene}$), 139.3, 138.5, 136.3, 135.2, 129.1, 128.6, 124.5, 105.7, 20.9 (*p*-CH_3), 18.8 (*o*-CH_3). IR (KBr, cm^{-1}): 3290, 2957, 2917, 1606, 1486, 1471, 1410, 1355, 1229, 1130, 1061, 950. Calcd for [(IMes)$PdCl_2$(pyrazole)] ($C_{24}H_{28}Cl_2N_4Pd$) (%): C, 52.43; H, 5.13; N, 10.19. Found (%): C, 52.67; H, 5.37; N, 10.41.

4.2.2 | [(IMes)$PdCl_2$(indazole)] (1b)

The procedure yielded 106 mg (88%) of pure **1b** as a yellow powder. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 11.56 (s, 1H, NH), 8.45 (s, 1H), 7.59–7.57 (m, 1H), 7.35–7.31 (m, 1H), 7.28–7.26 (m, 1H), 7.10 (br, 2H), 7.06 (br, 5H), 2.40

(s,12H, *o*-CH_3), 2.36 (s, 6H, *p*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 150.6 ($C_{carbene}$), 139.2, 138.6, 136.1, 134.9, 129.2, 128.2, 124.3, 122.0, 121.5, 121.2, 109.8, 21.1 (*p*-CH_3), 19.0 (*o*-CH_3). IR (KBr, cm^{-1}): 3290, 2918, 1626, 1485, 1471, 1412, 1376, 1354, 1245, 1230, 1092, 953, 858. Calcd for [(IMes)$PdCl_2$(indazole)] ($C_{28}H_{30}Cl_2N_4Pd$) (%): C, 56.06; H, 5.04; N, 9.34. Found (%): C, 56.22; H, 4.93; N, 9.45.

4.2.3 | [(IPr)$PdCl_2$(pyrazole)] (1c)

The procedure yielded 114 mg (90%) of pure **1c** as a yellow powder. ^{1}H NMR (CD_2Cl_2–DMSO-d_6 (3:1 *v*/v), 400 MHz, δ, ppm): 12.01 (s, 1H, NH), 7.75–7.73 (m, 1H), 7.49–7.31 (m, 9H), 6.15–6.13 (m, 1H), 3.09 (sept, J = 6.4 Hz, 4H, C*H*(CH_3)$_2$), 1.38 (d, J = 6.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.09 (d, J = 6.0 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2–DMSO-d_6 (3:1 *v*/v), 100 MHz, δ, ppm): 152.4 ($C_{carbene}$), 146.2, 138.0, 134.7, 129.4, 129.4, 125.4, 123.2, 104.5, 27.9 (*C*H(CH_3)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 22.4 (CH(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 3290, 3132, 2957, 2917, 1606, 1486, 1410, 1355, 1229, 1165, 1130, 1061, 1047, 856. Calcd for [(IPr)$PdCl_2$(pyrazole)] ($C_{30}H_{40}Cl_2N_4Pd$) (%): C, 56.83; H, 6.36; N, 8.84. Found (%): C, 57.04; H, 6.07; N, 8.62.

4.2.4 | [(IPr)$PdCl_2$(indazole)] (1d)

The procedure yielded 120 mg (88%) of pure **1d** as a yellow powder. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 11.59 (s, 1H, NH), 8.45 (s, 1H), 7.59–7.57 (m, 1H), 7.53–7.50 (m, 2H), 7.38–7.36 (m, 4H), 7.33–7.31 (m, 1H), 7.28–7.26 (m, 1H), 7.19 (br, 2H), 7.09–7.05 (m, 1H), 3.19 (sept, J = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 1.51 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.16 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 153.2 ($C_{carbene}$), 146.6, 138.6, 134.8, 134.5, 130.2, 128.1, 125.2, 124.0, 122.1, 121.4, 121.2, 109.8, 28.7 (*C*H(CH_3)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 3290, 3118, 2917, 2866, 1627, 1577, 1483, 1470, 1432, 1383, 1362, 1232, 1087, 998, 911. Calcd for [(IPr)$PdCl_2$(indazole)] ($C_{34}H_{42}Cl_2N_4Pd$) (%): C, 59.70; H, 6.19; N, 8.19. Found (%): C, 59.45; H, 5.99; N, 8.26.

4.2.5 | [(SIMes)$PdCl_2$(pyrazole)] (2a)

The procedure yielded 93 mg (85%) of pure **2a** as a yellow powder. ^{1}H NMR (CD_2Cl_2–DMSO-d_6 (3:1 *v*/v), 400 MHz, δ, ppm): 11.40 (s, 1H, NH), 7.19 (s, 1H), 6.93 (s, 1H), 6.44 (s, 4H), 5.61 (s, 1H), 4.93 (s, 4H), 1.98 (s, 6H, *p*-CH_3), 1.77 (s, 12H, *o*-CH_3). ^{13}C NMR (CD_2Cl_2–DMSO-d_6 (3:1 *v*/v), 100 MHz, δ, ppm): 181.8 ($C_{carbene}$), 137.8, 137.4, 136.5, 134.5, 129.1, 128.6, 104.5, 50.5, 20.1 (*p*-CH_3), 18.4 (*o*-CH_3). IR (KBr, cm^{-1}): 3347, 2922, 1628, 1491, 1455, 1436, 1375, 1310, 1268, 1246, 1025, 949, 842. Calcd for [(SIMes)$PdCl_2$(pyrazole)] ($C_{24}H_{30}Cl_2N_4Pd$) (%): C, 52.23; H, 5.48; N, 10.15. Found (%): C, 52.41; H, 5.66; N, 10.33.

4.2.6 | [(SIMes)$PdCl_2$(indazole)] (2b)

The procedure yielded 108 mg (90%) of pure **2b** as a yellow powder. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 11.52 (s, 1H, NH), 8.40 (s, 1H), 7.57–7.55 (m, 1H), 7.33–7.30 (m, 1H), 7.26–7.24 (m, 1H), 7.08–7.04 (m, 1H), 7.01 (br, 4H), 4.05 (s, 4H, NC*H*$_2$C*H*$_2$N), 2.61 (s, 12H, *o*-CH_3), 2.31 (s, 6H, *p*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 182.5 ($C_{carbene}$), 138.4, 136.9, 134.7, 134.4, 129.7, 129.5, 128.1, 122.0, 121.4, 121.2, 109.7, 51.1 (N*C*H$_2$*C*H$_2$N), 21.0 (*p*-CH_3), 19.2 (*o*-CH_3). IR (KBr, cm^{-1}): 3313, 2920, 1628, 1493, 1456, 1308, 1272, 1244, 955, 843. Calcd for [(SIMes)$PdCl_2$(indazole)] ($C_{28}H_{32}Cl_2N_4Pd$) (%): C, 55.87; H, 5.36; N, 9.31. Found (%): C, 56.03; H, 5.61; N, 9.22.

4.2.7 | [(SIPr)$PdCl_2$(pyrazole)] (2c)

The procedure yielded 115 mg (90%) of pure product **2c** as a yellow powder. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 11.56 (s, 1H, NH), 7.85(s, 1H), 7.44–7.2740 (m, 2H), 7.31–7.27 (m, 5H), 6.12(s, 1H), 4.07 (s, 4H, NCH_2CH_2N), 3.57 (sept, J = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 1.54 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.28 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 185.0 ($C_{carbene}$), 147.4, 138.7, 135.2, 129.3, 127.9, 124.3, 105.4, 53.7 (N*C*H$_2$*C*H$_2$N), 28.6 (*C*H(CH_3)$_2$), 26.7 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 3280, 2966, 1637, 1478, 1455, 1384, 1361, 1267, 1130, 1054, 1017, 801. Calcd for [(SIPr)$PdCl_2$(pyrazole)] ($C_{30}H_{42}Cl_2N_4Pd$) (%): C, 56.65; H, 6.66; N, 8.81. Found (%): C, 56.45; H, 6.33; N, 8.56.

4.2.8 | [(SIPr)$PdCl_2$(indazole)] (2d)

The procedure yielded 110 mg (80%) of pure **2d** as a yellow powder. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 11.56 (s, 1H, NH), 8.42 (s, 1H), 7.58–7.56 (s, 1H), 7.45–7.42 (m, 2H), 7.33–7.25 (m, 6H), 7.08–7.05 (m, 1H), 4.12 (s, 4H, NCH_2CH_2N), 3.62 (sept, J = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 1.58 (d, J = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.31 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 184.6 ($C_{carbene}$), 147.5, 138.6, 135.1, 134.4, 129.4, 128.1, 124.4, 122.1, 121.4, 121.2, 109.9, 53.8 (NCH_2CH_2N), 28.7 (*C*H(CH_3)$_2$), 26.7 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 3341, 2960, 2866, 1627, 1510, 1480, 1452, 1383, 1359, 1300, 1270, 1241, 1094, 1053, 962. Calcd for [(SIPr)$PdCl_2$(indazole)] ($C_{34}H_{44}Cl_2N_4Pd$) (%): C, 59.52; H, 6.46; N, 8.17. Found (%): C, 59.34; H, 6.77; N, 8.36.

4.3 | General Procedure for [(NHC)$PdCl_2$(azole)]-Catalyzed Suzuki–Miyaura Reaction

A sealable reaction tube was charged with aryl chloride (0.50 mmol), arylboronic acid (0.60 mmol), [(NHC)$PdCl_2$(azole)] (0.0005 mmol), NaOH (1.0 mmol) and EtOH (2.0 ml). The mixture was stirred at room temperature for 6 h. The filtrate was then concentrated and the residue was

subjected to purification via flash column chromatography to give the pure product.

4.4 | General Procedure for [(NHC)$PdCl_2$(azole)]-Catalyzed Buchwald–Hartwig Amination

A sealable reaction tube was charged with aryl chloride (0.50 mmol), amine (0.60 mmol), KO^{t}Bu (0.75 mmol), [(NHC)$PdCl_2$(azole)] (0.0005 mmol) and toluene (2.0 ml). The mixture was heated at 110 °C for 6 h. After cooling to room temperature, the filtrate was concentrated and the residue was subjected to purification via flash column chromatography to give the pure product.

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