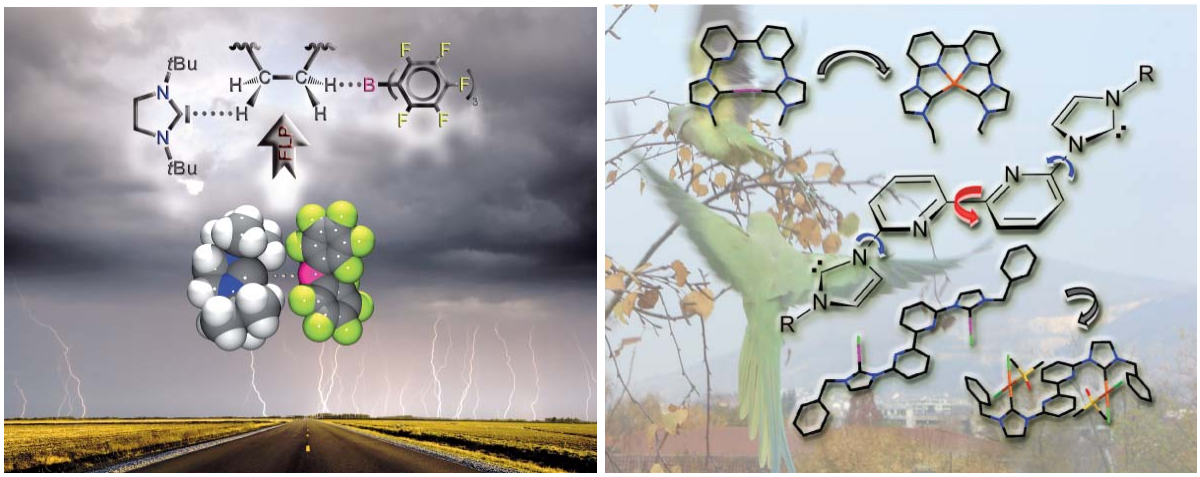
This paper is published as part of a *Dalton Transactions* themed issue on:

N-Heterocyclic Carbenes

Guest Editor Ekkehardt Hahn

Westfälische Wilhelms-Universität, Münster, Germany

Published in issue 35, 2009 of *Dalton Transactions*



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Synthesis, characterization and catalytic activity of novel *N*-heterocyclic carbene-palladium complexes†

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Received 1st April 2009, Accepted 19th June 2009
First published as an Advance Article on the web 21st July 2009
DOI: 10.1039/b906497b

The reaction of $Pd(OAc)_2$ with 1-(benzhydryl)-3-(alkyl)benzimidazolium salts **1a–d** yields *trans*-bis[1-(benzhydryl)-3-(alkyl)benzimidazolin-2-ylidene]dibromopalladium(II) complexes (**2a–d**) which were characterized by elemental analysis, NMR spectroscopy and the molecular structures of **2b**, and **2d** were determined by X-ray crystallography. The catalytic activity of $PdBr_2$bis(benzimidazolin-2-ylidene) complexes **2a–d** was evaluated in the direct arylation reaction of benzothiazole with bromobenzene derivatives.

Introduction

Since the first characterization of metal complexes containing *N*-heterocyclic carbene (NHC) ligands by Öfele[1] and Wanzlick[2] in 1968, the development of metal–NHC complexes by Lappert in the early 1970s,[3] and the isolation of the stable free NHC by the group of Arduengo in 1991,[4] much attention has been paid toward their properties and application.

NHCs show many interesting properties that make them valuable as ligands in catalysis. A combination of their powerful σ-donating and weak π-accepting character allows for the generation of a stronger bond to the metal than their phosphine homologues and leads to the formation of interestingly robust electron-rich metal complexes. Consequently, metal–NHC complexes tend to be air-stable, easy to handle and highly active in several catalytic transformations where harsh conditions are often required.[5] In recent years, an exceptionally large number of NHC complexes have emerged and have been used successfully in many catalytic transformations, notably the C–C and C–N cross-coupling reactions,[6,7] metathesis,[8] hydrosilylation,[9] transfer hydrogenation,[10] and furan synthesis.[11]

Heteroaromatics are important structural units frequently found in natural products,[12] pharmaceutically active substances, agrochemicals[13] and organic functional materials such as liquid crystals and fluorescent dyes.[14] Direct arylation of heterocycles has received considerable interest among synthetic chemists as it would eliminate the need for establishing a reactive functionality prior to C–C coupling enabling direct elaboration and expansion of the core motif. Direct transformation of a C–H bond into a C–C bond is a relatively clean and efficient method for meeting such goals.[15] In recent years, significant progress has been made toward the development of direct arylation of a wide variety of substrates using Pd,[16] Rh,[17] Ru,[18–20] and Ir[21] catalysts. For these reactions, the critical step is the C–H bond cleavage and metallation of the aromatic ring with the transition metal complex.

We have recently shown that NHC–ruthenium(II) species *in situ* generated from $[RuCl_2(p\text{-cymene})]_2$ and monoazolium salts under basic conditions were able to catalyze the direct arylation of 2-phenylpyridine by aryl bromides.[22]

We now report the synthesis of new palladium(II) complexes with electron-rich carbene ligands, arising from *N,N′*-dialkylbenzimidazolium salts, upon reaction with $Pd(OAc)_2$ precursor, and their application in catalytic C–H bond functionalization.

Results and discussion

Preparation of benzimidazolium salts

Dialkylbenzimidazolium salts, (**1a–d**) conventional functionalized NHC precursors, were synthesized by consecutive alkylation of 1- benzhydrylbenzimidazole with alkyl halides (Scheme 1).

According to Scheme 1, the salts (**1a–d**) were obtained in almost quantitative yield by quarternization of 1-benzhydrylbenzimidazole in DMF with alkyl halides.[23] The salts were air- and moisture stable both in the solid state and in solution. The structures of **1a–d** were determined by their characteristic spectroscopic data and elemental analyses. ^{13}C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet in the ^1H-decoupled mode at 142.7, 142.6, 142.4 and 153.8 ppm respectively for benzimidazolium bromides **1a–d**. The ^1H NMR spectra of the benzimidazolium salts further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets at 10.16, 9.95, 9.43 and 9.82 ppm respectively for **1a–d**. The IR data for benzimidazolium salts **1a–d** clearly indicate the presence of the –C=N– group with a ν(C=N) vibration at 1544, 1557, 1543 and 1596 cm^{-1} respectively for **1a–d**. The NMR values are similar to those found for other 1,3-dialkylbenzimidazolium salts.[23]

Preparation of palladium complexes 2

The formation of NHC–metal complexes is mainly based on four principal routes (Scheme 2): (i) *in situ* deprotonation of the corresponding azolium salts, (ii) complexation of the free

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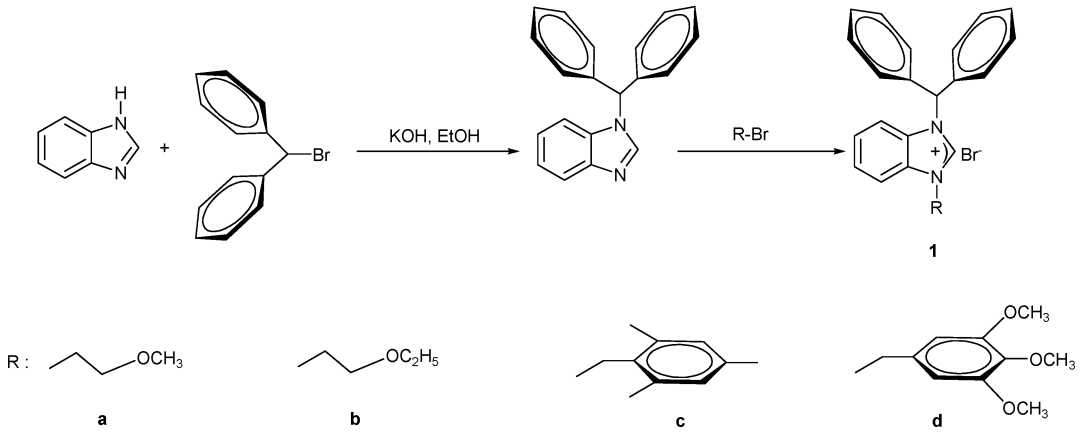
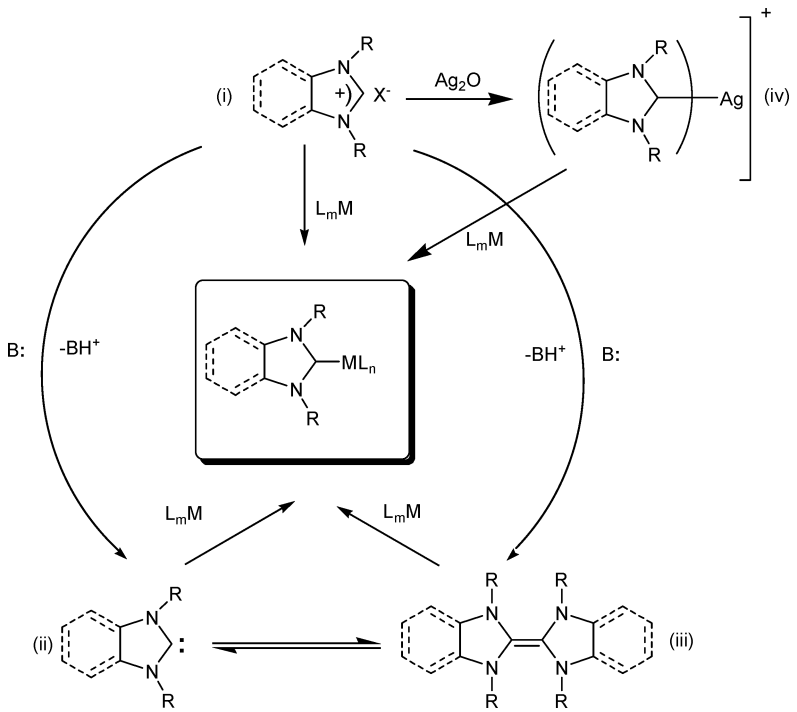
† CCDC reference numbers 716524 & 716525. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b906497b



Scheme 1 Synthesis of 1,3-dialkylbenzimidazolium bromides.



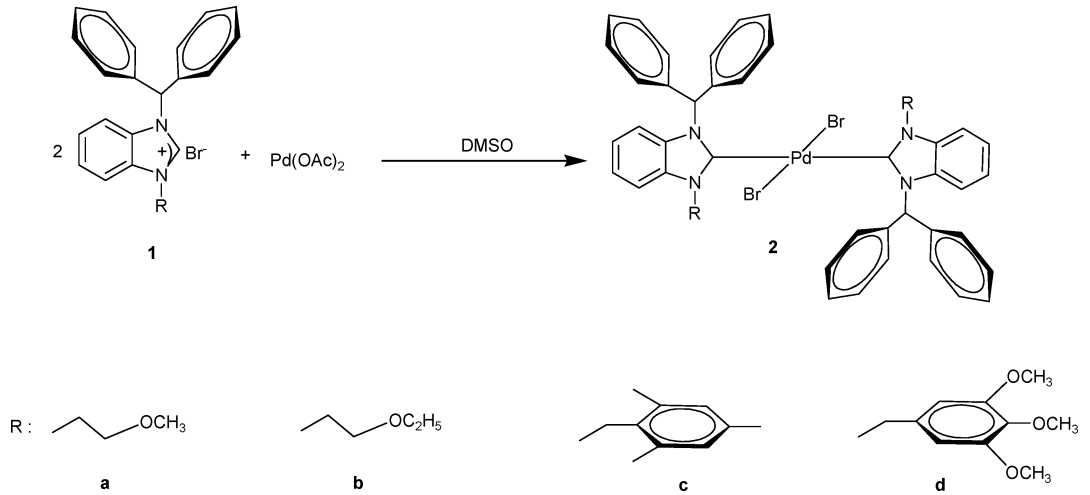
Scheme 2 General preparation of NHC complexes.

stable NHC, (iii) thermal cleavage of electron rich alkenes, and (iv) transmetallation from a silver–NHC complex.[24]

The reaction of benzimidazolium salts, with the $Pd(OAc)_2$ complex proceeded smoothly on heating at 30 °C for 3 h and then 120 °C for a further 6 h. The $PdBr_2$(1,3-dialkyl-benzimidazolin-2-ylidene)$_2$, complexes **2** as crystalline solids in 75–81% yield (Scheme 3).

Complexes **2a–d**, which were very stable in the solid state have been characterized by analytical and spectroscopic techniques. Palladium complexes exhibit a characteristic $\nu_{(NCN)}$ band typically at 1557, 1606, 1616 and 1595 cm^{-1} respectively for **2a–d**.[25] ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the range 182–184 ppm and are similar to those found in other carbene complexes. These new complexes showed typical spectroscopic signatures that were in line with those recently reported for other $PdBr_2$(*N*-heterocyclic carbene)$_2$ complexes.[26]

Structural characterization of 2b, and 2d. Crystals of **2b** and **2d** suitable for X-ray analysis were obtained from a chloroform solution layered with diethyl ether. The molecular structures of complexes have been confirmed by X-ray single-crystal analyses. Colorless single-crystals of **2b** and **2d** suitable for data collection were selected and performed on a STOE IPDS II diffractometer with graphite monochromated Mo-Kα radiation $\lambda = 0.71069$ Å. The structures were solved by direct-methods using SHELXS-97[27] and refined by full-matrix least-squares methods on F^2 using SHELXL-97[28] from within the WINGX[29,30] suite of software. The parameters for data collection and structure refinement of complexes **2b** and **2d** are listed in Table 1. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded



Scheme 3 Synthesis of palladium–NHC complexes.

Table 1 Parameters for data collection and structure refinement of **2b** and **2d**

	2b	**2d**
Empirical formula	$C_{48}H_{48}Br_2N_4O_2Pd$	$C_{60}H_{56}Br_2N_4O_6Pd\cdot 2(CHCl_3)$
Formula weight	979.12	1434.04
T/K	296	296
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.9725(3)	10.692(5)
b/Å	10.4541(4)	12.829(6)
c/Å	12.0262(4)	13.904(5)
α/°	81.773(3)	65.559(5)
β/°	86.671(3)	88.175(5)
γ/°	85.751(4)	67.876(4)
V/Å^3	1112.08(7)	1591.0(11)
Z	1	1
ρ_{calcd}/Mg m^{-3}	1.462	1.497
μ/mm^{-1}	2.26	1.85
F(000)	496	724
Crystal size/mm^3	0.44 × 0.29 × 0.22	0.44 × 0.24 × 0.14
θ Range for data collection/°	2.0–28.0	1.9–26.5
Reflections collected	28000	36044
Independent reflection	5130	6603
R(int)	0.068	0.050
Max./min. transmission	0.660 and 0.422	0.702 and 0.373
Data/restraints/parameters	5130/38/269	6603/0/370
Goodness-of-fit on F^2	1.05	1.05
R_1 ($I > 2\sigma(I)$)	0.038	0.035
wR_2 ($I > 2\sigma(I)$)	0.095	0.080
R_1 (all data)	0.045	0.047
wR_2 (all data)	0.098	0.084
$\Delta\rho_{max./min.}$/e Å^{-3}	0.58 and –0.67	0.52 and –0.56

to carbon were placed in calculated positions (C–H = 0.93–0.97 Å) and treated using a riding model with $U = 1.2$ times the U value of the parent atom for CH, CH_2 and CH_3. For the structure of **2b**, the large s.u. values and displacement parameters of some atoms in the molecule are caused by disorder of the ethoxyethyl group. The refinement of the disordered ethoxyethyl group was made anisotropically using PART and EADP restrictions. This disorder was modelled as two different orientations as A and B groups [hereafter A = O1a, C23a, C24a and B = O1b, C23b, C24b], seen in Fig. 1, with occupancy factors of 0.504(7) and 0.496(7), respectively. Molecular diagrams were created using ORTEP-III.[31] Geometric calculations were performed with Platon.[32] Molecular structures of **2b** and **2d** with selected data are presented in Figs. 1 and 2 respectively, and $\pi\cdots$ ring interactions are shown in Table 2.

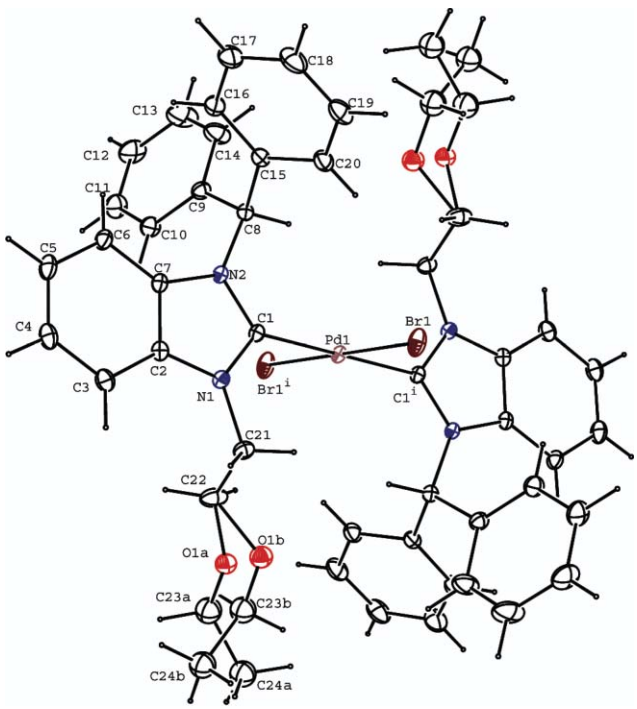


Fig. 1 ORTEP drawing of complex **2b** showing 40% probability thermal ellipsoids. Selected bond lengths [Å]: Pd1–Br1 = 2.4191(3), Pd1–C1 = 2.016(2), C1–N1 = 1.345(3), C1–N2 = 1.359(3), C2–N1 = 1.385(3), C7–N2 = 1.396(3), C8–N2 = 1.477(3), C8–C9 = 1.520(4), C21–N1 = 1.459(3); angles [°] : C1–Pd1–Br1 = 92.7(7), N1–C1–Pd1 = 124.6(18), N2–C1–Pd1 = 128.6(18), N1–C1–N2 = 106.5(2), N1–C2–C3 = 131.1(3), N2–C8–C9 = 112.4(2), C9–C8–C15 = 115.9(2), N1–C21–C22 = 112.2(3). Symmetry code: (i) 1 – x, 1 – y, 1 – z.

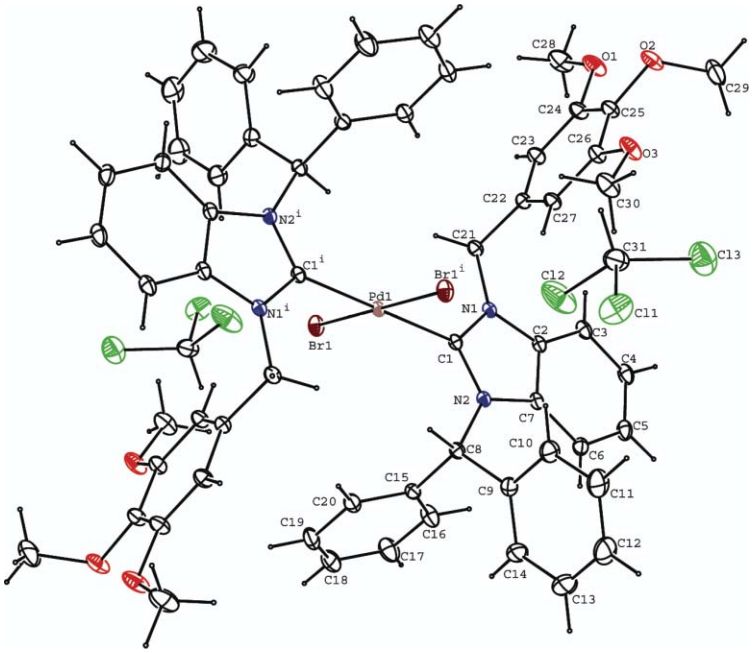


Fig. 2 ORTEP drawing of complex **2d** showing 40% probability thermal ellipsoids. Selected bond lengths [Å]: Pd1–Br1 = 2.4232(7), Pd1–C1 = 2.020(3), C1–N1 = 1.345(3), C1–N2 = 1.359(3), C2–N1 = 1.388(3), C7–N2 = 1.405(3), C8–N2 = 1.472(3), C8–C9 = 1.520(4), C21–N1 = 1.455(3), C21–C22 = 1.510(4); angles [°] : C1–Pd1–Br1 = 91.0(7), N1–C1–Pd1 = 125.7(18), N2–C1–Pd1 = 128.0(18), N1–C1–N2 = 106.2(2), N1–C2–C3 = 130.9(3), N2–C8–C9 = 112.0(2), C9–C8–C15 = 115.9(2), N1–C21–C22 = 113.1(2). Symmetry code: (i) 1 – *x*, 1 – *y*, 1 – *z*.

Table 2 π···ring interactions

2d			
C···H(I)	Cg(J)	H···Cg/Å	C–H···Cg/°
C12···H12	Cg(2)^{i}	3.3235	134.97
C19···H19	Cg(5)^{ii}	3.2306	130.29
C20···H20	Cg(5)^{ii}	3.3637	124.78

Cg(2): C2–C3–C4–C5–C6–C7, Cg(5): C22–C23–C24–C25–C26–C27. Symmetry codes: (i) –*x*, 2 – *y*, 1 – *z*; (ii) 1 – *x*, 1 – *y*, 1 – *z*.

Direct arylation of benzothiazole *via* C–H bond activation. We showed that NHC–palladium(II) species *in situ* generated from $Pd(OAc)_2$ and monoazolium salts under basic conditions were able to catalyze the direct arylation of aldehydes by aryl halides.[33,23e] Herein, we report a facile C-arylation of benzothiazole with aryl bromides catalyzed by well defined and stable palladium-NHC complexes. The influence of various bases such as Cs_2CO_3, K_2CO_3, K_3PO_4, NaH and KOBu^t was studied. It was observed that the bases Cs_2CO_3 and K_3PO_4 afforded good yields of the desired products. However, due to cost considerations K_3PO_4 was preferred over Cs_2CO_3. The effect of the various solvents on the reaction system was also examined. It was observed that nonpolar solvents such as toluene and xylene gave low yields of product probably due to the poor solubility of reactant and catalysts in the reaction medium. We found that the reactions performed in NMP with K_3PO_4 as the base at 130 °C gave better results than other bases. Control experiments indicated that the arylation of benzothiazole with bromobenzene did not occur in the absence of **2a**. Under these optimization conditions, bromobenzene, *p*-bromotoluene, *p*-bromoanisole and *p*-bromoacetophenone, reacted cleanly with benzothiazole in good yields (Table 3, entries 4, 6, 12 and 16).

Conclusions

From readily available starting materials, such as 1-(benzhydryl)-3-(alkyl)benzimidazolium salts, four novel $PdBr_2$(1,3-dialkyl-benzimidazolin-2-ylidene)$_2$ complexes (**2a–d**) have been prepared and characterized. Complexes **2b** and **2d** were characterized by single crystal X-ray diffraction studies. The efficiency of complexes **2a–d** as catalyst precursors for the arylation of benzothiazole with aryl bromides has also been established.

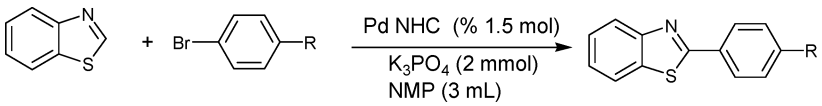
Experimental

All reactions for the preparation of benzimidazolium salts (**1**) and palladium-(NHC) complexes (**2**) were carried out under Ar in flame-dried glass-ware using standard Schlenk-type flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar. **1a–d** were prepared according to known methods.[23] All reagents were purchased from Aldrich Chemical Co. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab.

Synthesis of ligands

General procedure for the preparation of the benzimidazolium salts (1a–d). The benzimidazolium salts were prepared as **1a–c** according to our previous report.[23e] To a solution of

Table 3 Arylation of benzothiazole with aryl bromides



Entry	Cat.	R	Yield[a,b,c,d] (%)
1	**2a**	H	65
2	**2b**	H	61
3	**2c**	H	67
4	**2d**	H	81
5	**2a**	CH_3	63
6	**2b**	CH_3	70
7	**2c**	CH_3	59
8	**2d**	CH_3	69
9	**2a**	OCH_3	68
10	**2b**	OCH_3	73
11	**2c**	OCH_3	56
12	**2d**	OCH_3	80
13	**2a**	$COCH_3$	49
14	**2b**	$COCH_3$	47
15	**2c**	$COCH_3$	51
16	**2d**	$COCH_3$	58

[a] Reaction conditions: 1.5 mmol of *p*-R-C_6H_4Br, 1.0 mmol benzothiazole, 2 mmol K_3PO_4, 1.5 mol Pd, 3 mL NMP. [b] Purity of all compounds determined by NMR and the yield calculated based on the aryl bromide. [c] All reactions followed by GC. [d] Temperature 150 °C and time 30 h.

1-alkylbenzimidazoline (10 mmol) in DMF (10 mL) was slowly added alkylbromide (10 mmol) at 25 °C and the resulting mixture was stirred at 12 h at 80 °C. Et_2O (10 mL) was added to the reaction mixture. A white solid was precipitated in this period. The solid was washed with diethyl ether (3 × 15 mL), dried under vacuum. The precipitate was then crystallized from EtOH/Et_2O (1:2).

1-(Benzhydryl)-3-(3,4,5-trimethoxybenzyl)benzimidazolium bromide (1d). Yield: 4,91 g (90%); mp 253–254 °C; $\nu_{(CN)}$= 1595.66 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.61 (s, 3H, $CH_2C_6H_2(OCH_3)_3$-4), 3.74 (s, 6H, $CH_2C_6H_2(OCH_3)_3$-3,5), 5.67 (s, 2H, CH_2-(C_6H_2)-$(OCH_3)_3$-3,4,5), 6.90 (s, 2H, CH_2-(C_6H_2)-$(OCH_3)_3$-3,4,5), 7.41–8,35 (m, 15H, $CH(C_6H_5)_2$, Ar), 9.82 (s,1H,2-CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.0 ($CH_2C_6H_2(OCH_3)_3$-3,5), 56.7 ($CH_2C_6H_2(OCH_3)_3$-4), 60.6 (CH_2-(C_6H_2)-$(CH_3)_3$-3,4,5), 64.8 ($CH(C_6H_5)_2$), 106.7, 115.1, 127.5, 127.6, 127.7, 127.9, 129.8, 129.9, 130.1, 132.0, 132.8, 138.3, 142.7 (Ar), 153.8 (2-CH). Anal. Calc. for $C_{30}H_{29}N_2O_3Br$: C, 66.06; H, 5,36; N, 5.14. Found: C, 66.02; H, 5.39; N, 5.22%.

Synthesis of complexes *trans*-bis[1-(Benzhydryl)-3-(methoxyethyl)benzimidazolin-2-ylidene]dibromopalladium(II) (2a). 1-(Benzhydryl)-3-(methoxyethyl)benzimidazolium bromide (**1a**) (0.42 g, 1 mmol) and $Pd(OAc)_2$ (0.11 g, 0.5 mmol) were solved in DMSO (15 mL). The resulting mixture was stirred for 3 h at room temperature and then for 6 h at 120 °C. The solvent was removed under reduced pressure. The solid was washed with ether (3 × 10 mL) and dried under vacuum. The crude product was then crystallized from CH_2Cl_2/Et_2O (1:2). Yield: 0.36 g (76%); mp 220–221 °C; $\nu_{(CN)}$ = 1557cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.27 (s, 6H, OCH_3), 4.08 (t, 4H, J = 6 Hz, NCH_2CH_2O), 4.97 (t, 4H, J = 6 Hz, NCH_2CH_2O), 8.51 (s, 2H, $CH(C_6H_5)_2$), 6.74–7.58 (m, 28H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.2 (OCH_3), 67.5 (NCH_2CH_2O), 71.5 (NCH_2CH_2O), 48.4 ($CH(C_6H_5)_2$), 111.3, 113.5, 122.6, 127.9, 128.4, 129.0, 129.6, 133.6, 135.9, 137.6 (Ar), 183.7 ($C_{carbene}$). Anal. Calc. for $C_{46}H_{44}O_2N_4Br_2Pd$: C, 58.04; H, 4.66; N, 5.89. Found: C, 58.07; H, 4.71; N, 5.83%.

***trans*-bis[1-(Benzhydryl)-3-(ethoxyethyl)benzimidazolin-2-ylidene]dibromo-palladium(II) (2b).** Compound **2b** was prepared in the same way as **2a**, from 1-(benzhydryl)-3-(ethoxyethyl)benzimidazolium bromide (**1b**) (0.44 g, 1 mmol) and $Pd(OAc)_2$ (0.11 g, 0.5 mmol) in DMSO (5 mL). Yield: 0.37 g (75%); mp 281–283 °C; $\nu_{(CN)}$ = 1606cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, 6H, J = 6.9 Hz, OCH_2CH_3), 3.43 (quart., 4H, J = 6.9 Hz, OCH_2CH_3), 4.12 (t, 4H, J = 6 Hz, NCH_2CH_2O), 4.98 (t, 4H, J = 6. Hz, CH_2CH_2O), 8.50 (s, 2H, $CH(C_6H_5)_2$, 6.73–7.57 (m, 28H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0 (OCH_2CH_3), 67.9 (OCH_2CH_3), 66.8 (NCH_2CH_2O), 69.2 (NCH_2CH_2O), 48.2 ($CH(C_6H_5)_2$), 111.4, 113.3, 122.5, 128.4, 129.0, 133.8, 135.9, 137.6 (Ar), 183.9 ($C_{carbene}$). Anal. Calc. For $C_{48}H_{48}Br_2N_4O_2Pd$: C, 58.88; H, 4.94, N, 5.72. Found: C, 58.92; H, 4.99; N, 5.69%.

***trans*-bis[1-(Benzhydryl)-3-(2,4,6-trimethylbenzyl)benzimidazolin-2-ylidene]dibromo-palladium(II) (2c).** Compound **2c** was prepared in the same way as **2a**, from 1-(benzhydryl)-3-(2,4,6-trimethylbenzyl)benzimidazolium bromide (**1c**) (0.50 g, 1 mmol) and $Pd(OAc)_2$ (0.11 g, 0.5 mmol) in DMSO (15 mL). Yield: 0.45 g (81%); mp 299–300 °C; $\nu_{(CN)}$= 1616 cm^{-1}. ^1H NMR (400 Mhz, $CDCl_3$): δ = 2.32 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,6), 2.37 (s, 6H, $CH_2C_6H_2(CH_3)_3$-4), 5.93 (s, 4H, CH_2-(C_6H_2)-$(CH_3)_3$), 6.95 (s, 4H, CH_2-(C_6H_2)-$(CH_3)_3$), 8.83 (s, 2H, $CH(C_6H_5)_2$), 7.38–7.73 (m, 28H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1 ($CH_2C_6H_2(CH_3)_3$-4), 21.4 ($CH_2C_6H_2(CH_3)_3$-2,6), 53.5 (CH_2-(C_6H_2)-$(CH_3)_3$-2,4,6), 67.4 ($CH(C_6H_5)_2$), 114.6, 114.7, 122.1, 122.4, 127.8, 128.3, 128.4, 128.8, 129.6, 134.7, 135.0, 138.0, 138.4, 153.6 (Ar), 182.0 ($C_{carbene}$). Anal. Calc. for $C_{60}H_{58}Br_2N_4Pd$: C, 65.43; H, 5.31; N, 5.09. Found: C, 65.41; H, 5.30; N, 5.07%.

***trans*-bis[1-(Benzhydryl)-3-(3,4,5-trimethoxybenzyl)benzimidazolin-2-ylidene]dibromo-palladium(II) (2d).** Compound **2d** was prepared in the same way as **2a**, from 1-(benzhydryl)-3-(3,4,5-trimethoxybenzyl)benzimidazolium bromide (**1d**) (0.56 g, 1 mmol) and $Pd(OAc)_2$ (0.11 g, 0.5 mmol) in DMSO (15 mL). The crude product was then crystallized from $CHCl_3/Et_2O$ (1:2). Yield: 0.56 g (78%); mp 275–277 °C; $\nu_{(CN)}$= 1595 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 12H, $CH_2C_6H_2(OCH_3)_3$-3,5), 3.89 (s, 6H, $CH_2C_6H_2(OCH_3)_3$-4), 6.05 (s, 4H, CH_2-(C_6H_2)-$(OCH_3)_3$-3,4,5), 6.91 (s, 4H, CH_2-(C_6H_2)-$(OCH_3)_3$-3,4,5), 8.64 (s, 2H, $CH(C_6H_5)_2$), 6.54–7.40 (m, 28H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.9 ($CH_2C_6H_2(CH_3)_3$-3,5), 60.8 ($CH_2C_6H_2(CH_3)_3$-4), 65.9 (CH_2-(C_6H_2)-$(CH_3)_3$-3,4,5), 67.5 ($CH(C_6H_5)_2$), 105.3, 111.4, 113.6, 122.7, 122.8, 127.9, 128.4, 128.7, 129.0, 131.3, 134.6, 134.8, 137.5, 138.1 (Ar), 184.0 ($C_{carbene}$). Anal. Calc. for $C_{60}H_{56}Br_2N_4O_6Pd{\cdot}2(CHCl_3)$: C, 51.96; H, 4.01; N, 3.91. Found: C, 51.92; H, 4.02; N, 3.93%.

General procedure for the arylation of benzothiazole. The Pd–NHC complex (% 1.5 mol), aryl bromides (1.5 mmol), benzothiazole (1 mmol), K_3PO_4 (2.0 mmol) and NMP (3 mL) were all added to a small Schlenk tube and the mixture was heated at 150 °C for 30 h in an oil bath. EtOAc were added to the cold reaction mixture. The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The remaining residue was purified by column chromatography on silica gel (EtOAc/hexane mixture) to yield the arylated products. Conversion and ratios were determined by ^1H NMR and by GC analyses.

Acknowledgements

This work was financially supported by the Technological and Scientific Research Council of Turkey TUBİTAK-CNRS (France) [TBAG-U/181 (106T716)], Inönü University Research Fund (İ.Ü. B.A.P: 2009/13) and the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased from grant no. F279 of the University Research Fund).

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