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Highly Active, Well-Defined (Cyclopentadiene)(N-heterocyclic carbene)palladium Chloride Complexes for Room-Temperature Suzuki–Miyaura and Buchwald–Hartwig Cross-Coupling Reactions of Aryl Chlorides and Deboronation Homocoupling of Arylboronic Acids

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Abstract: A new class of well-defined N-heterocyclic carbene (NHC)-(cyclopentadiene)palladium chloride complexes such as CpPd(NHC)Cl wasw synthesized from the readily available starting NHC-palladium(II) chloride dimers. These air-stable, coordinatively saturated NHC-Pd complexes bearing the cyclopentadiene (Cp) unit exhibit high catalytic activity in the room temperature Suzuki–Miyaura and Buchwald–Hartwig cross-coupling reactions involving unactive aryl chlorides as the substrates. In addition, they are found to be extremely efficient catalysts in the deboronation homocoupling of arylboronic acids at room temperature.

Keywords: cross-coupling; homocoupling; N-heterocyclic carbenes; palladium

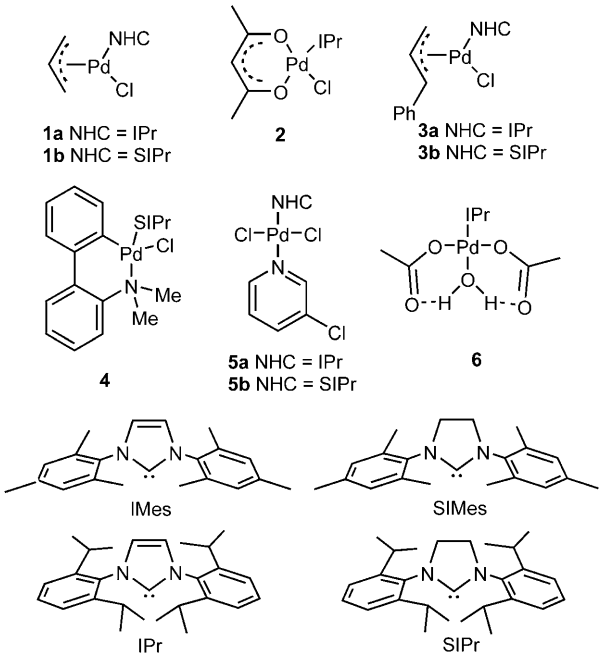
Introduction

Transition metal-mediated cross-coupling reactions are one of the most powerful tools and widely used methods to construct C–C or C–heteroatom bonds.[1] Among them, the Suzuki–Miyaura reaction,[2] involving the coupling between an aryl halide and an organoboron reagent catalyzed by a palladium/ligand system, has emerged as a captivating means for synthesis of biaryl compounds due to their air- and moisture-stable properties, low toxicity, tolerance towards an extensive range of functional groups, and easy preparation of the corresponding organoboron reagents. A great number of catalytic systems has been developed for effecting the coupling of the aryl bromides and iodides with the arylboronic acids during the past two decades. In view of the wide diversity, ready availability and low cost of aryl chlorides relative to aryl bromides and iodides, the use of aryl chlorides as the coupling substrates remains as the very attractive target.[3] Although giant efforts utilizing active and unactive aryl chlorides as the substrates have been made by employing various electron-rich, bulky tertiary phosphines as the ligands,[4] to maintain an efficiently catalytic transformation, usually an excess of the costly tertiary phosphine ligands in these Pd/ligand catalytic system is required.[5] Additionally, their extreme air-sensitivity and degradable properties at high temperature,[6] along difficulties with the removal of phosphine ligand and ligand decomposition by-product , have seriously limited their application in the fine chemical and pharmaceutical industries.

Over the past decade, application of N-heterocyclic carbenes as supporting ligands in transition metal-mediated homogeneous catalysis has become increasingly popular.[7] Because of the bulky substituents on the imidazole nitrogens, higher thermal stability and better σ-donating properties relative to the common tertiary phosphine ligands, which are in favour of the oxidative-addition and reductive-elimination steps of the cross-coupling catalytic cycle, N-heterocyclic carbenes have proven to be excellent alternatives in numerous transition metal-catalyzed cross-coupling reactions involving tertiary phosphines. Well-defined

NHC-containing palladium(II) precatalysts,[8] in addition to the above-mentioned inherent merits of NHC ligands, consist of an accurate ratio (optimally 1:1) of the Pd/ligand that avoids the use of excess costly ligand. Particularly, the NHC-Pd complexes with a ratio close to 1 of the Pd/ligand generally exhibit enhanced reactivity associated with the formation of a highly active monoligated [Pd(0)L] species.[9]

Recently, several types of air-stable, well-defined NHC-Pd complexes such as (NHC)Pd(allyl)Cl **1**,[10] (NHC)Pd(acac)Cl **2**,[11] (NHC)Pd(cinnamyl)Cl **3**,[12] NHC-containing N-C-palladacycle **4**,[13] PEPPSI **5**[14] and $Pd(OAc)_2(IPr)(H_2O)$ **6**[15] have been developed (Scheme 1), and these complexes were found to be high active precatalysts in various cross-coupling reactions including the Suzuki–Miyaura, Negishi, Kumada–Tamao–Corriu, Buchwald–Hartwig reactions, and the arylation of ketones. All these NHC-Pd(II) species, bearing one dominant NHC ligand, two anionic ligands, and/or other neutral 'throw-away' ligands (such as 3-chloropyridine in PEPPSI), exhibit a 1:1 ratio of the NHC ligand/Pd. These precatalysts were thought to be activated through various pathways,[10a,13c,14d] liberating in all cases an active [(NHC)Pd(0)] species into the catalytic cycle. Besides the dominant NHC ligand, another ancillary ligation is also crucial to their catalytic performance. Indeed, (NHC)Pd(allyl)Cl **1** required activation at 70 °C to perform effectively in aryl aminations, while the corresponding (NHC)Pd(cinnamyl)Cl **3** could be easily activated at room temperature,[12a] leading to an increased concentration of catalytically active Pd(0) species. To the best of our knowledge, there are not many Cp-Pd complexes known to date. In view of extreme sensitivity of the Cp ring to reductive removal from the Cp-Pd complexes and in order to develop easily-activated, highly active, well-defined NHC-Pd(II) precatalysts, we have focused our efforts on synthesis of new Cp-containing NHC-Pd(II) complexes. These CpPd(NHC)Cl precatalysts can be easily activated at room temperature to produce the desired active catalyst [(NHC)Pd(0)], exhibiting very high activity in the C–C and C–N cross-coupling reactions involving an aryl chloride as one of the coupling partners. Additionally, they are found to be extremely efficient catalysts in the deboronation homocoupling of arylboronic acids at room temperature. We herein report the synthesis and structure of these NHC-Pd(II) complexes, as well as their catalytic activity in the C–C and C–N bond formation reactions.

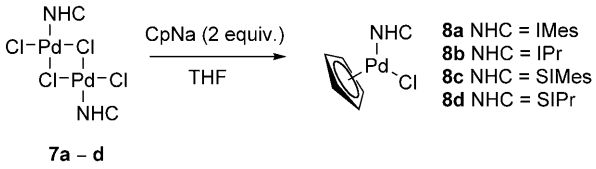


Scheme 1. Well-defined NHC-Pd complexes.

Results and Discussion

Synthesis of CpPd(NHC)Cl Complexes 8a–d

As shown in Scheme 2, in a very straightforward manner, by treating the requisite NHC-$PdCl_2$ dimers **7a–d** at room temperature with two equivalents of



Scheme 2. Synthesis of CpPd(NHC)Cl complexes

freshly prepared CpNa (CpNa = sodium cyclopentadienylide) in a solution of tetrahydrofuran (THF), the desired Cp-containing NHC-Pd complexes, CpPd(IMes)Cl **8a**, CpPd(IPr)Cl **8b**, CpPd(SIMes)Cl **8c**, and CpPd(SIPr)Cl **8d**, were conveniently obtained in generally excellent yields (95–98%). The starting NHC-$PdCl_2$ dimers **7** could be readily prepared either from $PdCl_2(PhCN)_2$ through the direct displacement of nitrile ligands with the free carbenes,[16] or from $[Pd(\eta^3\text{-allyl})Cl]_2$ dimer *via* a two-step sequence with high overall yields.[17] Once the CpPd complexes are formed, the work-up and crystallization can be performed in air without any disadvantageous impact on yield. Although these CpPd(NHC)Cl complexes were found to decompose gradually in solution, they exhibit enough stability in air, thus allowing for indefinite storage and easy handling. The proposed structures for them were firmly supported by the ^1H and

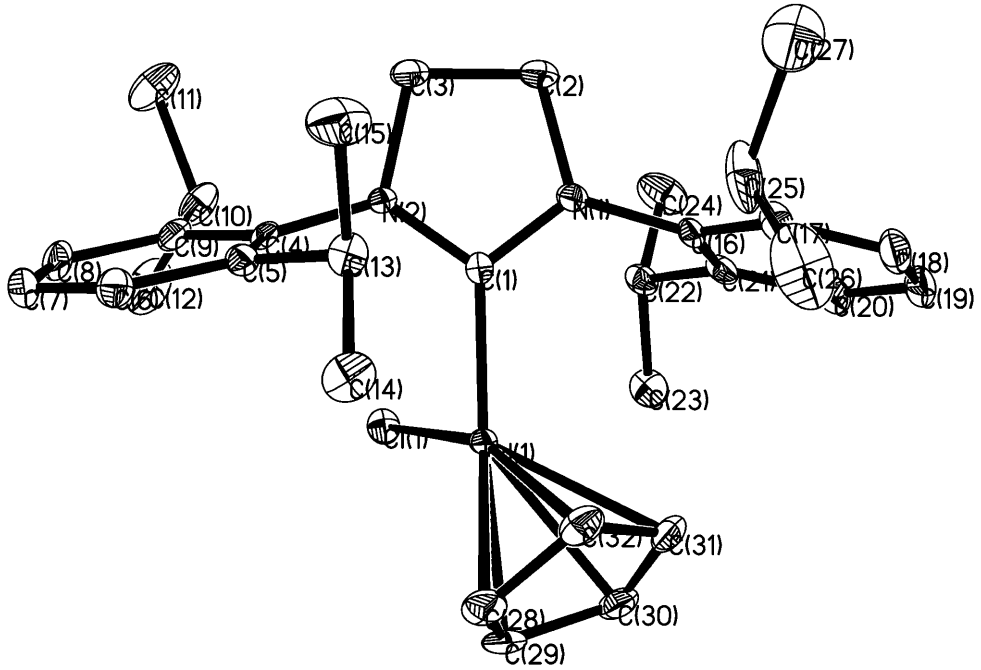


Figure 1. The crystal structure of complex **8d** (all hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: Pd–C(1) 1.977(2), Pd–C(28) 2.292(3), Pd–C(29) 2.290(2), Pd–C(30) 2.445(3), Pd–C(31) 2.401(3), Pd–C(32) 2.209(3), Pd–Cl(1) 2.3257(7); N(1)–C(1)–N(2) 107.90(19), N(1)–C(1)–Pd 125.32(17), N(2)–C(1)–Pd 126.34(17), C(1)–Pd-–(28) 135.04(9), C(1)-Pd-Cl(1) 90.62(6).

^{13}C NMR spectral data which show one carbene ligand, and one characteristic η^5-bonded cyclopentadienyl ligand. To further confirm the structures of this family of complexes, suitable crystals for single-crystal X-ray diffraction analysis of compounds **8a**, **8b**, and **8d** were obtained by slow diffusion of *n*-pentane into ether solution.[18] Representatively, the crystal structure of **8d** reveals η^5-coordination of the Cp ring, opposite to the Cl atom, around the Pd center (Figure 1).

Study of the Catalytic Activity of CpPd(NHC)Cl Complexes in the Suzuki–Miyaura Reaction

Using 4-methylphenylboronic acid and 4-chloroanisole as the coupling partners, the catalytic activity of this class of NHC-Pd complexes **8a–d** in the Suzuki–Miyaura cross-coupling reaction was examined intensively. Based on the extensive screen, 2-propanol and KO-*t*-Bu are found to be the most efficient solvent and base, thus giving the optimal coupling results. Under the optimal reaction conditions, to our delight, all four Cp-containing NHC-Pd complexes can be easily activated at room temperature and allow for the coupling to proceed in high yield at room temperature (Figure 2). Among them, CpPd(IPr)Cl **8b** and CpPd(SIPr)Cl **8d** each afforded a 100% conversion for the corresponding aryl chloride within 2 h at a 1 mol% catalyst loading. Additionally, it is notable that, just as reported previously,[12a,13c] the use of common reagent grade 2-propanol has no obvious deterious influence on the coupling yields.

As mentioned above, besides the NHC ligands, other ancillary ligands in the well-defined NHC-Pd complexes have much to do with their catalytic performance in the cross-coupling reactions.[8a] A variety of well-defined NHC-Pd complexes **1–5** therefore wase synthesized according to the literature methods[10–14] and the effect of ancillary ligands on the catalytic activity in the Suzuki–Miyaura reaction was evaluated. As shown in Figure 2, (NHC)Pd(acac)Cl **2** and NHC-$PdCl_2$ dimer **7** cannot catalyze the coupling reaction at room temperature. Although (NHC)Pd(allyl)Cl **1** afforded no more than a 10% yield for the coupling reaction, by simple change of the allyl group with the cinnamyl group, the resulting (NHC)Pd(cinnamyl)Cl **3** can be easily activated at room temperature and provides a 100% conversion for aryl chloride within 2 h. Additionally, NHC-containing palladacycle **4** and pyriding-containing complexes **5** were found to exhibit predominant catalytic activity in the coupling reaction. Compared with above-mentioned NHC-Pd complexes, the CpPd(NHC)Cl complexes, especially **8b** and **8d**, have also proven to be highly efficient catalysts for the Suzuki–Miyaura cross-coupling reactions at room temperature.

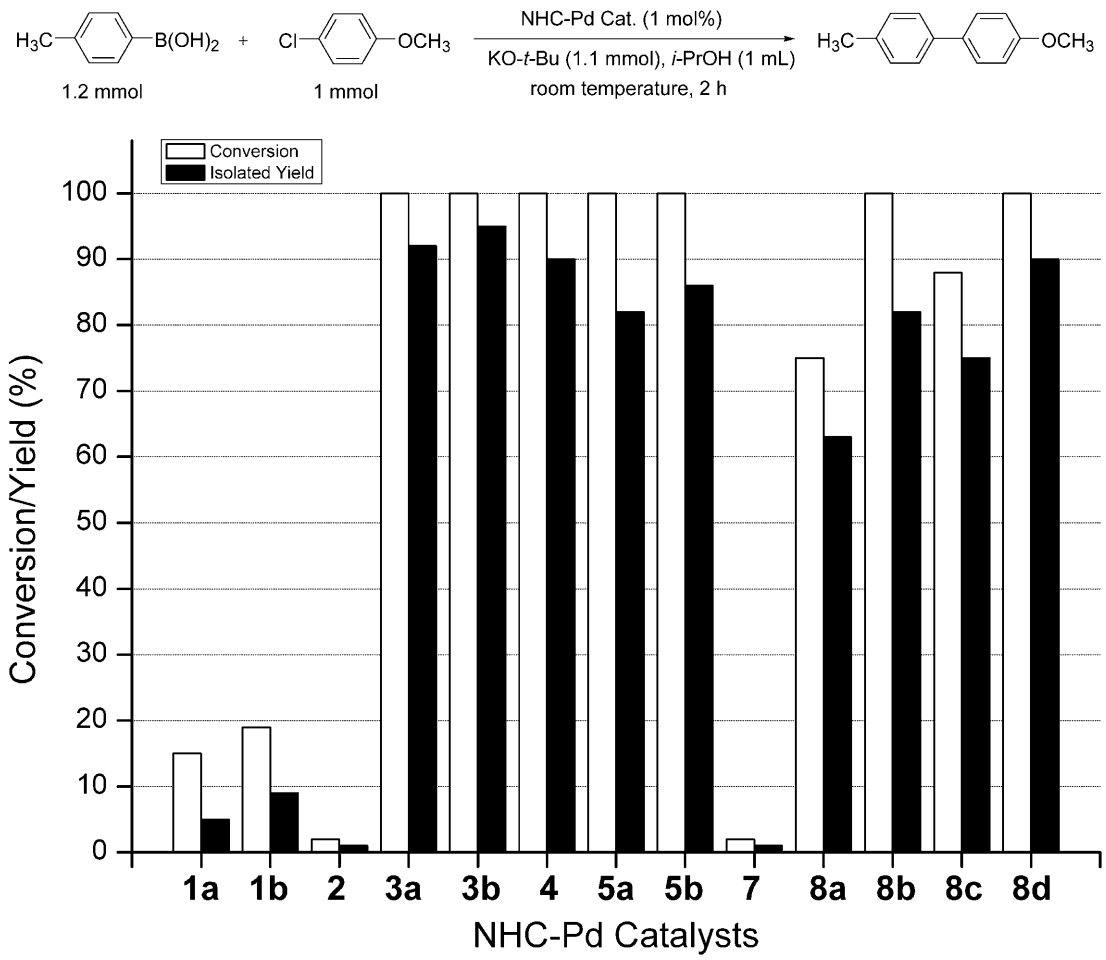


Figure 2. Effect of ancillary ligands on catalytic performance in the Suzuki–Miyaura coupling reaction. Conversion ratios were determined by a GC/MS method using undecane as internal standard. Isolated yields were reported as an average of two experiments. Reagent grade 2-propanol was used. For NHC-$PdCl_2$ dimer **7**, NHC = SIPr.

Encouraged by these promising early results, to further validate the catalytic utility of the Cp-containing NHC-Pd complexes, we then submitted the complexes to the Suzuki–Miyaura reaction involving a variety of arylboronic acids and unactive aryl chlorides. As expected, in all cases unactive aryl chlorides coupled smoothly with the arylboronic acids at room temperature in high yields using **8d** as the catalyst at a 1 mol% loadings (Table 1). It is noteworthy that sterically hindered aryl chlorides and/or arylboronic acids could be effectively coupled under the reaction conditions (Table 1, entries 7, 9, 11, and 12), indicating that di- and tri-*ortho*-substituted biaryls can be readily synthesized by utilizing the present catalytic system. However, it is somewhat disappointing that the coupling of 2-substituted 1-halonaphthalene with 2-methyl-1-naphthaleneboronic acid affords the desired *tert-ortho*-substituted biaryls in poor yields at room temperature even with higher catalyst loadings and prolonged reaction times (Table 1, entry 13).

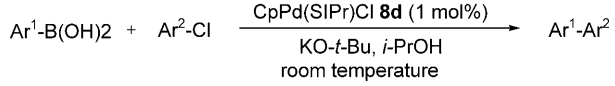
Study of the Deboronation Homocoupling of Arylboronic Acids Catalyzed by CpPd(NHC)Cl Complexes

In our initial experiments on the Suzuki–Miyaura coupling reaction, we observed the formation, to various extents depending on the CpPd(NHC)Cl complexes used, of the corresponding deboronation homocoupling products from the arylboronic acids (Table 2). With CpPd(IMes)Cl **8a** as the precatalyst, the symmetric biaryl was obtained as a side product in a yield of 15% (Table 2, entry 1). The Pd-mediated deboronation homocoupling[19] of arylboronic acids provides an efficient, straightforward method to synthesize symmetrical biaryls, which are present widely in natural products, electronic materials, liquid crystals, find use as chiral ligands employed in homogeneous catalysis, and are active pharmaceutical ingredients. Additionally, other transition metals, such as Rh,[20] Au,[21] V,[22] Cu,[23] and Cr,[24] can be used to me-

diate biaryl formation from the corresponding arylboronic acids *via* a deboronation homocoupling pathway. However, as far as we know, no reports on the deboronation homocoupling of arylboronic acids catalyzed by NHC-Pd complexes have appeared to date.

To further investigate the behavior of this family of Cp-containing NHC-Pd complexes in the homocoupling reaction, a variety of arylboronic acids bearing different groups and substituted patterns, in conjugation with different CpPd(NHC)Cl complexes **8a–d**, were subject to the deboronation homocoupling reac-

Table 1. Suzuki–Miyaura cross-coupling reactions of aryl chlorides at room temperature.[a]



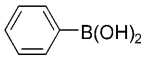
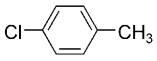
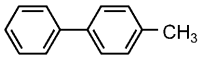
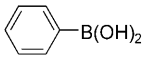
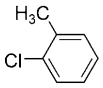
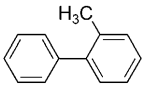
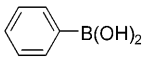
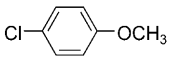
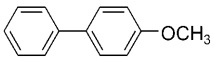
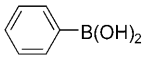
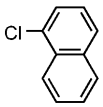
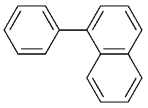
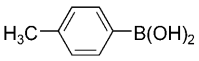
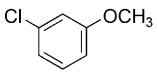
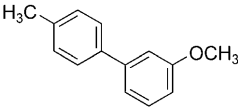
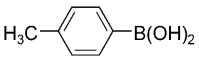
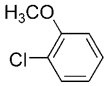
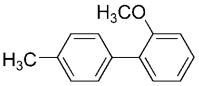
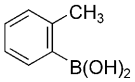
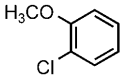
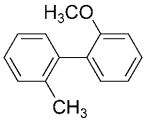
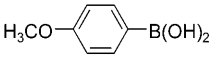
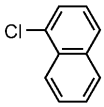
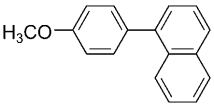
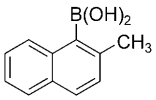
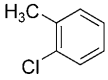
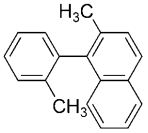
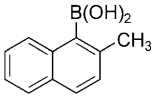
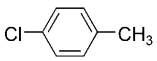
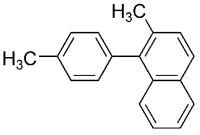
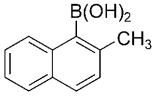
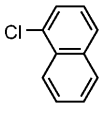
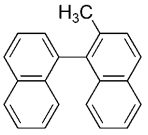
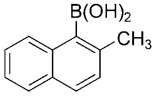
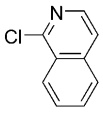
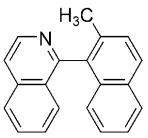
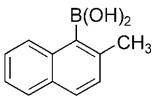
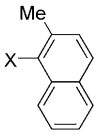
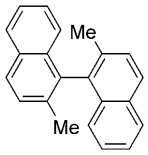
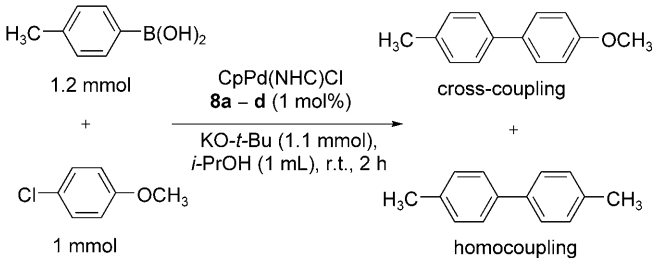
Entry	Ar^1-B(OH)$_2$	Ar^2Cl	Product	Yield [%][b]
1				92[c]
2				88
3				94[c]
4				89
5				96[c]
6				88
7				84
8				87
9				79[d]
10				82
11				75[d]
12				69[d]

Table 1. (Continued)

Entry	Ar^1-B(OH)$_2$	Ar^2Cl	Product	Yield [%][b]
13				X = Br, 12[e]; X = I, 17[e]

[a] *Reaction conditions:* aryl chloride (1 mmol); arylboronic acid (1.2 mmol); CpPd(SIPr)Cl **8d** (1 mol%); KO-*t*-Bu (1.1 mmol); reagent grade 2-propanol (1 mL); T = room temperature (23 °C); Reaction time t = 20 h. Reaction time was not optimized.
[b] Isolated yields upon an average of two runs.
[c] Reaction time t = 12 h.
[d] 1.5 mmol arylboronic acid were used.
[e] 2 mmol 2-methyl-1-naphthaleneboronic acid and 2 mol% CpPd(SIPr)Cl **8d** were used; Reaction time t = 36 h.

Table 2. Homocoupling side reactions of arylboronic acids in the cross-coupling reaction.



Entry	NHC-Pd catalyst	Yield [%][a,b]	
		Cross-coupling reaction	Homocoupling reaction
1	**8a**	65	15
2	**8b**	82	7
3	**8c**	75	11
4	**8d**	90	5

[a] Isolated yields, as an average of two runs.
[b] Reagent grade 2-propanol was used.

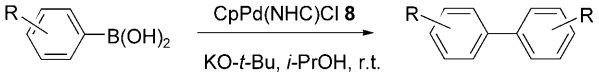
tion. Results from the tests are outlined in Table 3. Among the four Cp-containing NHC-Pd complexes, SIPr performs best in the homocoupling reaction of phenylboronic acid at room temperature (Table 3, entry 4). For extensively substituted arylboronic acids, the yields obtained depended highly on the steric factors of substitutents when CpPd(SIPr)Cl **8d** was used as the catalyst. In all cases, *p*- and *m*-substituted arylboronic acids gave the corresponding biaryls in excellent yields, while a poor yield was obtained for *o*-methylphenylboronic acid. Furthermore, no homocoupling product was observed for 2-methyl-1-naphthylboronic acid and only 15% deboronation product was identified along with most recovered arylboronic acid (Table 3, entry 10). In contrast, with 2-methoxy-1-naphthylboronic acid, 2-methoxynaphthelene was isolated in almost quantitative yield under the same reaction conditions (Table 3, entry 11), suggesting that *o*-methoxy group has an accelerating effect on the deboronation of arylboronic acid.

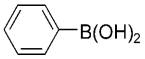
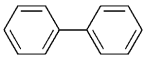
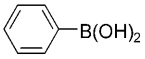
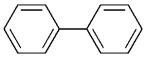
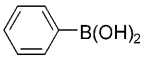
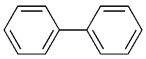
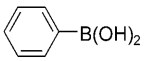
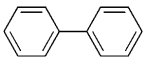
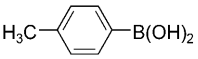
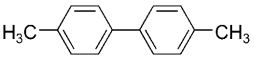
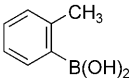
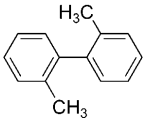
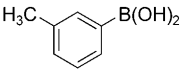
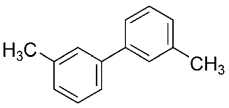
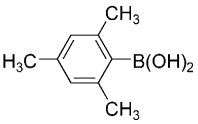
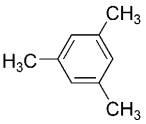
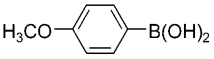
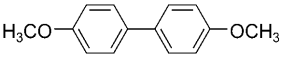
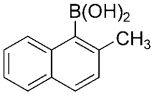
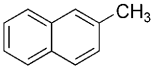
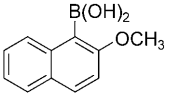
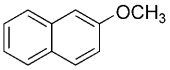
Study of the Catalytic Activity of CpPd(NHC)Cl Complexes in the Buchwald–Hartwig Reaction

Transition metal-mediated *N*-arylamination reactions, namely the Buchwald-Hartwig reaction, are one of the widely used methods for C–N bond formation.[25] Recently, applications of N-heterocyclic carbenes (NHCs) as ligands in *N*-arylaminations have become increasingly popular due principally to the higher efficiency of NHC-Pd complexes in arylamination.[8]

Previous reports[10a,15,26] have shown that SIPr performs better than IPr in the Buchwald–Hartwig amination, and the same situation has been identified in our Cp-containing NHC-Pd complexes. Moreover, 1,2-dimethoxyethane (DME) and NaO-*t*-Bu were discovered to be the best choice for solvent and base in the *N*-arylamination process. By combination of these conditions, and using the CpPd(NHC)Cl complex **8d** as catalyst, diverse aryl chlorides can be coupled smoothly with various primary and secondary amines in high yields at room temperature (Table 4). It is noteworthy that the reactions of sterically encumbered aryl chlorides (Table 4, entry 6 and 7) or amines (Table 4, entry 9 and 10), as well as a heteroaromatic chloride (Table 4, entry 8), all proceeded in high yields at room temperature. Particularly, *N*-arylpiperazine units are often seen in active pharmaceutical ingredients (APIs) in medicinal chemistry. Direct *N*-arylamination of piperazine using the present catalytic system provides an efficient approach to these biologically active compounds (Table 4, entries 7 and 8). In addition, *N*-arylation of chiral primary alkylamines under the catalytic conditions has also proven to be a superior alternative method for the synthesis of chiral *N*-arylamine derivatives (Table 4, entry 12).

Table 3. NHC-Pd-mediated deboronation homocoupling of arylboronic acids at room temperature.[a]



Entry	NHC-Pd catalyst	Arylboronic acid	Homocoupling product	Yield [%][b]
1	**8a**			84
2	**8b**			95
3	**8c**			88
4	**8d**			98
5	**8d**			98
6	**8d**			28
7	**8d**			91
8	**8d**			9[c]
9	**8d**			95
10	**8d**			15[d]
11	**8d**			99[e]

[a] *Reaction conditions:* arylboronic acid (2 mmol); CpPd(NHC)Cl **8** (1 mol%); KO-*t*-Bu (2.5 mmol); reagent grade 2-propanol (2 mL); T = room temperature (25 °C); t = 24 h. Reaction time was not optimized.

[b] Isolated yields given as an average of two runs.

[c] No homocoupling product was observed, only 9% deboronation product was isolated with most starting boronic acid recovered.

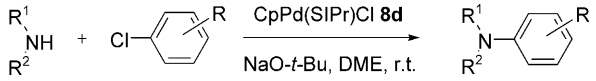
[d] No homocoupling product was observed, only 15% deboronation product was isolated with most starting boronic acid recovered.

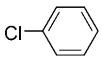
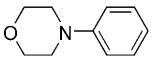
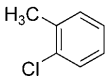
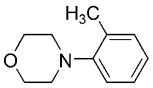
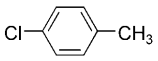
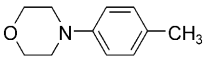
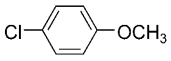
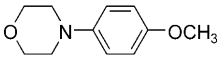
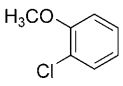
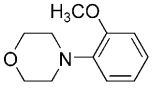
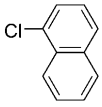
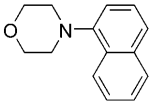
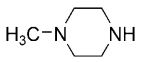
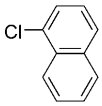
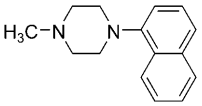
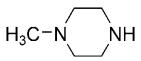
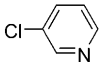
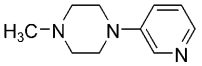
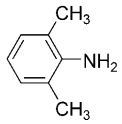
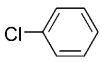
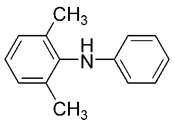
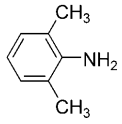
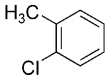
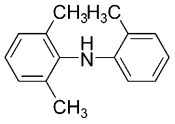
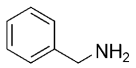
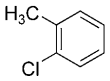
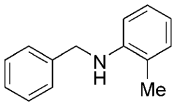
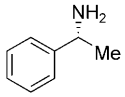
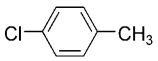
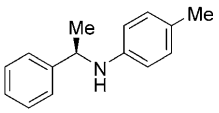
[e] No homocoupling product was observed, and almost quantitative deboronation product was isolated.

Conclusions

In summary, we have synthesized a new class of well-defined NHC-Pd complexes. These air-stable Cp-containing complexes exhibited highly catalytic activity in the Suzuki–Miyaura and Buchwald–Hartwig cross-coupling reactions. At room temperature, diverse arylboronic acids and amines can be coupled smoothly with unactive aryl chlorides in high yields using CpPd(SIPr)Cl **8d** as the precatalyst. In addition, these novel Cp-containing NHC-Pd complexes were found to be highly efficient catalysts in the deboronation homocoupling reactions of arylboronic acids. Although the exact activated mechanism for these coordinatively saturated NHC-Pd precatalysts is not yet clear, the facile activation [from Pd(II) to Pd(0) species] at room temperature and the resulting high catalytic activity in the coupling reactions should be attributed to the potential for reductive removal of the Cp group from the corresponding CpPd complexes. Results from our study confirm again that, apart from the dominant NHC ligands, other ancillary ligands surrounding the palladium center have much to do with the catalytic performance. By simple modification of

Table 4. Buchwald–Hartwig cross-coupling reactions of aryl chlorides at room temperature.[a]



Entry	Amine	Aryl chloride	Product	Time [h]	Yield [%][b]
1				2	96
2				4	86
3				2	94
4				2	93
5				4	88
6				4	89
7				4	83
8				12	88
9				12	92
10				12	83
11				12	85
12				12	82[c]

[a] *Reaction condition:* aryl chloride (1 mmol), amine (1.1 mmol), CpPd(SIPr)Cl **8d** (1 mol%), NaO-*t*-Bu (1.1 mmol), DME (1 mL). T = Room temperature (23 °C).
[b] Isolated yields give as an average of two runs.
[c] (*R*)-(+)-1-Phenylethylamine was used.

the allyl group in (NHC)Pd(allyl)Cl **1** to the cinnamyl group, a dramatic improvement in catalytic performance was achieved by Nolan et al.[12] In this regard, replacement of the Cp group in CpPd(NHC)Cl **8a–d** by the unsymmetrical indenyl group will lead to an obvious change in their catalytic activity. Studies about the latter system are currently ongoing in our laboratories.

Experimental Section

General Comments

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were distilled from appropriate drying agents prior to use. All aryl chlorides and amines were used as received. Arylboronic acids were prepared from the corresponding aryl bromides according to the commonly reported procedures and puri-

fied as described by Espinet.[27] Flash chromatography was performed on silica gel (silica gel 60, 200–300 mesh). ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker-300 or Bruker-400 MHz spectrometer at ambient temperature in $CDCl_3$. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. Melting points are uncorrected. The starting NHC-$PdCl_2$ dimers **7a–d** were prepared from the corresponding imidazolium salts (IMes·HCl and IPr·HCl) and imidazolinium salts (SIMes·HBF_4 and SIPr·HBF_4) following the literature method with excellent overall yields (generally $>95\%$).[17]

Synthesis of CpPd(NHC)Cl Complexes; General Procedure

To a stirred suspension of the corresponding $PdCl_2$-carbene dimers **7a–d** (0.4 mmol) in THF (20 mL) was added dropwise sodium cyclopentadienylide solution (0.8 mmol, 1.5 M in THF; (freshly prepared from sodium dispersion6 in THF with freshly cracked cyclopentadiene) at room temperature. Once the sodium cyclopentadienylide solution had been added, the solution color became green gradually from the original orange. The reaction mixture was stirred overnight at room temperature. At that time, the mixture was directly subjected to flash column chromatography to give the corresponding CpPd(NHC)Cl complexes **8a–d** as a green crystals.

CpPd(IMes)Cl (8a): Following general procedure, 390 mg of **8a** (95% yield) were obtained as a green crystals; mp 200–202 °C; ^{1}H NMR: $\delta=7.13$ (s, 2H, NHC), 7.02 (s, 4H, aryl), 5.18 (s, 5H, Cp), 2.37 (s, 6H, $CH_3\times2$), 2.18 (s, 12H, $CH_3\times4$); ^{13}C NMR: $\delta=162.4$, 139.1, 136.3, 135.7, 129.1, 123.7, 98.2, 21.2, 18.4; anal. valcd. for $C_{26}H_{29}ClN_2Pd$ (MW 511.39): C 61.06, H 5.72, N 5.48; found: C 61.00, H 5.73, N 5.30.

CpPd(IPr)Cl (8b): Following general procedure, 465 mg of **8b** (97% yield) were obtained as deep green crystals; mp 176–178 °C; ^{1}H NMR) $\delta=7.49$ (t, 2H, $J=7.7$ Hz, aryl), 7.33 (d, 4H, $J=7.7$ Hz, aryl), 7.19 (s, 2H, NHC), 5.11 (s, 5H, Cp), 2.92 (m, 4H, $J=6.8$ Hz, $CH\times4$), 1.39 (d, 12H, $J=6.8$ Hz, $CH_3\times4$), 1.11 (d, 12H, $J=6.8$ Hz, $CH_3\times4$); ^{13}C NMR: $\delta=167.8$, 146.2, 136.4, 130.1, 124.8, 124.0, 98.3, 28.7, 26.0, 22.7; anal. calcd. for $C_{32}H_{41}ClN_2Pd$ (MW 595.55): C 64.54, H 6.94, N 4.70; found: C 64.55, H 6.83, N 4.80.

CpPd(SIMes)Cl (8c): Following general procedure, 395 mg of **8c** (96% yield) were obtained as green crystals; mp 183–185 °C; ^{1}H NMR: $\delta=6.98$ (s, 4H, aryl), 5.14 (s, 5H, Cp), 4.00 (s, 4H, NHC), 2.40 (s, 6H, $CH_3\times2$), 2.33 (s, 12H, $CH_3\times4$); ^{13}C NMR: $\delta=195.8$, 138.3, 136.5, 136.4, 129.4, 98.6, 51.0, 21.1, 18.6, anal. calcd. for $C_{26}H_{31}ClN_2Pd$ (MW 513.41): C 60.82, H 6.09, N 5.46; found: C 60.95, H 6.03, N 5.39.

CpPd(SIPr)Cl (8d): Following general procedure, 470 mg of **8d** (98% yield) were obtained as deep green crystals; mp 186–187 °C; ^{1}H NMR: $\delta=7.41$ (t, 2H, $J=7.8$ Hz, aryl), 7.26 (d, 4H, $J=7.8$ Hz, aryl), 5.05 (s, 5H, Cp), 4.08(s, 4H, NHC), 3.37 (m, 4H, $J=6.8$ Hz, $CH\times4$), 1.45 (d, 12H, $J=6.8$ Hz, $CH_3\times4$), 1.25 (d, 12H, $J=6.8$ Hz, $CH_3\times4$); ^{13}C NMR: $\delta=$ 198.6, 147.3, 137.0, 129.3, 124.4, 99.1, 53.5, 28.7, 26.6, 23.5, anal. calcd. for $C_{32}H_{43}ClN_2Pd$ (MW 597.57): C 64.32, H 7.25, N 4.69; found: C 64.35, H 7.21, N 4.70.

Suzuki–Miyaura Cross-Coupling Reactions of Aryl Chlorides; General Procedure

In the air to a Schlenk tube that closed with a screw cap fitted with a septum and was equipped with a magnetic stir bar were added in turn potassium *tert*-butoxide (1.2 mmol, 116 mg), boronic acid (1.2 mmol), and CpPd(SIPr)Cl **8d** (0.01 mmol, 6 mg). The tube was then caped with a rubber septum and evacuated and backfilled with argon. This sequence was repeated three times. Aryl chloride (1 mmol) was injected through the septum, followed by addition of reagent grade 2-propanol (1 mL). The mixture was then stirred at room temperature for 20 h. After that time, water (5 mL) was added to the reaction mixture, the organic layer was extracted with diethyl ether (10 mL×3), dried over magnesium sulfated, and the solvent was evaporated under vacuum. The product was purified by flash chromatography on silica gel.

Deboronation Homocoupling Reactions of Arylboronic Acids; General Procedure

In the air to a Schlenk tube that closed with a screw cap fitted with a septum and was equipped with a magnetic stir bar were added in turn potassium *tert*-butoxide (1.2 mmol, 116 mg), boronic acid (1.2 mmol), and CpPd(SIPr)Cl **8d** (0.01 mmol, 6 mg). The tube was then caped with a rubber septum and evacuated and backfilled with argon. This sequence was repeated three times. Reagent grade 2-propanol (1 mL) was injected through the septum. The mixture was then stirred at room temperature for the indicated period of time. Water (5 mL) was then added to the reaction mixture, the organic layer was extracted with diethyl ether (10 mL× 3), dried over magnesium sulfated, and the solvent was evaporated under vacuum. The product was purified by flash chromatography on silica gel.

Buchwald-Hartwig Cross-Coupling Reactions of Aryl Chlorides; General Procedure

In the air, sodium *tert*-butoxide (1.1 mmol, 106 mg) and CpPd(SIPr)Cl **8d** (0.01 mmol, 6 mg) were charged in turn to a Schlenk tube equipped with a magnetic bar, and sealed with a screw cap fitted with a septum. The tube was then evacuated and backfilled with argon. This sequence was repeated three times. 1,2-Dimethoxyethane (DME) (1 mL), amine (1 mmol) and aryl chloride (1.1 mmol) were injected in turn *via* a syringe through the septum. The mixture was then stirred at room temperature for the indicated period of time. When no further conversion was observed, the reaction mixture was diluted with ethyl acetate (5 mL) and transferred to a round-bottomed flask. The reaction tube was rinsed with additional ethyl acetate (10 mL) and combined mixture was concentrated onto silica gel, and purified by flash chromatography.

Acknowledgements

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[18] For the crystal structures of NHC-Pd complexes **8a** and **8b**, see the Supporting Information. CCDC 714852, 714853, and714854 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.

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