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Benzimidazol-2-ylidene ligated palladacyclic complexes of *N*,*N*-dimethylbenzylamine – Synthesis and application to C–C coupling reactions

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ABSTRACT

Palladacyclic complexes derived from *N*,*N*-dimethylbenzylamine (dmba) and the benzimidazol-2-ylidene ligands: 1,3-di(cyclohexyl)benzimidazol-2-ylidene (BzImCy), 1,3-di(*tert*-butyl)benzimidazol-2-ylidene (BzIm^{t}Bu) and 1,3-di(1-adamantyl)benzimidazol-2-ylidene (BzImAd) were prepared. The yield for (BzImCy)Pd(Cl)dmba (**2a**) was 72% but yields for the more sterically encumbering analogues: (BzImAd)Pd(Cl)dmba (**2b**) and (BzIm^{t}Bu)Pd(Cl)dmba (**2c**) were 34% and 38%, respectively. The complexes were obtained as off-white, moisture- and air-stable crystalline solids and were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, CHN analysis and IR spectroscopy. Complex **2c** was further characterized by X-ray diffraction studies. The catalytic activity of all three complexes was explored for the Suzuki–Miyaura and Heck–Mizoroki coupling reactions of simple aryl bromides.

1. Introduction

The strong σ-donating properties of N-heterocyclic carbenes (NHCs) and the ability to tune their electronic and steric properties by varying the backbone and N-substituents have made them particularly useful as ligands, since they form strong metal–carbon bonds with a variety of metals [1–3]. They are also useful as organocatalysts [4]. Since the isolation of the first stable free NHC by Arduengo in 1991 [5], NHCs have emerged as active, robust and versatile ancillary ligands for several metal mediated homogeneous catalytic reactions including Pd-catalyzed C–C coupling reactions [6–10]. The air-, moisture- and thermally-stable nature of NHC complexes has led to an increase in their application to homogeneous catalytic transformations, and arguably rivaling phosphine ligands as versatile and attractive ligand alternatives [1,8].

In Pd-mediated cross-coupling reactions, the active form of the catalyst is believed to be a mono-ligated NHC-Pd(0) species, however, a variety of other co-ligands such as *p*-quinone, pyridine (Pyr) derivatives and chelating ligands such as acetylacetonate (acac) are necessary for stabilizing the pre-catalyst, and also serve to facilitate efficient delivery of the metal into the catalytic cycle [11–15]. Consequently, *N*,*N*-dimethylbenzylamine is one such sacrificial ligand, which enables the formation of the pre-catalyst, and through reductive degradation it can be dislodged in a controlled manner during the catalyst activation process [8,11]. The chelating structure of this ligand in palladacycles confers a degree of thermal stability, minimizing susceptibility to decomposition to metallic Pd, thereby making them attractive as catalysts for cross-coupling reactions [16]. Relative to their phosphine counterparts, palladacycles containing NHC ligands are less explored [11]. Despite this, NHC-ligated palladacycles have successfully catalyzed a variety of useful reactions such as the Heck–Mizoroki, Suzuki–Miyaura coupling, α-arylation of ketones and dehydrohalogenation reactions [8,10,17].

In this work, we are investigating palladacyclic complexes of dmba containing benzimidazol-2-ylidene ligands by combining the strongly donating and sterically demanding properties of the NHC ligands with the stability of the palladacycle framework. Complexes containing benzimidazol-2-ylidene ligands such as (BzIm)Pd(acac)Cl and (BzIm)Pd(Pyr)Cl_2 were previously prepared in our laboratory [18] and our ongoing interest in NHCs and their palladium(II) complexes prompted us to explore the synthesis and catalytic behavior of these Pd-dmba-benzimidazol-2-ylidene complexes. Analogous air- and moisture-stable palladacyclic complexes, with unsymmetrical benzimidazol-2-ylidenes and

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dimethylamino ligands in a mutually *trans* arrangement have been reported by Günay et al. [19]. The flexible and robust framework of palladacycles is believed to be responsible for their high turnovers in coupling reactions [17]. The choice of *N*-alkyl substituted NHCs relative to their aryl counterparts was based on the tendency of these former systems to have stronger electron donor properties [20,21].

2. Experimental

2.1. General – Materials and instruments

Reactions and manipulations were carried out under an inert, dry atmosphere of argon using standard air-free techniques with solvents purified and dried according to standard procedures [22], and deoxygenated prior to use. Selected reactions were performed in air and without special anhydrous precautions. The compounds 1,3-di(1-adamantyl)benzimidazolium chloride, 1,3-di (cyclohexyl)benzimidazolium chloride and 1,3-di(*tert*-butyl)benzimidazolium chloride, were obtained from Kamal Pharmachem Inc. and were used as received. Other chemicals were obtained from Kamal Pharmachem Inc., Sigma–Aldrich and BDH Chemicals and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACE 200 or 500 MHz Fourier Transform spectrometer and referenced to the residual protons in the incompletely deuterated solvents. Chemical shifts are reported in parts per million (δ, ppm) relative to tetramethylsilane (TMS). IR spectra were obtained on Bruker Vector 22 and Tensor 37 spectrometers. CHN analyses were performed on a PE 2400 CHNS/O Analyzer at the UWI, Mona, Jamaica.

2.2. Synthesis of complexes

2.2.1. Representative synthesis of NHC-palladacycles

A modified literature procedure [11,23] was employed in the preparation of the NHC-ligated palladacycles. For a typical reaction, the benzimidazolium chloride (2 equiv.), di-(μ-chlorobis(*N*,*N*)-dimethylbenzylamine)dipalladium (1 equiv.), K_2CO_3 (10 equiv.) were added to a reaction flask equipped with a stirring bar and subsequently purged with argon gas. 1,4-Dioxane (3 mL) was then added and the mixture was refluxed for 24 h. The mixture was then filtered and the sample purified by flash column chromatography using hexanes:CH_2Cl_2:EtOAc (5:5:1) as eluent.

*2.2.1.1. (BzImCy)Pd(dmba)Cl (**2a**).* Complex **2a** was obtained as an off-white crystalline solid (yield: 287.5 mg, 72%). ^{1}H NMR ($CDCl_3$; δ_H (ppm)): 7.63 (m, 2H, *meta*-CH (BzImCy)); 7.22 (m, 2H, *ortho*-CH (BzImCy)); 7.02 (d, 1H, *J* = 7.1 Hz, Ar-C*H*); 6.92 (t, 1H, *J* = 7.2 Hz, Ar-C*H*); 6.64 (t, 1H, *J* = 7.3 Hz, Ar-C*H*); 6.12 (d, 1H, *J* = 7.3 Hz, Ar-C*H*); 5.68 (m, 2H, NCH); 3.95 (s, 2H, CH_2 (benzyl)); 2.88 (s, 6H, $N(CH_3)_2$); 2.22 (m, 5H, CH_2 (cyclohexyl)); 1.89 (m, 9H, CH_2 (cyclohexyl)); 1.28 (m, 6H, CH_2 (cyclohexyl)); ^{13}C NMR ($CDCl_3$; δ_C (ppm)): 184.2 (Pd-NCN); 148.5, 148.0, 136.7, 134.0, 125.1, 123.6, 122.1, 121.9, 112.6 (Ar-C); 72.2 (CH_2 (benzyl)); 62.5 (NCH); 50.3 ($N(CH_3)_2$); 30.9, 30.7, 26.3, 26.2, 25.5 (CH_2 (cyclohexyl)). ν/cm^{-1} 3045, 2933, 2856, 1608, 1576, 1475, 1445, 1370, 1352, 1217, 1021, 955, 896, 850, 738. *Anal.* Calc. for $C_{28}H_{38}N_3ClPd$: C, 60.02; H, 6.87; N, 7.53. Found: C, 59.34; H, 6.58; N, 7.30%.

*2.2.1.2. (BzImAd)Pd(dmba)Cl (**2b**).* Complex **2b** was obtained as an off-white crystalline solid (yield: 119.2 mg, 34%). ^{1}H NMR ($CDCl_3$) δ_H 7.97 (m, 2H, *meta*-CH (BzImAd)); 7.19 (m, 2H, *ortho*-CH (BzImAd)); 6.94 (d, 1H, *J* = 7.4 Hz, Ar-C*H*); 6.89 (t, 1H, *J* = 7.3 Hz, Ar-C*H*); 6.63 (m, 1H, Ar-C*H*); 6.03 (d, 1H, *J* = 7.4 Hz, Ar-C*H*); 3.87 (s, 2H, CH_2 (benzyl)); 3.15 (m, 12H, CH_2 (adamantyl)); 2.86 (s, 6H, $N(CH_3)_2$); 2.27 (s, br, 6H, CH (adamantyl)); 1.76 (m, 12H, CH_2 (adamantyl)). ^{13}C NMR ($CDCl_3$) δ_C 178.4 (Pd-NCN); 151.0, 146.8, 136.1, 134.7, 125.4, 123.1, 121.9, 120.7, 116.2 (Ar-C); 72.6 (CH_2 (benzyl)); 62.0 ($NC(CH_2)_3$); 51.3 ($N(CH_3)_2$); 42.2, 36.2 (CH_2 (adamantyl)); 30.6 (CH (adamantyl)). ν/cm^{-1} 3045, 2980, 2905, 2858, 2840, 1578, 1453, 1375, 1332, 1292, 1104, 864, 844, 740, 663, 626. *Anal.* Calc. for $C_{36}H_{46}N_3ClPd.CHCl_3$: C, 56.83; H, 6.06; N, 5.37. Found: C, 56.87; H, 6.05; N, 5.29%.

*2.2.1.3. (BzIm^{t}Bu)Pd(dmba)Cl (**2c**).* Complex **2c** was isolated as an off-white crystalline solid (yield: 211.5 mg, 38%). ^{1}H NMR ($CDCl_3$) δ_H 7.76 (m, 2H, *meta*-CH (BzIm^{t}Bu)); 7.15 (m, 2H, *ortho*-CH (BzIm^{t}Bu)); 6.94 (d, 1H, *J* = 7.2 Hz, Ar-C*H*); 6.85 (t, 1H, *J* = 7.3 Hz, Ar-C*H*); 6.59 (t, 1H, *J* = 7.2 Hz, Ar-C*H*); 6.02 (d, 1H, *J* = 7.5 Hz, Ar-C*H*); 3.85 (s, 2H, CH_2 (benzyl)); 2.80 (s, 6H, $N(CH_3)_2$); 2.22 (s, br, 18H, C$(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ_C 179.2 (Pd-NCN); 150.6, 147.1, 135.8, 135.1, 125.5, 123.3, 122.1, 121.3, 115.4 (Ar-C); 72.4 (CH_2 (benzyl)); 60.1 ($NC(CH_3)_3$); 51.3 ($N(CH_3)_2$); 31.5 ($C(CH_3)_3$). ν/cm^{-1} 3055, 3004, 2971, 2912, 2834, 1580, 1477, 1402, 1373, 1332, 1228, 1182, 1128, 1024, 996, 936, 854, 744. *Anal.* Calc. for $C_{24}H_{34}N_3ClPd$: C, 56.92; H, 6.77; N, 8.30. Found: C, 57.07; H, 6.59; N, 8.22%. Single crystals were obtained from a solution of Hexanes:EtOAc:CH_2Cl_2 (5:5:1) following slow evaporation.

2.2.2. General procedure for the Heck–Mizoroki reaction of aryl bromides and methyl acrylate

A typical reaction is given below for the Heck–Mizoroki coupling reactions, employing a modified literature protocol [24,25].

(BzIm)Pd(Cl)dmba (4.5 mg, 2 mol%), Cs_2CO_3 (262 mg, 0.80 mmol) and a stirring bar were placed in a dry Radley™ tube. The tube was stoppered and the contents flushed with argon gas.[1] 1,4-Dioxane (1 mL) was then added *via* syringe followed by methyl acrylate (0.054 mL, 0.60 mmol) and the aryl halide[2] (0.05 mL, 0.40 mmol). The resulting mixture was refluxed for 24 h. After refluxing, the reaction mixture was filtered, and the desired coupled product purified by column chromatography using hexanes:EtOAc (12:1) as eluent.

2.2.3. General procedure for the Suzuki–Miyaura reaction of aryl bromides and phenylboronic acid

A typical reaction is given below for the Suzuki–Miyaura coupling reactions, employing a modified literature protocol [26,27].

(BzIm)Pd(Cl)dmba (4.5 mg, 2 mol%), Cs_2CO_3 (275 mg, 0.84 mmol), phenylboronic acid (73.6 mg, 0.60 mmol) and a stirring bar were placed in a dry Radley™ tube. The tube was stoppered and the contents flushed with argon gas.[1] 1,4-Dioxane (1 mL) was then added *via* syringe followed by the aryl halide[2] (0.05 mL, 0.40 mmol). The resulting mixture was heated for 24 h. After heating, the reaction mixture was filtered, and the desired coupled product purified by column chromatography using hexanes:EtOAc (12:1) as eluent.

3. Results and discussion

3.1. Synthesis and characterization of complexes

The synthesis of the desired (BzIm)Pd(Cl)dmba complexes, was based on the principle that halide-bridged palladacyclic dimers can be cleaved by nucleophiles such as NHCs to produce monomeric Pd-complexes [23,28]. Several NHC-ligated palladacyclic pre-catalysts of *N*,*N*-dimethylbenzylamine (dmba) have been prepared

[1] The same procedure was followed for the reactions performed in air, except that the purging of the reaction tube with argon was omitted.

[2] Under inert conditions, for the solid aryl halide, 4-bromoacetophenone (80.0 mg, 0.40 mmol) was weighed and placed in the Radley™ tube before purging with argon.

using the principle of the substitution of a bridging chloride of the dimer [Pd(dmba)(μ-Cl)]$_2$ by isolated free NHCs [8,11,29]. Consequently, in this study, complexes **2a**, **2b** and **2c** were prepared *via* a convenient version of a one-pot synthesis from the dimer [Pd(dmba)(μ-Cl)]$_2$ and the corresponding benzimidazolium salts (*ca.* 1:2 equiv. respectively) with potassium carbonate as base (Scheme 1). The complexes were obtained as air- and moisture-stable solids, in yields of 72%, 34% and 38%, comparable to existing one-pot synthetic procedures in the current literature [11,19,23]. Purification by column chromatography was necessary before characterization.

The low yields obtained for **2b** and **2c** can be attributed to the decomposition of some of the metal precursor to palladium black. Additionally the greater steric bulk imposed by the adamantyl and *t*-butyl N-substituents on the benzimidazole framework, relative to the cyclohexyl group may also be an influential factor. The steric repulsion between the bulky backbone (aromatic bridge) and the sterically demanding N-substituents result in larger values for % V_{Bur} (descriptor characterizing ligand steric demand) [30,31] as the greater steric demand limits access to, and therefore coordination/complexation, at the metal center. The greater steric bulk of the adamantyl and *t*-butyl substituents relative to the cyclohexyl moiety has been demonstrated by Scott et al. [32] and Huang et al. [33] *via* synthetic, structural and thermochemical studies. The stereoelectronic properties of NHCs bearing these bulky N-substituents influence synthetic outcomes, and are directly related to the carbene lone pair availability and overlap with the metal orbitals [20,33].

The mechanism of the formation of these NHC-ligated palladacycles is however, still unclear. Kantchev et al. [11] proposed a mechanism *via* the formation of a short-lived π-complex with the precursor azolium salt, thereby increasing the acidity of the proton (im-H^2) and facilitating complexation. They discounted the possibility of an *in situ* generated NHC intermediate, since *N*-alkyl substituted NHCs are known to react sluggishly with the *in situ* generated dimer [Pd(dmba)(μ-Cl)]$_2$. On the contrary, Gökçe et al. [23] attributed the formation of some related (NHC) Pd(dmba)Cl complexes, prepared from the azolium salt and NaH in the presence of the parent dimer [Pd(dmba)(μ-Cl)]$_2$, to the generation of the free NHC *in situ* with subsequent cleavage of the dimer to form the desired complex.

3.2. NMR spectroscopy

Diagnostic resonances in the ^{1}H and ^{13}C NMR spectra confirm the successful preparation of the NHC-palladacycles of *N*,*N*-dimethylbenzylamine. The carbene carbon of the benzimidazol-2-ylidene ligands of **2a**, **2b** and **2c** occurred at δ_C 184.2, 178.4 and 179.2, respectively, such that the observed trend for the carbene carbon resonances relative to the benzimidazol-2-ylidenes is BzImCy > BzIm^{t}Bu > BzImAd. These carbon resonances are consistent with assignments found in the literature for similar complexes [9,23,34]. The methylene carbon of the benzylamine moiety resonated in the range δ_C 72.2–72.6. The nitrogen bound methyl carbons occurred as one peak resonating at δ_C 50.3, 51.3 and 51.3, for **2a**, **2b** and **2c**, respectively, compared with two closely spaced peaks for similar carbons in the precursor [Pd(dmba)(μ-Cl)]$_2$, observed at δ_C 52.8 and 52.6.

Chemical shifts for the dmba protons of some imidazol-2-ylidene and imidazolin-2-ylidene analogues of these (BzIm)Pd(Cl)dmba systems generally occurred further upfield relative to the parent dimer [8,11,23,34]. This shift to higher fields has been attributed to the increased σ-donicity of the NHC ligands [23]. However, this general upfield shift was not observed for all the bulky benzimidazol-2-ylidene ligated systems **2a**, **2b**, and **2c**. In the ^{1}H NMR spectrum, a singlet signal at δ_H 3.95, 3.87 and 3.85 for **2a**, **2b**, **2c**, respectively, integrating for two protons distinguished the methylene protons of the *N*,*N*-dimethylbenzylamine moiety, compared to δ_H 3.93 in the parent dimer. The nitrogen-bound methyl protons occurred as a broad singlet integrating for 6 protons at δ_H 2.88, 2.86, 2.80 for **2a**, **2b**, **2c**, respectively, relative to δ_H 2.85 for the dimer [Pd(dmba)(μ-Cl)]$_2$.

3.3. Crystal structure

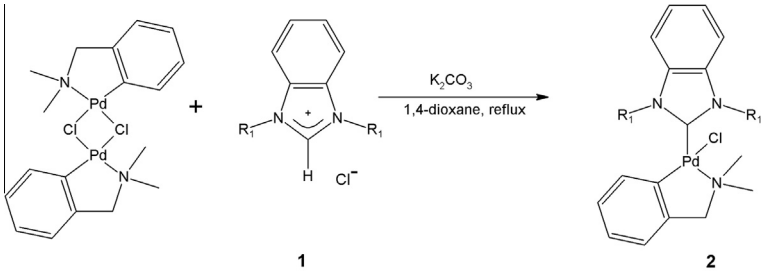
In the crystal structure of **2c** (Fig. 1), the 1,3-di(*tert*-butyl)benzimidazol-2-ylidene ligand lies *trans* to the dimethylamino moiety. Crystal and experimental data are provided in Table 1 and selected bond-lengths and bond angles are listed in Table 2. The N2–C1–N1 bond angle is 106.85(17)° and is characteristic of singlet benzimidazol-2-ylidenes which usually measures approximately 107° [11]. The C2–C3 (bridge) bond length is 1.398(3) Å. The Pd1–C1 and Pd1–C10 bond lengths are 1.988(2) Å and 2.000(2) Å, respectively, and are consistent with the usual range for Pd–C bonds [19,23]. The bond lengths for Pd1–Cl1 and Pd1–N3 are 2.4173(5) Å and 2.1295(17) Å, respectively, and are comparable to the values observed for similar bonds in the literature [8,19,23]. There is a distorted square planar geometry about the palladium(II) center, a consequence of the Pd being a part of the five-membered palladacyclic ring. The angles C1–Pd1–Cl1 and C1–Pd1–C10 are 88.53(6)° and 94.77(8)°, respectively, and the arrangement of the benzimidazol-2-ylidene is non-coplanar with respect to the palladacyclic ring and a more perpendicular relationship exists between the moieties. A search of the literature revealed that complexes **2a**, **2b** and **2c** have not been previously reported.

3.4. Catalysis

In a preliminary study, the catalytic activity of pre-catalysts **2a**, **2b** and **2c** was assessed for the Heck–Mizoroki and Suzuki–Miyaura reactions involving simple aryl bromides. Benzimidazol-2-ylidenes are known to exhibit intermediate behavior between imidazol-2-ylidenes and imidazolin-2-ylidines [35]. Results from studies on the electron-donating properties of various imidazolin-2-ylidenes and imidazol-2-ylidenes suggest that within a particular class of NHCs, the electronic differences are relatively small. Experimental data suggest that electron-donor properties are unlikely to play a significant role in the observed differences in catalytic activity for imidazol-2-ylidenes *versus* imidazolin-2-ylidines [36,37] Consequently, for the benzimidazol-2-ylidenes explored in this study, the electronic properties of the ligands are not expected to be significantly different and so any difference in the catalytic activity is likely attributed to the difference in steric properties of the benzimidazol-2-ylidenes.

3.4.1. Heck–Mizoroki coupling

3.4.1.1. Formation of methyl 4-methoxycinnamate and methyl 4-acetylcinnamate. Table 3 summarizes the results for the Heck–Mizoroki coupling of 4-methoxybromobenzene and 4-bromoacetophenone with methyl acrylate. The reactions performed under inert atmosphere showed no significant difference in the activities of the pre-catalysts for the formation of methyl 4-methoxycinnamate, and all pre-catalysts **2a**, **2b**, **2c** performed poorly with yields of only 20%, 18% and 9%, respectively, (entries 1, 3 and 4). Pre-catalyst **2a** performed equally poorly in air, for the formation of methyl 4-methoxycinnamate with a yield of 20% (entry 2). Under inert conditions, **2b** and **2c** showed improved performance for the coupling of the activated aryl halide, 4-bromoacetophenone with methyl acrylate. The bulkier pre-catalysts were more active towards the formation of methyl 4-acetylcinnamate; with yields of 66% and 41% for **2b** and **2c** respectively, (entries 6 and 8) whereas a yield of only 11% (entry 5) was obtained for the less



a : R_1 = cyclohexyl, 72%
b : R_1 = 1-adamantyl, 34%
c : R_1 = *t*-butyl, 38%

Scheme 1. Synthesis of (BzIm)Pd(dmba)Cl complexes.

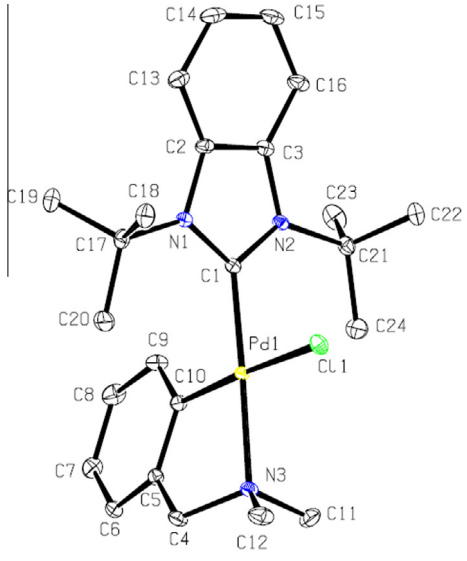


Fig. 1. An ORTEP representation of chloro[1,3-di(*tert*-butyl)benzimidazol-2-ylidene](*N*,*N*-dimethylbenzylamine)palladium(II), **2c**. Displacement ellipsoids are represented at the 30% probability level and hydrogen atoms are omitted for clarity.

bulky cyclohexyl derivative. However, pre-catalyst **2b** displayed reduced activity in air, with a moderate 47% yield of methyl 4-acetylcinnamate (entry 7). It is apparent that the greater steric bulk of **2b** and **2c** is playing a role in possibly enhancing the reductive elimination step in the catalytic cycle [20,38] thereby increasing catalytic efficiency.

3.4.2. Suzuki–Miyaura coupling

3.4.2.1. Formation of 4-methoxybiphenyl and 4-acetylbiphenyl. Suzuki–Miyaura coupling reactions generally require milder conditions relative to the Heck–Mizoroki couplings [39]. Initially, the reactions were conducted at 50 °C for this study. However, a higher temperature was required to improve yields for some pre-catalysts, and so, some reactions were subsequently conducted at 101 °C, contingent on the performance at lower temperature (Table 4). For each Suzuki–Miyaura coupling reaction, the yields of the desired biphenyl derivatives ranged from poor to excellent for all three pre-catalysts (Table 4).

The bulkier pre-catalysts **2b** and **2c** performed better than the less bulky cyclohexyl system, **2a** under inert atmosphere for the formation of 4-methoxybiphenyl at 50 °C, with **2b** giving a very good yield of 83% and **2c** a 36% yield (entries 3 and 4). Upon increasing the temperature to 101 °C, the yield for **2a** improved significantly to 94% (entry 1); but this had little or no effect on the performance of **2b** (85%, entry 3). The increase in yield for **2c** (54%, entry 4) was reasonable, though not remarkably so. At 50 °C, pre-catalysts **2a** and **2b** outperformed **2c** for the formation

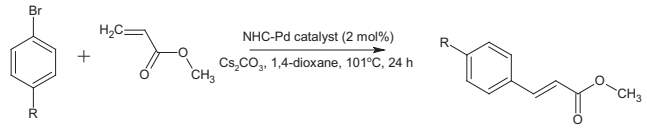
Table 1
X-ray experimental data for **2c**.

Empirical formula	$C_{24}H_{34}ClN_3Pd$
Formula weight	506.39
T (K)	147(2)
λ (Å)	0.71073
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	12.5455(4)
b (Å)	15.8780(5)
c (Å)	23.7632(8)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4733.6(3)
Z	8
ρ_{calc} (Mg/m^3)	1.421
Absorption coefficient (mm^{-1})	0.912
$F(000)$	2096
Crystal size (mm)	0.43 × 0.25 × 0.21
θ (°)	2.24–27.51
Index ranges	$-16 \leqslant h \leqslant 16$, $-16 \leqslant k \leqslant 20$, $-30 \leqslant l \leqslant 25$
Reflections collected	24689
Independent reflections [R_{int}]	5430 [0.0321]
Completeness to θ = 27.51°	99.8%
Absorption correction	Semi-empirical from equivalents
Maximum, minimum transmission	0.7456, 0.6823
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5430/0/270
Goodness-of-fit (GOF) on F^2	1.025
Final R indices [$I > 2\sigma(I)$] R_1, wR_2	0.0255, 0.0564
R indices (all data) R_1, wR_2	0.0431, 0.0645
Largest difference peak and hole (e Å^{-3})	0.396 and −0.663

Table 2
Selected bond lengths and bond angles for **2c**.

Bond lengths (Å)	
Pd(1)–C(1)	1.988(2)
Pd(1)–C(10)	2.000(2)
Pd(1)–N(3)	2.1295(17)
Pd(1)–Cl(1)	2.4173(5)
C(2)–C(3)	1.398(3)
Bond angles (°)	
C(1)–Pd(1)–Cl(1)	88.53(6)
C(1)–Pd(1)–C(10)	94.77(8)
N(2)–C(1)–N(1)	106.85(17)
C(1)–Pd(1)–N(3)	176.95(7)

Table 3
Evaluation of NHC-Pd complexes for the Heck–Mizoroki coupling of 4-methoxybromobenzene and 4-bromoacetophenone with methyl acrylate.

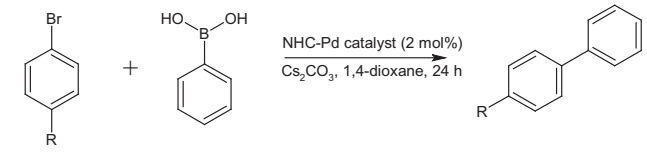


R = OCH_3, $COCH_3$

Entry	Pre-catalyst		R	Yield[a] (%)
1	(BzImCy)Pd(dmba)Cl	**2a**	OCH_3	20
2	(BzImCy)Pd(dmba)Cl	**2a**		20[b,*]
3	(BzImAd)Pd(dmba)Cl	**2b**		18
4	(BzIm^{t}Bu)Pd(dmba)Cl	**2c**		9
5	(BzImCy)Pd(dmba)Cl	**2a**	$COCH_3$	11
6	(BzImAd)Pd(dmba)Cl	**2b**		66
7	(BzImAd)Pd(dmba)Cl	**2b**		47[b,*]
8	(BzIm^{t}Bu)Pd(dmba)Cl	**2c**		41

[a] Yields are based on the aryl-halide.
[b] Reaction performed in air.
[*] Pd black was not observed.

Table 4
Evaluation of NHC-Pd complexes for the Suzuki–Miyaura coupling of 4-methoxybromobenzene and 4-bromoacetophenone with phenylboronic acid.



R = OCH_3, $COCH_3$

Entry	Pre-catalyst		R	Yield[a] (%)	
				50 °C	Reflux
1	(BzImCy)Pd(dmba)Cl	**2a**	OCH_3	7[*]	94[*]
2	(BzImCy)Pd(dmba)Cl	**2a**		–	99[b,*]
3	(BzImAd)Pd(dmba)Cl	**2b**		83	85[*]
4	(BzIm^{t}Bu)Pd(dmba)Cl	**2c**		36	54[*]
5	(BzImCy)Pd(dmba)Cl	**2a**	$COCH_3$	>99[*]	–
6	(BzImCy)Pd(dmba)Cl	**2a**		45[b,*]	99[b,*]
7	(BzImAd)Pd(dmba)Cl	**2b**		94	–
8	(BzIm^{t}Bu)Pd(dmba)Cl	**2c**		51	88

[a] Yields are based on the aryl-halide.
[b] Reaction performed in air.
[*] Pd black was not observed.

of the 4-acetylbiphenyl under argon, with yields of >99%, 94% and 51%, respectively (entries 5, 7 and 8). However, the performance of **2c** was enhanced to 88% (entry 8), by increasing the temperature. Under reflux and in air, pre-catalyst **2a** showed no loss of activity in the formation of both 4-methoxybiphenyl and 4-acetylbiphenyl with 99% yield, (entries 2 and 6), but at the lower temperature **2a** showed some loss of activity for the formation of the latter, with 45% yield (entry 6).

Overall, pre-catalyst **2b** was generally more active than **2a** and **2c** for both types of coupling reactions investigated.

4. Conclusions

Three relatively bulky benzimidazol-2-ylidene ligated palladacyclic complexes of *N*,*N*-dimethylbenzylamine that are stable to air, moisture and long term storage, were prepared and successfully catalyzed the Heck–Mizoroki and Suzuki–Miyaura coupling reactions with poor to excellent yields of the coupled products under inert conditions. The selected C–C coupling reactions done in air with pre-catalysts **2a** and **2b**, without stringent anhydrous techniques, were effectively mediated and with comparable activities to those conducted under inert atmosphere, in most instances. The steric nature of the NHC ligands appears to be a significant factor, influencing the yields of the complexes as well as their catalytic activities in the coupling reactions.

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Appendix A. Supplementary material

CCDC 1456395 contains the supplementary crystallographic data for **2c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.04.048.

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