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Ag(I) and Pd(II) complexes of a 1,3-dibenzhydryl substituted benzannulated *N*-heterocyclic carbene: Unexpected rearrangement, structures and catalytic studies

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ABSTRACT

Reaction of the sterically bulky 1,3-dibenzhydrylbenzimidazolium bromide (Bh_2-bimyH$^+$Br$^-$) (**A**) with $Pd(OAc)_2$ in DMSO yielded a mono(carbene) Pd(II) complex **1** with a *N*-bound benzimidazole derivative, which resulted from an unusual NHC rearrangement reaction. Reaction of **A** with Ag_2O, on the other hand, cleanly gave the Ag(I) carbene complex [AgBr(Bh_2-bimy)] (**2**), which has been used as a carbene-transfer agent to prepare the acetonitrile complex *trans*-[$PdBr_2(CH_3CN)(Bh_2$-bimy)] (**3**). Dissociation of acetonitrile from complex **3** and subsequent dimerization afforded the dinuclear Pd(II) complex [$PdBr_2(Bh_2$-bimy)]$_2$ (**4**) in quantitative yield. All complexes were fully characterized by multinuclear NMR spectroscopies, ESI mass spectrometry and X-ray diffraction analysis. Furthermore, the catalytic activity of complex **4** in aqueous Suzuki–Miyaura cross-coupling reactions was studied and compared with that of its previously reported less bulky analogue [$PdBr_2(^i Pr_2$-bimy)]$_2$.

1. Introduction

N-heterocyclic carbenes (NHCs) have been recognized as powerful ligands in organometallic chemistry and homogenous catalysis [1]. In particular, Pd complexes of unsaturated imidazolin-2-ylidenes and saturated imidazolidin-2-ylidenes have been developed as highly reactive precatalysts in C–C and C–N coupling reactions [2]. Catalytic applications of benzannulated carbenes, on the other hand, have received less attention, although this class of carbenes occupies an interesting intermediate position between the former two and thus exhibits unique properties [3]. Therefore, we have been focusing on benzannulated NHCs in our research, especially on those with bulky *N*-substituents [4], as the steric bulk is commonly believed to promote the reductive elimination step occurring in the catalytic cycle of Heck-type C–C coupling reactions. Recently, we reported the synthesis and catalytic activities of several Pd(II) complexes with the bulky 1,3-diisopropylbenzimidazolin-2-ylidene ligand [4a,b]. As a continuation of our research, we herein present the syntheses, structural characterizations and preliminary catalytic studies of complexes with the even bulkier 1,3-dibenzhydrylbenzimidazolin-2-ylidene ligand.

2. Result and discussion

2.1. Synthesis and characterization of complexes

A general method to synthesize Pd(II) bis(carbene) complexes involves the reaction of basic $Pd(OAc)_2$ with two equiv of azolium salts under in situ deprotonation of the latter to form the corresponding carbene ligand [5]. Surprisingly, our initial attempt to synthesize such a complex by reacting $Pd(OAc)_2$ with the very sterically bulky 1,3-dibenzhydrylbenzimidazolium bromide (Bh_2-bimyH$^+$Br$^-$, **A**) in DMSO at 75 °C under air was unsuccessful. Instead, an unexpected mono(carbene) Pd(II) complex (**1**) with a remarkably rearranged *N*-coordinated 1,2-disubstituted benzimidazole derivative [2-(1-benzhydrylbenzimidazol-2-yl)-benzophenone] was isolated in a good yield of 70% as a yellow solid (Scheme 1). Besides complex **1**, this reaction also afforded a minor compound (**X**) tentatively assigned to the initially targeted bis(carbene) complex [$PdBr_2(Bh_2$-bimy)$_2$], which is insoluble in DMSO and thus precipitated from the reaction media (vide infra).

Complex **1** is well soluble in halogenated and the more polar solvents acetone, DMF and DMSO, but insoluble in nonpolar solvents such as hexane and diethyl ether. The formation of complex **1** was supported by its positive mode ESI mass spectrum, which shows an isotopic pattern centered at $m/z = 1101$ corresponding to the $[M-Br]^+$ fragment. In addition, the identity of complex **1** was further corroborated by ^{13}C NMR spectroscopy. The signals for the CO carbon and the NCN carbon in the unusual 1,2-disubstituted benzimidazole ligand arise at 195.3 and 172.4 ppm, respectively. The $C_{carbene}$ resonates at 153.7 ppm, which is comparable

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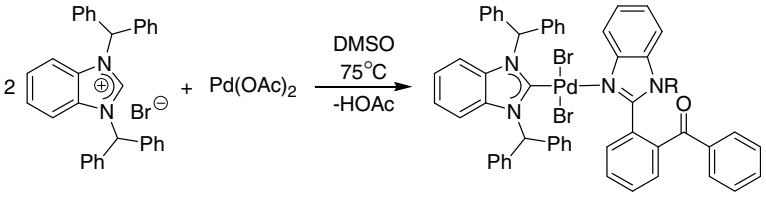


Scheme 1. Synthesis of complex **1**.

with the reported values for *trans*-dihalo-(benzimidazolin-2-ylidene) Pd(II) complexes with *N*-heterocyclic co-ligands [4g].

Single crystals of complex **1** suitable for X-ray diffraction were obtained as solvate **1** · $2(CH_3)_2CO$ by slow evaporation of a concentrated acetone solution. Its molecular structure is depicted in Fig. 1 and cystallographic data are listed in Table 1. The palladium center in complex **1** is coordinated by two bromo ligands, one NHC ligand and the 1,2-disubstituted benzimidazole in a trans fashion. The deviation angle of the carbene ring from the $PdBr_2CN$ coordination plane is 79.31. Similarly, the *N*-bound benzimidazole plane is twisted from the coordination plane with a torsion angle of 68.02°. The Pd1–C1 and Pd1–N3 bonds amount to 1.9579(18) and 2.0909(15) Å, respectively, which are in the expected range.

Notably, several examples of unusual NHC rearrangement/decomposition reactions have been reported in the literature that generally lead to a C–N bond cleavage between the heterocylic ring and the *N*-alkyl or *N*-aryl substituents [6]. However, the formation of the 1,2-disubstituted benzimidazole ligand in complex **1** is still unique as it apparently requires at least three steps: (i) C–N cleavage between the *N*-heterocyclic ring and one benzhydryl substituent; (ii) *ortho*-C–H activation of the aromatic ring in this benzhydryl substituent and subsequent rearrangement to the 2-position of the heterocycle; (iii) oxidation of the methine group in the initial benzhydryl substituent to form a benzophenone derivative.

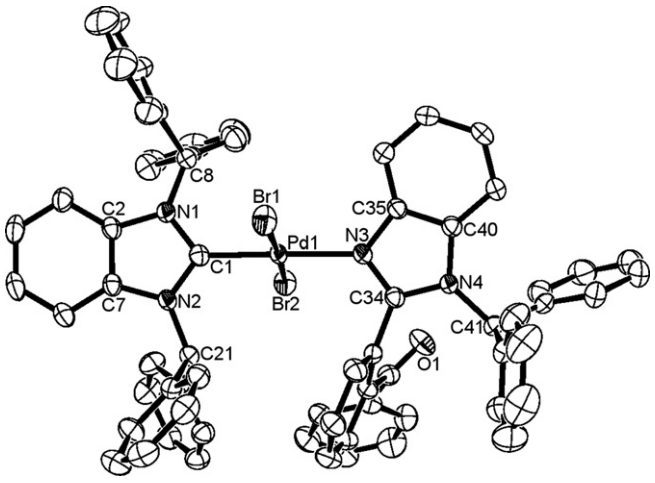


Fig. 1. Molecular structure of complex **1** showing 50% probability ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 1.9579(18), Pd1–Br1 2.4346(5), Pd1–Br2 2.4230(5), Pd1–N3 2.0909(15), C1–N1 1.353(2), C1–N2 1.351(2), N1–C2 1.398(2), N1–C8 1.480(2), N2–C7 1.400(2), N2–C21 1.474(2), C2–C7 1.392(3), N3–C34 1.321(2), N3–C35 1.391(2), N4–C34 1.362(2), C1–Pd1–Br1 86.66(5), C1–Pd1–Br2 89.84(5), N3–Pd1–Br1 91.35(5), N3–Pd1–Br2 92.18(5), N1–C1–N2 107.14(15), C1–N1–C2 110.32(15), C1–N2–C7 110.00(15), C34–N3–C35 106.17(14), N3–C34–N4 112.13(15).

At present, the mechanism for this unusual rearrangement and the formation of complex **1** is still unclear. However, we believe that the presence of palladium, aerial oxygen and the use of relatively high temperature are crucial for this process. When the reaction was carried out either in the absence of palladium, under nitrogen atmosphere or at ambient temperature (ceteris paribus), no formation of complex **1** or 2-(1-benzhydrylbenzimidazol-2-yl)-benzophenone was detected. Furthermore, complex **1** may result from the decomposition of complex **X**. To investigate this possibility, we heated complex **X** in either DMSO at 75 °C or in refluxing acetonitrile overnight under air, but no reaction took place. Further heating in DMSO to 130 °C led to an intractable product mixture, from which complex **1** could not be identified.

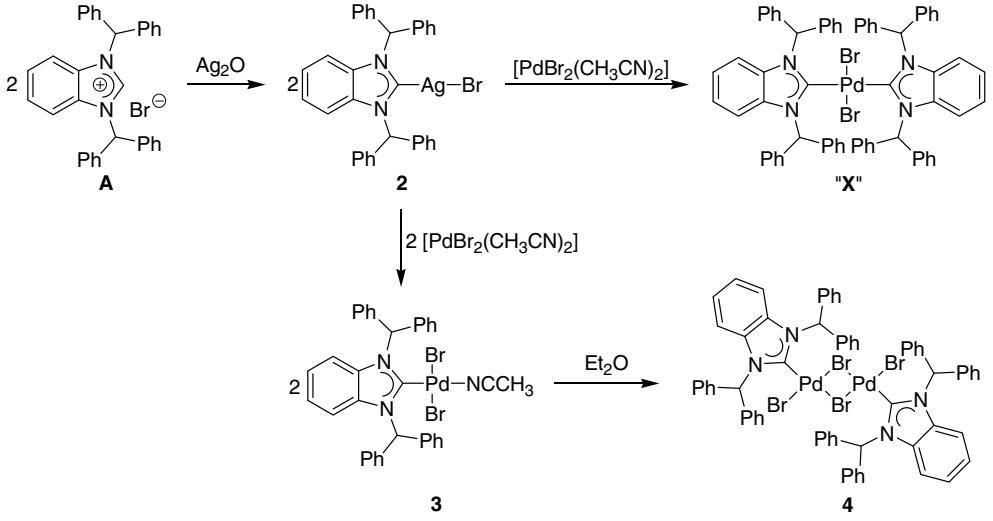
With the attempt to obtain the desired bis(carbene) complex $[PdBr_2(Bh_2\text{-bimy})_2]$, we explored the milder Ag-carbene-transfer method developed by Lin et al. [7]. The silver monocarbene complex $[AgBr(Bh_2\text{-bimy})]$ (**2**), which should subsequently serve as a carbene-transfer agent, was synthesized in an excellent yield of 93% by the reaction of Ag_2O with 2 equiv. of salt **A** in CH_2Cl_2 at ambient temperature (Scheme 2). The characteristic downfield signal for the NCHN proton in salt **A** is absent in the ^1H NMR spectrum of complex **2**, corroborating the formation of a carbene complex. Furthermore, the ^{13}C NMR spectrum shows a downfield resonance at 192.1 ppm arising from the coordinated carbene carbon. This carbenoid signal is broad and does not show $^{13}C–^{107,109}Ag$ coupling, which is consistent with the labile nature of the $Ag–C_{carbene}$ bond. The ESI mass spectrum of complex **2** is dominated by an isotopic cluster centered at $m/z = 1101$ corresponding to the $[AgL_2]^+$ (L = Bh_2-bimy) fragment in the positive mode and an isotopic envelope at $m/z = 267$ corresponding to the $[AgBr_2]^-$ fragment in the negative mode, suggesting an ion-pair structure of complex **2** in the gas phase [7].

Single crystals of complex **2** suitable for X-ray diffraction were obtained from a mixed CH_2Cl_2/Et_2O solution upon standing. It may be worth noting that complex **2** represents one of only few reported benzimidazolin-2-ylidene Ag(I) complexes, which have been crystallographically characterized [7,8], as imidazolin-2-ylidenes have prevailed in the field of silver-NHC chemistry [9]. As shown in Fig. 2, complex **2** is a neutral monomer, in which the coordination geometry deviates from linearity with an C1–Ag1–Br2 angle amounting to 170.81(13)°. The Ag1–C1 bond length is 2.081(5) Å and similar to those reported for other benzimidazolin-2-ylidene Ag(I) complexes [7,8]. Different from other halobenzimidazolin-2-ylidene Ag(I) complexes, complex **2** shows neither intermolecular Ag···Ag nor Ag···Br interactions at all, presumably due to the pronounced steric bulk of the benzhydryl substituents.

Having established the straightforward formation and identity of the silver carbene complex, we conveniently reacted in situ generated **2** with $[PdBr_2(CH_3CN)_2]$ in subsequent reactions. When this reaction was carried out in a L:Pd ratio of 2:1, formation of the dibromo-bis(carbene) complex $[PdBr_2(Bh_2\text{-bimy})_2]$ was expected (Scheme 2). After filtration of the AgBr precipitate and drying of

Table 1
Selected X-ray crystallographic data for complexes **1–4**

	1 · $2(CH_3)_2CO$	**2**	**3**	**4** · $2CHCl_3$
Formula	$C_{72}H_{62}Br_2N_4O_3Pd$	$C_{33}H_{26}AgBrN_2$	$C_{35}H_{29}Br_2N_3Pd$	$C_{68}H_{54}Br_4Cl_6N_4Pd_2$
Formula weight	1297.48	638.34	757.83	1672.29
Color, habit	Orange, block	Colorless, plate	Yellow, block	Orange, block
Crystal size (mm)	0.38 × 0.20 × 0.20	0.24 × 0.10 × 0.08	0.54 × 0.32 × 0.10	0.56 × 0.42 × 0.16
Temperature (K)	223(2)	223(2)	223(2)	223(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	11.581(2)	17.5789(11)	16.6225(12)	21.2354(10)
b (Å)	15.459(4)	9.1363(6)	10.6140(8)	17.7672(8)
c (Å)	18.044(4)	18.2095(12)	18.0485(14)	18.5717(9)
α (°)	69.890(13)	90	90	90
β (°)	89.00(2)	114.853(2)	101.962(2)	110.1270(10)
γ (°)	82.013(14)	90	90	90
V (Å^3)	3002.4(12)	2653.7(3)	3115.2(4)	6579.1(5)
Z	2	4	4	4
D_c (g cm^{-3})	1.435	1.598	1.616	1.688
Radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	1.692	2.290	3.189	3.264
θ range (°)	1.20–27.50	1.35–27.48	1.52–27.50	1.02–27.50
Unique data	39475	18198	21635	46299
Maximum, minimum transmission	0.7284, 0.5657	0.8380, 0.6094	0.7410, 0.2777	0.6232, 0.2622
Final R indices	R_1 = 0.0311,	R_1 = 0.0574,	R_1 = 0.0454,	R_1 = 0.0415,
[$I > 2\sigma(I)$]	wR_2 = 0.0813	wR_2 = 0.1362	wR_2 = 0.0934	wR_2 = 0.0993
R indices (all data)	R_1 = 0.0394,	R_1 = 0.0889,	R_1 = 0.0769,	R_1 = 0.0637,
	wR_2 = 0.0873	wR_2 = 0.1490	wR_2 = 0.1041	wR_2 = 0.1093
Goodness-of-fit (GoF) on F^2	1.067	1.020	0.973	1.029
Peak/hole (e Å^{-3})	0.662/−0.299	2.265/−0.483	1.077/−0.441	2.259/−0.786



Scheme 2. Synthesis of complexes **2–4**.

the filtrate under vacuo, a yellowish powder was obtained. This compound is only sparingly soluble in halogenated solvents and acetonitrile, but insoluble in more polar solvents such as DMSO and DMF. The ^{1}H NMR spectrum of this compound in $CDCl_3$ is identical to that of the minor complex **X** obtained by the reaction of $Pd(OAc)_2$ and salt **A** in DMSO (vide supra), which shows only aromatic protons in the range of 6.82–7.36 ppm and a singlet at 8.69 ppm presumably arising from the CH protons of the benzhydryl substituents. Due to the poor solubility, its ^{13}C NMR spectrum could not be obtained despite prolonged acquisition time. Attempts to confirm the identity of this compound by ESI or FAB MS were also unsuccessful as the mass spectra measured under various temperature and different voltages showed only one identifiable peak at m/z = 451 corresponding to the $[HL]^+$ fragment of salt **A**. In addition, the C, H, N values found by elemental analysis (C, 66.78; H, 4.95; N, 4.56%) deviate from the calculated values for target complex $[PdBr_2(Bh_2\text{-bimy})_2]$ (C, 67.91; H, 4.49; N, 4.80%) despite many efforts of purification. Hence, the identity of complex **X** as $[PdBr_2(Bh_2\text{-bimy})_2]$ remains uncertain.

We then attempted to synthesize a monocarbene Pd(II) complex by reacting in situ generated complex **2** with $[PdBr_2(CH_3CN)_2]$ in a L:Pd ratio of 1:1 in acetonitrile. Immediate precipitation of AgBr was observed, and as expected, the mono(carbene) complex *trans*-$[PdBr_2(CH_3CN)(Bh_2\text{-bimy})]$ (**3**) was obtained as air-stable yellow crystals from the filtrate (Scheme 2). The ^{1}H NMR spectrum of complex **3** in CD_3CN is rather simple. The signal for the CH protons of the benzhydryl groups arises as a singlet at 8.54 ppm, which is shifted downfield by 0.79 ppm compared to the analogous resonance of salt **A**. The ^{1}H NMR spectrum of the same product in $CDCl_3$, on the other hand, is more complicated. It shows three

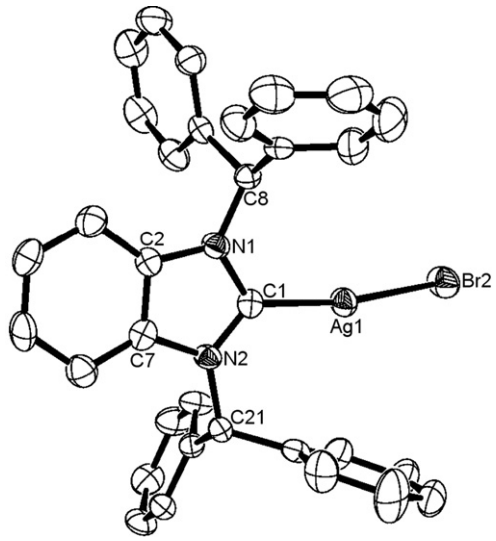
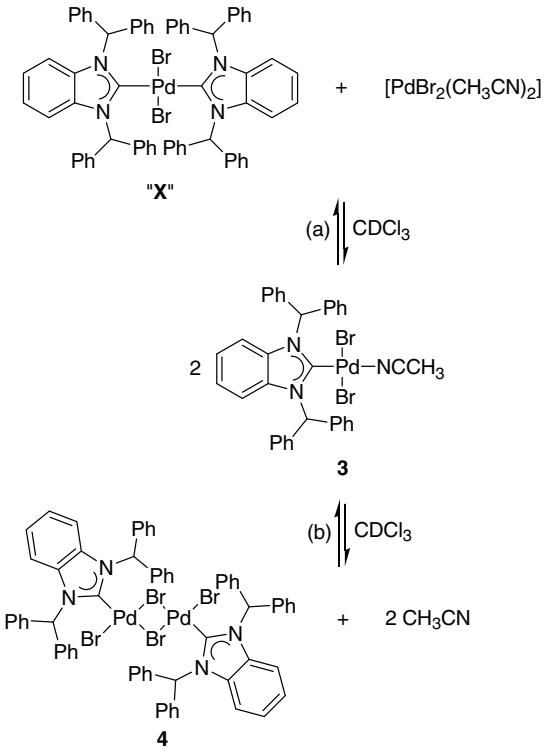


Fig. 2. Molecular structure of complex **2** showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1–C1 2.081(5), Ag1–Br2 2.4253(6), C1–N1 1.363(6), C1–N2 1.340(6), N1–C8 1.481(6), N1–C2 1.392(6), N2–C21 1.477(6), N2–C7 1.399(6), C2–C7 1.398(7), C1–Ag1–Br2 170.81(13), C1–N1–C2 110.4(4), C1–N2–C7 111.2(4).

singlets at 8.58, 8.70 and 8.76 ppm in an intensity ratio of approximately 1:0.5:2, which remains largely unchanged after 1 day. After comparison with ^{1}H NMR spectra of isolated and authentic samples, we assigned the three resonances to the benzhydryl CH protons in complex **3** (8.58 ppm), complex **X** (8.70 ppm) and the dimeric complex $[PdBr_2(Bh_2\text{-bimy})]_2$ (**4**) (8.76 ppm) (vide infra), respectively.

Apparently, the lability of the CH_3CN ligand gives rise to two dynamic processes that can be observed when pure complex **3** was dissolved in $CDCl_3$ (Scheme 3): (a) two molecules of complex **3** undergo ligand exchange to form complex **X** {tentatively $[PdBr_2(Bh_2\text{-bimy})_2]$} and $[PdBr_2(CH_3CN)_2]$; (b) two molecules of complex **3** form the dimeric complex $[PdBr_2(Bh_2\text{-bimy})]_2$ (**4**) under CH_3CN dissociation. A comparison of the integrals for the aforementioned resonances suggests that process (b) is kinetically more favored, which should allow for a selective preparation of complex **4** (vide infra).



Scheme 3. Proposed dynamic processes of complex **3** in $CDCl_3$.

However, complex **3** is stable in CH_3CN and thus single crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated CH_3CN solution. Its molecular structure depicted in Fig. 3 shows a square-planar geometry around the palladium center with a weakly bonded acetonitrile ligand in trans position to the NHC. The Pd1–C1 (1.938(4) Å) and Pd1–N3 (2.077(4) Å) bond lengths are comparable to the corresponding bond parameters of the diisopropylbenzimidazolin-2-ylidene analogue *trans*-$[PdBr_2(CH_3CN)(^iPr_2\text{-bimy})]$ [4a]. In addition, the Pd1–N3–C34 angle (167.9(4)°) is smaller than that for *trans*-$[PdBr_2(CH_3CN)(^iPr_2\text{-bimy})]$ (175.35(18)°).

As mentioned above, the lability of the acetonitrile ligand in complex **3** and the preference for process (b) (vide supra) should allow for a selective preparation of the dimeric complex **4**. Indeed, it was found that upon washing of complex **3** with diethyl ether, dissociation of acetonitrile from the metal center readily occurred to yield the dimeric complex $[PdBr_2(Bh_2\text{-bimy})]_2$ (**4**) as an orange powder (Scheme 2). The formation of complex **4** was confirmed by ^{1}H NMR spectroscopy, which shows the absence of the methyl signal from the acetonitrile ligand and a slight downfield shift for the benzhydryl CH proton. The other ^{1}H and ^{13}C chemical shifts for the NHC ligand remain largely unchanged upon dissociation of acetonitrile and formation of complex **4**. Notably, our attempt to prepare complex **4** directly from salt **A** and $Pd(OAc)_2$ in the presence of KBr in DMSO at 90 °C failed and gave rise to an intractable product mixture, although the same synthetic route worked very well for the 1,3-diisopropylbenzimidazolin-2-ylidene analogue $[PdBr_2(^iPr_2\text{-bimy})]_2$ [4a]. The failure is presumably attributed to the decomposition of the carbene ligand under the relatively harsh reaction conditions.

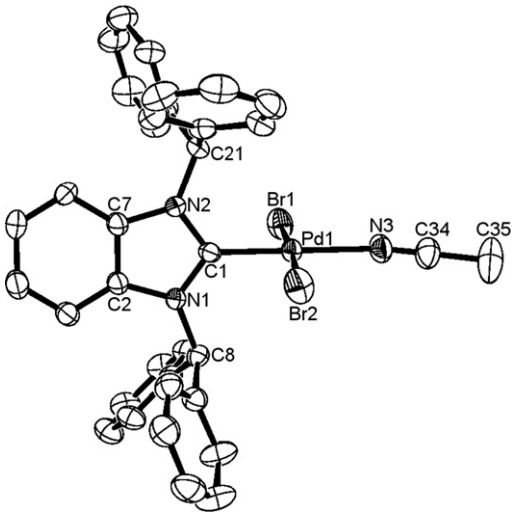


Fig. 3. Molecular structure of complex **3** showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 1.938(4), Pd1–Br1 2.4075(6), Pd1–Br2 2.4279(6), Pd1–N3 2.077(4), C1–N1 1.349(4), C1–N2 1.351(4), N1–C8 1.481(4), N1–C2 1.406(5), N2–C21 1.479(4), N2–C7 1.411(5), C2–C7 1.395(5), N3–C34 1.111(5), C34–C35 1.454(7), C1–Pd1–Br1 87.92(11), C1–Pd1–Br2 89.08(11), N3–Pd1–Br1 88.41(10), N3–Pd1–Br2 94.64(10), N1–C1–N2 107.6(3), C1–N1–C2 110.0(3), C1–N2–C7 110.1(3), Pd1–N3–C34 167.9(4).

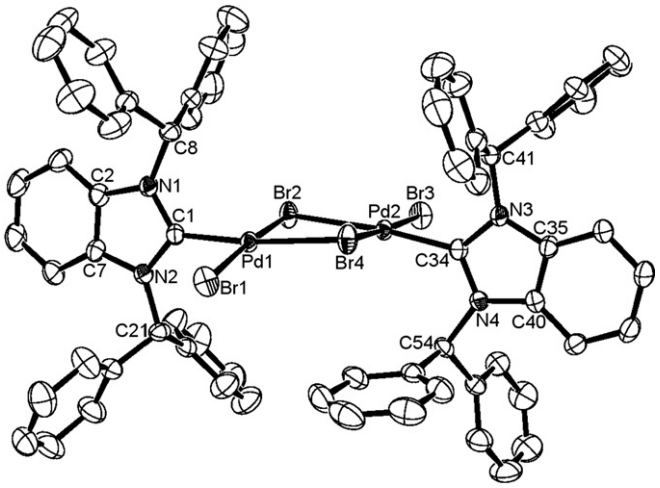


Fig. 4. Molecular structure of complex **4** showing 50% probability ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 1.957(3), Pd1–Br1 2.4161(5), Pd1–Br2 2.4439(5), Pd1–Br4 2.5085(4), Pd2–C34 1.949(3), Pd2–Br2 2.5225(4), Pd2–Br3 2.4038(5), Pd2–Br4 2.4454(5), C1–N1 1.350(4), C1–N2 1.346(4), N1–C8 1.475(4), N1–C2 1.402(4), N2–C21 1.480(4), N2–C7 1.410(4), C2–C7 1.395(5), C34–N3 1.344(4), C34–N4 1.346(4), N3–C41 1.483(4), N3–C35 1.399(4), N4–C54 1.490(4), N4–C40 1.404(4), C1–Pd1–Br1 89.69(10), C1–Pd1–Br2 90.09(10), Br2–Pd1–Br4 88.359(15), Br1–Pd1–Br4 92.515(16), Pd1–Br2–Pd2 90.711(15), Pd1–Br4–Pd2 91.008(15), C34–Pd2–Br3 86.24(10), C34–Pd2–Br4 91.86(10), Br2–Pd2–Br3 94.286(16), Br2–Pd2–Br4 88.007(15), N3–C34–N4 107.9(3), C34–N3–C35 109.7(3), C34–N4–C40 109.4(3).

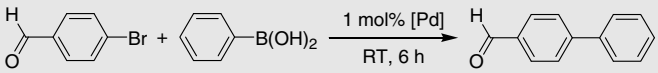
The molecular structure of solvate **4** · $2CHCl_3$ determined by X-ray diffraction analysis is illustrated in Fig. 4. Complex **4** contains two essentially square-planar Pd(II) centers coordinated by one carbene, one terminal bromo and two bridging bromo ligands with the carbene ligands oriented anti to each other. The carbene ring planes are almost perpendicular to the $PdCBr_3$ coordination planes with dihedral angles of 78.22 and 88.66°. Different from the 1,3-diisopropylbenzimidazolin-2-ylidene analogue that has a planar $[Pd_2Br_2]$ ring [4a], the $[Pd_2Br_2]$ ring in complex **4** is slightly bent with a hinge angle of ca. 165°. The two Pd–$C_{carbene}$ bond distances of 1.957(3) and 1.949(3) Å have slightly elongated compared to that in the precursor complex **3**, which is in line with less Lewis acidic metal centers in complex **4**. Furthermore, among the three types of Pd–Br bonds in this complex, the Pd–Br bonds trans to the carbene ligands are significantly longer than the other two types due to the strong trans influence of the NHC.

2.2. Catalysis

Previously, we have shown that the dimeric complex $[PdBr_2(^iPr_2\text{-bimy})]_2$ bearing the bulky 1,3-diisopropylbenzimidazolin-2-ylidene ligand serves as a very good precatalyst for aqueous Suzuki–Miyaura cross-coupling reactions [4a]. Herein, we wanted to compare its performance to that of complex **4** bearing the even bulkier 1,3-dibenzhydrylbenzimidazolin-2-ylidene ligand. The coupling of 4-bromobenzaldehyde with phenylboronic acid with 0.5 mol% of complex **4** and a reaction time of 6 h at ambient temperature was chosen as a standard test reaction to study the effects of various solvents. As shown in Table 2, the reaction carried out in pure water as "green" solvent gave the highest yield of 100%, whereas that in CH_3CN afforded the lowest yield of only 26%. Reactions in a CH_3CN/H_2O mixture or toluene gave near-quantitative yields. The same solvent trend was observed when $[PdBr_2(^iPr_2\text{-bimy})]_2$ was employed as the precatalyst for the same reaction [4a].

Subsequently, the comparison of both catalyst precursors was extended to various substrates using water as the reaction media.

Table 2
Effect of the solvent on the Suzuki–Miyaura cross-coupling reactions catalyzed by **4**[a]



Entry	Solvent	Yield (%)[b]
1	H_2O	100
2	CH_3CN/H_2O (1:1 in volume)	97
3	Toluene	97
4	CH_3CN	26

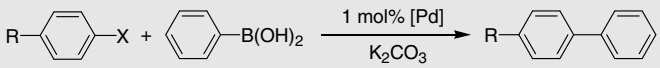
[a] *Reaction conditions:* 1 mmol of 4-bromobenzaldehyde; 1.2 mmol of phenylboronic acid; 3 ml of solvent; 1.5 equivalents of K_2CO_3; 0.5 mol% of **4**; under nitrogen atmosphere.
[b] Yields were determined by ^1H NMR spectroscopy for an average of two runs.

For the coupling of activated 4-bromoacetophenone, the two complexes gave the same yield of 89% after 6 h (entry 1, Table 3). However, their activities were found to be very different in the coupling of deactivated aryl bromides. For instance, complex **4** gave generally higher yields in the coupling of electron-rich 4-bromotoluene or 4-bromoanisole (entries 2/3, Table 3). It was observed that in reactions with deactivated substrates the reaction mixture turned to black within a few minutes. Hence, it is likely that the real catalysts in these reactions are colloidal palladium(0) nanoparticles, which has been reported by other research groups when different catalyst precursors were used in Suzuki–Miyaura [10] or Mizoroki–Heck [11] reactions with less reactive substrates and at elevated temperatures. The difference in the catalytic activities of complex **4** and $[PdBr_2(^iPr_2\text{-bimy})]_2$ observed here may lead to the hypothesis that the two complexes with different *N*-substituents generate active palladium(0) colloids of different sizes, which exhibit different catalytic activities. Furthermore, the comparison between entry 2 and 4 in Table 3 suggests that the CH_3CN/H_2O mixture is a better solvent system than pure H_2O for the coupling of deactivated 4-bromotoluene. On the other hand, pure H_2O is the best choice of solvent for the activated 4-bromobenzaldehyde. A simple extrapolation of optimized conditions from one substrate type to another is thus not always feasible.

We also found that using the CH_3CN/H_2O mixture as solvent, the coupling of electron-rich 4-bromotoluene or 4-bromoanisole catalyzed by complex **4** could occur at ambient temperature, giving yields of 84% and 31%, respectively, after 2 h (entries 5/7, Table 3). These reactions could go to completion in a short time when the reaction temperature was raised to 85 °C (entries 6/8, Table 3). In an attempt to test the reusability of the active catalyst in the coupling of 4-bromotoluene (entry 6, Table 3), it was found that a second run still afforded a good yield of 83% after 0.5 h (ceteris paribus). Furthermore, aerobic conditions did not cause loss of yield, which is evident when entries 4 and 6 (Table 3) are compared. However, the coupling of 4-chlorobenzaldehyde and 4-chloroacetophenone were more difficult and afforded only low yields of 8% and 36%, respectively, even at 85 °C (entries 9/10, Table 3). Surprisingly, addition of $[N(n\text{-}C_4H_9)_4]Br$ (TBAB), which is commonly used as a phase-transfer catalyst and promoter did not lead to any significant improvements (entries 11/12, Table 3). In the case of 4-bromotoluene and 4-bromoanisole a TBAB-addition prevents the formation of active Pd(0) species at ambient temperature due to its stabilizing effect and thus no conversion was observed (entries 13/14, Table 3).

We have also attempted to study the kinetics of the coupling reaction using 4-bromotoluene at ambient temperature. To our surprise, after 12 min a high yield of 80% was already obtained, but longer reaction times did not improve the yield to a great extend. This observation corroborates the proposal that palladium(0)

Table 3
Suzuki–Miyaura cross-coupling reactions[a]



Entry	Aryl halide	Solvent	t (h)	Temperature (°C)	Yield (%)[b]
1	4-Bromoacetophenone	H_2O	6	RT	89(89)[c]
2	4-Bromotoluene	H_2O	12	85	80(55)[c]
3	4-Bromoanisole	H_2O	12	85	80(28)[c]
4	4-Bromotoluene	CH_3CN/H_2O (1:1 in volume)	1	85	100(100)[c]
5	4-Bromotoluene	CH_3CN/H_2O (1:1 in volume)	2	RT	84(61)[d]
6	4-Bromotoluene	CH_3CN/H_2O (1:1 in volume)	0.5	85	100[d]
7	4-Bromoanisole	CH_3CN/H_2O (1:1 in volume)	2	RT	31[d]
8	4-Bromoanisole	CH_3CN/H_2O (1:1 in volume)	2	85	100[d]
9	4-Chlorobenzaldehyde	CH3CN/H_2O (1:1 in volume)	5	85	8[d]
10	4-Chloroacetophenone	CH3CN/H_2O (1:1 in volume)	5	85	36[d]
11	4-Chlorobenzaldehyde	CH_3CN/H_2O (1:1 in volume)	5	85	14[d,e]
12	4-Chloroacetophenone	CH_3CN/H_2O (1:1 in volume)	5	85	32[d,e]
13	4-Bromotoluene	CH_3CN/H_2O (1:1 in volume)	2	RT	0[d,e]
14	4-Bromoanisole	CH_3CN/H_2O (1:1 in volume)	2	RT	0[d,e]

[a] *Reaction conditions:* 1 mmol of aryl halide; 1.2 mmol of phenylboronic acid; 3 ml of solvent; 1.5 equivalents of K_2CO_3; 0.5 mol% of **4** or $[PdBr_2(^iPr_2\text{-bimy})]_2$.
[b] Yields were determined by ^1H NMR spectroscopy for an average of two runs; values in brackets are the yield for the reactions catalyzed by $[PdBr_2(^iPr_2\text{-bimy})]_2$.
[c] Reactions were carried out under nitrogen atmosphere.
[d] Reactions were carried out under air.
[e] With addition of 1.5 equivalents of $[N(n\text{-}C_4H_9)_4]Br$.

colloids are the real catalysts. It seems that after converting ~80% of the substrates the initially smaller colloids have substantially grown in size, which results in self-deactivation due to the resulting smaller active surface area.

3. Conclusion

We obtained an unexpected mono(carbene) Pd(II) complex (**1**) with a *N*-bound 1,2-disubstituted benzimidazole derivative when the sterically bulky 1,3-dibenzhydrylbenzimidazolium bromide (**A**) was reacted with $Pd(OAc)_2$ in DMSO at 75 °C. The formation of complex **1** involves an unique NHC rearrangement reaction, the mechanism of which remains to be investigated. This rearrangement reaction was not observed in the preparation of the Ag(I) carbene complex [AgBr(Bh_2-bimy)] (**2**) under milder reaction conditions. A transmetallation protocol using complex **2** successfully afforded the acetonitrile complex *trans*-[$PdBr_2(CH_3CN)(Bh_2$-bimy)] (**3**), which was found to undergo two dynamic processes in deuterochloroform solution. Dissociation of acetonitrile in complex **3** allowed for an easy synthesis of the dimeric complex $[PdBr_2(Bh_2\text{-bimy})]_2$ (**4**) in a quantitative yield. Furthermore, a comparison of the catalytic activities revealed that complex **4** is a good catalyst precursor in Suzuki–Miyaura cross-coupling reactions and exhibits superior activity for deactivated aryl bromides than its previously reported analogue $[PdBr_2(^iPr_2\text{-bimy})]_2$ [4a].

4. Experimental

4.1. General considerations

Unless otherwise noted all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. Salt **A** was prepared as previously reported [12]. ^1H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 and AMX 500 spectrometer and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane. Mass spectra were measured using a Finnigan MAT LCQ (ESI or FAB) spectrometer. Infrared spectra were recorded with a Varian 3100 FT-IR spectrometer using KBr pellet. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

4.2. Synthesis of trans-dibromo(1,3-dibenzhydrylbenzimidazolin-2-ylidene)(2-(1-benzhydrylbenzimidazol-2-yl)-benzophenone) palladium(II) (**1**)

A mixture of $Pd(OAc)_2$ (67 mg, 0.3 mmol) and salt **A** (318 mg, 0.6 mmol) was dissolved in DMSO (8 ml) and stirred at 75 °C overnight. The resulting suspension was filtered through a sintered funnel. The solvent of the filtrate was removed by vacuum distillation and the residue was subjected to column chromatography (SiO_2, ethyl acetate: hexane = 1:4). The 4th band (R_f = 0.45) was collected and dried under reduced pressure to give complex **1** as a yellow solid (248 mg, 0.21 mmol, 70%). ^1H NMR (300 MHz, $CDCl_3$): δ 9.10 (s, 1H, CH), 8.32 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 8.11 (s, 1H, CH), 7.76–6.72 (m, 43H, Ar-H & CH), 6.32 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): 195.8 (s, CO), 172.9 (s, NCN), 154.2 (s, $C_{carbene}$), 141.4, 139.3, 138.4, 138.3, 138.2, 138.1, 137.6, 137.3, 135.6, 135.5, 134.6, 134.5, 132.7, 132.0, 131.9, 131.4, 130.9, 130.5, 130.4, 130.1, 129.9, 129.8, 129.7, 129.4, 129.1, 129.05, 129.0, 128.9, 128.8, 128.6, 128.2, 128.1, 124.1, 123.2, 123.0, 122.8, 120.7, 114.1, 113.6 (s, Ar-C), 68.7, 68.2, 65.5 (s, CH). IR (KBr pellet) $\tilde{\nu} = 1660\ cm^{-1}$ (s, C=O). Anal. Calc. for $C_{66}H_{50}Br_2N_4OPd$: C, 67.10; H, 4.27; N, 4.74. Found: C, 67.14; H, 4.42; N, 4.59%. MS (ESI): m/z = 1101 $[M-Br]^+$.

4.3. Synthesis of 1,3-dibenzhydrylbenzimidazolin-2-ylidene silver(I) bromide (**2**)

A mixture of Ag_2O (23 mg, 0.1 mmol) and salt **A** (106 mg, 0.2 mmol) was suspended in CH_2Cl_2 (15 ml) and stirred at ambient temperature for 7 h shielded from light. The reaction mixture was filtered through celite and the solvent of the filtrate was removed in vacuo to give the crude product as a white solid. Crystallization from a concentrated CH_2Cl_2/Et_2O solution afforded the product as colorless crystals (119 mg, 0.093 mmol, 93%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.35–7.15 (m, Ar-H & CH). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 192.1 (br, $C_{carbene}$), 137.2, 134.2, 129.1, 128.6. 128.2, 124.1, 113.4 (s, Ar-C), 68.1 (s, CH). Anal. Calc. for $C_{33}H_{26}AgBrN_2$:

C, 62.09; H, 4.11; N, 4.39. Found: C, 61.79; H, 4.11; N, 4.37%. MS (ESI): m/z = 1009 $[2M-AgBr_2]^+$, 267 $[AgBr_2]^-$.

4.4. Synthesis of trans-dibromo(1,3-dibenzhydrylbenzimidazolin-2-ylidene)(acetonitrile)palladium(II) (**3**)

A mixture of Ag_2O (23 mg, 0.1 mmol) and salt **A** (106 mg, 0.2 mmol) was suspended in CH_2Cl_2 (10 ml) and stirred at ambient temperature for 7 h shielded from light. The resulting mixture was directly filtered into a solution of $[PdBr_2(CH_3CN)_2]$, which in turn was prepared in situ by heating $PdBr_2$ (53 mg, 0.2 mmol) in CH_3CN (20 ml) under reflux conditions for 6 h. The reaction mixture was stirred at ambient temperature for 24 h and gradually lightened up from initially red to yellow. The resulting suspension was filtered through a sintered funnel and the residue was washed by CH_3CN repeatedly until the filtrate is colorless. The solvent of the filtrate was removed under vacuum to give an orange residue. Washing the residue with small portions of ice-cold CH_3CN followed by drying in vacuo afforded the pure product as a yellow powder (82 mg, 0.11 mmol, 54%). ^1H NMR (500 MHz, CD_3CN): δ 8.54 (s, 2 H, CH), 7.43–7.35 (m, 20 H, Ar-H), 6.91 (m, 2 H, Ar-H), 6.83 (m, 2 H, Ar-H), 1.96 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): 165.7 (s, $C_{carbene}$), 138.2, 135.1, 130.0, 129.4, 129.2, 124.0 (s, Ar-C), 118.3 (s, CN), 114.8 (s, Ar-C), 69.2 (s, CH), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Anal. Calc. for $C_{35}H_{29}Br_2N_3Pd$: C, 55.47; H, 3.86; N, 5.54. Found: C, 55.81; H, 4.26; N, 5.39%. MS (ESI): m/z = 678 $[M-Br]^+$, 1353 $[2M-2CH_3CN-Br]^+$.

4.5. Synthesis of di-μ-bromobis(1,3-dibenzhydrylbenzimidazolin-2-ylidene)dibromodipalladium(II) (**4**)

Complex **3** (76 mg, 0.1 mmol) was suspended in Et_2O (20 ml) and stirred at ambient temperature overnight. The resulting mixture was filtered through a sintered funnel and the residue was washed by Et_2O again (10 ml × 3). Drying the residue in vacuo afforded the product as an orange powder (71 mg, 0.049 mmol, 99%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 4 H, CH), 7.44–7.31 (m, 40 H, Ar-H), 6.88 (m, 4 H, Ar-H), 6.82 (m, 4 H, Ar-H). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 165.2 (s, $C_{carbene}$), 137.5, 135.1, 129.8, 129.4, 129.0, 123.6, 114.5 (s, Ar-C), 69.4 (s, CH). Anal. Calc. for $C_{66}H_{52}Br_4N_4Pd_2$: C, 55.29; H, 3.66; N, 3.91. Found: C, 55.00; H, 3.73; N, 3.81%. MS (ESI): m/z = 1353 [M−Br].

4.6. General procedure for the Suzuki–Miyaura cross-coupling reaction

In a typical run, a Schlenk-tube was charged with a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), potassium carbonate (1.5 mmol), precatalyst (0.005 mmol) and $[N(n\text{-}C_4H_9)_4]Br$ (1.5 mmol) (for entries 11–14 in Table 3). The reaction vessel was degassed under vacuum and filled with nitrogen. The solvent (3 ml) was then added to the mixture using a syringe. The reaction mixture was vigorously stirred at the appropriate temperature. After the desired reaction time, the solution was allowed to cool and quenched by adding 5 ml of aqueous HCl solution (2.4 M). Dichloromethane (10 ml) was added to the reaction mixture and the organic phase was extracted with water (6 × 5 ml) and dried over $MgSO_4$. The solvent was removed by evaporation to give a crude product, which was analyzed by ^1H NMR spectroscopy.

4.7. X-Ray diffraction studies

Diffraction data for complexes **1–4** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using SHELXL-97 [13] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in Table 1.

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Appendix A. Supplementary material

CCDC 686371, 686372, 686373 and 686374 contains the supplementary crystallographic data for (**1**), (**2**), (**3**) and (**4**). 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 doi:10.1016/j.jorganchem.2008.06.037.

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