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Synthesis, characterization and catalytic properties of *cis*-dibromo{1,1'-di [3,4,5-trimethoxybenzyl]-3,3'-butylenedibenzimidazol-2,2'-diylidene}palladium (II)

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ABSTRACT

An *N*-heterocyclic carbene palladium-based complex, *cis*-dibromo{1,1'-di[3,4,5-trimethoxybenzyl]-3,3'butylenedibenzimidazol-2,2'-diylidene}palladium(II), has been synthesized and characterized by elemental analysis, IR spectroscopy and ¹H- and ¹³C-NMR spectroscopy. The crystal and molecular structure of the title compound was determined by single-crystal X-ray diffraction. The title compound consists of a 1,1'-di[3,4,5trimethoxybenzyl]-3,3'-butylenedibenzimidazole and two bromo ligands coordinated to a palladium atom in a distorted square-planar *cis*-system. Two benzoimidazole rings are connected to each other by a C₄H₈ bridge. The substituted benzimidazole ligand forms a bidentate chelate with palladium, bonding *via* the carbene carbon atoms. There are two independent molecules A and B in the asymmetric unit. The Pd—Br bonds are 2.4675(14) and 2.4601(13)Å, and the Pd—C_{carbene} bonds are 1.985(9) and 1.986(9)Å for molecule A. Each A and B molecule is stabilized with intra- and inter-molecular hydrogen bonds and C—H…π interactions. The palladium-carbene complex was tested as a catalyst in the direct arylation of benzothiazole with arylbromides. The most suitable reaction conditions for the direct arylation of benzothiazole with arylbromides are NMP, K₃PO₄, Pd–NHC and 130 °C.

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Heteroaryl groups directly connected by single Csp^2 — Csp^2 bonds to heteroaryl moieties are present as core structures in many biologically active compounds, naturally-occurring substances, agrochemicals, and optical and photochromic materials in polymer science [1,2]. The most useful method to prepare for these important derivatives is the metal-catalyzed cross-coupling of aryl halides with heteroaryl derivatives [3]. A viable solution could be the use of palladium(II) complexes with suitable ligands, which should increase the stability of the catalyst under reaction conditions without negatively affecting its reactivity. One type of ligand would be an *N*heterocyclic carbene.

N-heterocyclic carbene (NHC) ligands appear particularly suited to this purpose, in that it is known that their palladium(II) complexes possess a high thermal and hydrolytic stability, even under strongly acidic conditions [4].

Recently, our research group has focused on *N*-heterocyclic carbene derivative ligands and their metal complexes for synthesis, characterization, crystal structure and catalytic activity [5–14]. In this contribution, we pursue further our previous work on the chelating biscarbene palladium(II) complex. *Bis*(benzimidazolium) salt as the

NHC precursor, was synthesized by treatment of 1-substituted benzimidazole with 1,4-dibromobuthane according to the literature [10]. Because of the 1,4-butylene linker group is more flexible than the other more commonly used bridges such as methylene, o-xylylene etc. [15] we select 1,4-butylene group as a bridge/linker group. The reaction of the *bis*(benzimidazolium) salt with Pd(OAc)₂ in dimethyl sulfoxide resulted in the Palladium–NHC complex (**2**) as a crystalline solid (Scheme 1) [16]. The spectroscopically pure **2**, which is very stable in the solid state, was characterized by analytical and spectroscopic techniques [16]. The FT-IR spectroscopy, ¹H- and ¹³C–NMR spectroscopy, and elemental analysis data of the title compound confirm the proposed structure [16,17]. The crystal structure of this new complex [17,18], as well as its applications in the direct arylation of benzothiazole with arylbromides [19] is described.

The complex exhibits signals slightly upfield in comparison with the parent carbene precursor (1); as expected, the C₂–H signal is absent. Correspondingly, the ¹³C–NMR spectrum of the title compound shows the characteristic coordinated carbene signal at 173.8 ppm, which is in the typical range observed for Pd–NHC complexes. The IR data for the Pd–carbene complex clearly indicate the presence of the C–N group with a ν_{CN} vibration at 1462 cm⁻¹.

The molecular structure of the title compound was confirmed by the result of a single crystal X-ray structure determination. The molecular structure of **2**, with the atom-numbering scheme, is shown

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Scheme 1. Synthesis of palladium-NHC complex.

in Fig. 1. Selected bond lengths and angles are listed in the caption of Fig. 1 [20]. The asymmetric unit of the title compound contains two crystallographically independent molecules A and B. There is very little difference between the bond lengths and angles of these molecules.

The coordination geometry around the palladium atom is square planar, with C_{carben} and Br atoms *cis* to each other. There is a small amount of distortion of the square plane towards a tetrahedron. The palladium atom is displaced slightly at a distance of 0.018 Å from the coordination plane defined by the C1–C12–Br1–Br2 atoms. The Br1–Pd1–Br2 angle of 94.74(5)° and the C1–Pd–C12 angle of 93.3(4)° agree well with values reported for structures of the type *cis*-PdL₂X₂ (L: Carben derivative ligands) [21–23].

The Pd—Br bond in the title complex is somewhat shorter than the average of 2.484 ± 0.023 Å calculated for 44 Pd–Br distances in 22 palladium–NHC complexes reported in the Cambridge Structural Database [24]. The corresponding Pd—Br bond length values [2.4580



Fig. 1. The molecular structure of *cis*-dibromo{1,1′-di[3,4,5-trimethoxybenzyl]-3,3′butylenedibenzimidazol-2,2′-diylidene}palladium(II). Thermal ellipsoids are shown at the 50% probability level. Pd1–C12 1.985(9), Pd1–C1 1.986(9), Pd1–Br2 2.4601(13), Pd1–Br1 2.4675(14), N1–C1 1.339(12), N1–C2 1.419(11), N1–C19 1.474(11), N2–C1 1.340(11), N2–C7 1.420(12), N2–C8 1.460(11), N3–C12 1.377(11), N3–C13 1.395(13), N3–C11 1.445(12), N4–C12 1.309(11), N4–C18 1.390(12), N4–C29 1.437(11) Å, C12– Pd1–C1 93.3(4), C12–Pd1–Br2 84.7(3), C1–Pd1–Br2 177.7(2), C12–Pd1–Br1 178.9(3), C1–Pd1–Br1 87.3(3), Br2–Pd1–Br1 94.74(5), C1–N1–C2 110.8(7), C1–N1–C19 125.6 (7), C2–N1–C19 123.6(7), C1–N2–C7 110.9(7), C1–N2–C8 125.1(7), C7–N2–C8 123.9) (7), C12–N3–C13 108.9(8), C12–N3–C11 125.8(8), C13–N3–C11 124.9(8), C12–N4–C18 111.4(7), C12–N4–C29 126.5(7), C18–N4–C29 112.1(8), N1–C1–N2 106.8(7), N1–C1– Pd1 128.1(6), N2–C1–Pd1 125.1(7), N2–C8–C9 113.0(8), C10–C9–C8 114.3(7), C9– C10–C11 114.3(9), N3–C11–C10 111.0(8), N4–C12–N3 107.5(8), N4–C12–Pd1 128.3 (6), N3–C12–Pd1 124.2(7), N1–C19–C20 113.4(7), N4–C29–C30 115.5(8)°.

(6) and 2.4622(6)] in {1,1'-dibenzyl-3,3'-ethylenediimidazolin-2,2' diylidene}palladium(II) dibromide [21], follow a similar trend to those in the title compound. In addition, the Pd—Br bond distances are shorter than the platinum complex, (1,1'-dimethyl-3,3'-methylene-4-diimidazolin-2,2'-diylideneplatinum(II) dibromide) (2.4976 (11) and 2.4883(13)Å) [26].

The $Pd-C_{carben}$ bond in the title complex is somewhat shorter than the average of 1.997 ± 0.019 Å calculated for 14 Pd-C_{carben} distances in 9 Pd-NHC complexes reported to the Cambridge Structural Database [24]. The corresponding Pd-Ccarben bond length values [1.959(6)-1.993(2)] in the compounds {1,1'-di(4-methoxybenzyl)-3,3'-ethylenediimidazolin-2,2'diylidene}palladium(II) dibromide, {1,1'-di(3-methoxybenzyl)-3,3'-ethylenediimidazolin-2,2' diylidene}palladium(II) dibromide, {1,1'-di(4-fluorobenzyl)-3,3'ethylenediimidazolin-2,2'diylidene}palladium(II) dibromide, {1,1'dibenzyl-3,3'-ethylenediimidazolin-2,2'diylidene}palladium(II) dibromide, and {1,1'-di(1-naphthalenemethyl)-3,3'-ethylenediimidazolin-2,2'diylidene}palladium(II) dibromide [21], [1.980(8)-1.994 (8)] in the compounds diiodo(methylenebis(imidazo[1,5-a]-pyridine-3-ylidene))palladium(II) and dibromo(methylenebis(imidazo[1,5-a]pyridine-3-ylidene))palladium(II) [22], and [1.983(5) and 1.971(5)Å] in dibromo(1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene)palladium(II) [25] follow a similar trend to those in the title compound. In addition, the $\text{Pd-}C_{\text{carben}}$ distances are also slightly shorter than the other $Pd-C_{carben}$ single bonds; 1-(o-methoxybenzyl)-3-tert-butylimidazol-2-ylidene)₂PdCl₂ (2.036(5)Å) [27], trans-{3-(2-((2,6-diisopropylphenyl)-imino)propyl)-1-methylimidazol-2ylidene}PdCl₂, (2.037(1)Å) [28], [($\kappa^{1-nPr}CN^{CHPh}$)₂PdCl₂], (2.067(10) Å) [29], *bis*(1-(benzoxazolin-2-yl)-3-mesitylimidazol-2-ylidene) diiodo palladium(II) (2.016(5)Å) [30], and bis(1,3-bis-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene)palladium(II) chloride (2.035 (2)Å) [12]. The Pd—C_{carben} bond lenght values (Pd1–C12, 1.985(9) and Pd1–C1, 1.986(9)Å) differ, but are only slightly greater than those in the similar platinum complex [1.963(10) and 1.950(10) Å] [30].

The benzimidazole ring is almost planar and the maximum deviations from planarity are -0.030(8)Å for atom N1 and 0.034 (10)Å for atom C13. The dihedral angle of two benzimidazole moieties is 89.7(3)°. In addition, the benzoimidazole moiety (N1,N2, C1–C7) forms dihedral angles of 82.8(4)° and 8.6(4)° with the mean planes through the 3,4,5-trimethoxybenzyl rings (C20:C25) and (C30: C35), respectively.

The crystal structure of the title compound is stabilized by intermolecular C—H...Br and C—H...O; and by intramolecular C—H...N and C—H...O van der Waals contact which link the molecules into a three-dimensional molecular network (Fig. 2) [31]. In addition, the packing is stabilized by C—H... π interactions [31].

The arylation reaction of thiazoles has been studied by Miura and Nomura. They have described that the palladium catalyzed direct arylation of thiazole with aryl bromides in DMF [32,33]. We describe here successively the reactions of substituted bromobenzene derivatives with benzothiazole. Initially, the direct arylation of benzothiazole with bromobenzene was chosen as a model reaction and the roles of various reaction parameters on the yield for the coupling of bromobenzene with benzothiazole in the presence of 1.5 mol% Pd catalyst were investigated. The influence of various organic and



Fig. 2. Packing diagram for 2 complex.

inorganic bases such as K_3PO_4 , Cs_2CO_3 , KO^rBu , and K_2CO_3 was studied for the standard reaction (Table 1, entries 1–4). It was observed that the all bases afforded good yields of the desired product. However, due to cost considerations K_3PO_4 was preferred. The effect of various solvents on the reaction system was also studied (Table 1, entries 4– 7). It was observed that *N*-methylpyrrolidone was effective in providing higher conversions whereas solvents like toluene, DMF, dioxane showed lower conversions. Finally, we studied the influence of a higher reaction temperature. At 150 °C instead of 130 °C, some side-products were also formed. Then using the most suitable reaction conditions (NMP, K₃PO₄, Pd–NHC, 130 °C) we examined the scope and limitation of this reaction with a variety of aryl bromides. Table 1 summarizes the results obtained for these reactions. We have demonstrated how to produce higher yields for the Pd–NHC catalyzed direct arylation of benzothiazole (Table 1, entry 9). The presence of electron donating substituents appears to have a minor effect on the reaction yields. Bromobenzenes with electron donating groups, such as *p*-bromoanisole and *p*-bromotoluene, took longer reaction times (Table 1, entries 8 and 9) compared with bromobenzene. Without a catalyst, the blank reaction indicated that the arylation of benzotiazole with bromobenzene gave products from the aryl bromide substrate.

Table 1

Palladium catalyzed direct arylation of benzothiazole and aryl bromides^a.

	\bigcirc	\sim + Br		<i>Bis</i> (NHC)-Pd		
Entry	R	Base	Solvent	Time(h)	Product	Yield (%)
1	Н	K ₂ CO ₃	NMP	20		21
2	Н	Cs ₂ CO ₃	NMP	20		20
3	Н	KO ^t Bu	NMP	20		25
4	Н	K ₃ PO ₄	NMP	20		58
5	Н	K ₃ PO ₄	DMF	20		10
6	Н	K ₃ PO ₄	Toluene	20		23
7	Н	K ₃ PO ₄	Dioxane	20		35
8	CH ₃	K ₃ PO ₄	NMP	24		65
9	OCH ₃	K ₃ PO ₄	NMP	24	OCH3	74
10	COCH ₃	K ₃ PO ₄	NMP	20		53

^a Reaction conditions: 1.5 mmol of R-C₆H₄Br, 1.0 mmol of benzothiazole, 1.5 mol%Pd catalyst, 130 °C. Purity of compounds was checked by NMR and yields are based on benzothiazole. All reactions were monitored by GC and GC-MS.

In conclusion, we have designed and synthesized a novel air stable palladium-*N*-heterocyclic carbene complex. The molecular and crystal structure of the palladium complex was elucidated. The complex is found to exhibit good catalytic activity in the direct arylation of benzothiazole with arylbromides.

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- [16] All reactions for the preparation of bis(benzimidazolium) salt and chelating Pd (NHC) complex were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals were obtained from Sigma Aldrich and Fluka. (Scheme 1). 1.0 mmol of bis(benzimidazolium) salt and Pd(OAc)₂ (0.22 g, 1.0 mmol) were dissolved in 5 mL DMSO and stirred at room temperature for 2 h, afterwards the mixture was heated for 5 h at 50 °C and later 2 h at 90 °C and 0.5 h 120 °C. The volatile compounds were removed in vacuum and the precipitate was washed twice with 5 mL THF. The complex was recrystallized by dichloromethane:diethyl ether (1:3) at room temperature. Cis-dibromo{1,1'-di[3,4,5trimethoxybenzyl]-3,3'-butylenedibenzimidazol-2,2'-diylidene}palladium (II), Yield: 0.62 g (68%). M.p.: $204-205 \,^{\circ}\text{C}$, $v_{(CN)}$: 1462 cm^{-1} . ¹H NMR (399.9 MHz, CDCl₃) d = 7.50-7.13 (m, 4H, NC₆H₄N), 7.41(d, 2H, J = 8.1 Hz, NC₆H₄N), 7.06 (d, 2H, J = 8.1 Hz, NC₆H₄N), 6.48 (s, 4H, CH₂C₆H₂(OCH₃)₃-3,4,5), 6.15 (d, 2H, 2H, 2H) = 8.1 Hz, NC₆H₄N), 7.41 (d, 2H, 2H) = 8.1 Hz, NC₆H₄N), 7.41 (d, 2H, 2H) = 8.1 Hz, NC₆H₄N), 7.41 (d, 2H, 2H) = 8.1 Hz, NC₆H₄N), 7.41 (d, 2H) = 8.1 Hz, NC $J = 15.6 \text{ Hz}, CH_2C_6H_2(OCH_3)_3 - 3,4,5), 5.16 (d, 2H, J = 15.6 \text{ Hz}, CH_2C_6H_2$ (OCH₃)₃-3,4,5), 5.95 and 4.68 (m, 4H, -CH₂CH₂CH₂CH₂-), 3.81 (s, 6H, CH₂C₆H₂ (OCH₃)₃-3,4,5), 3.61 (s, 12H, CH₂C₆H₂(OCH₃)₃-3,4,5), 2.32 and 1.51 (m, 4H, $-CH_2CH_2CH_2CH_2-$). ¹³C NMR (100.5 MHz, CDCl₃) d = 173.8 ($C_{carbene}$), 153.7, 137.6, 134.1, 133.7, 130.5, 123.9, 111.9, 110.3, 104.4 and 102.2 (NC₆H₄N and CH₂C₆H₂ (OCH₃)₃-3,4,5), 60.9 (CH₂C₆H₂(OCH₃)₃-3,4,5), 56.2 (CH₂C₆H₂(OCH₃)₃-3,4,5), 56.0 (CH₂C₆H₂(OCH₃)₃-3,4,5), 44.1 (-CH₂CH₂CH₂CH₂CH₂), 24.6 (-CH₂CH₂CH₂CH₂CH₂). Anal. Calc. for C₃₈H₄₂N₄O₆PdBr₂: C, 49.77; H, 4.62; N, 6.11. Found: C, 49.65; H, 4.74; N, 6.24%
- [17] Melting point was determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm⁻¹ with a ATI UNICAM 1000 spectrometer. The elemental analyses were performed at TUBITAK (Ankara, Turkey) Microlab. ¹H- and ¹³C-NMR spectra were recorded with a Varian AS 400 Merkur spectrometer operating at 400 MHz (¹H) (¹³C) in CDCl₃ with tetramethylsilane as an internal reference. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet and m = multiplet signal. Single crystal X-ray data were collected on a Rigaku AFC8S Mercury CCD diffractometer [Molecular Structure Corporation & Rigaku (2006). CrystalClear, MSC, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan] using monochromated Mo-Kα radiation. The structure was solved [Sheldrick, G. M.

(2008). SHELXTL Version 6.10, Acta Cryst. A64, 112–122.] by direct and conventional Fourier methods. Full-matrix least-squares refinement was [Sheldrick, G. M. (2008). SHELXTL Version 6.10, Acta Cryst. A64, 112–122.] based on F^2 . Apart from hydrogen all atoms were refined anisotropically; hydrogen atom coordinates were calculated at idealized positions and refinement are given in reference [18]. PLATON [ALLSpek (2010) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands] was used to determine that a void of 373 Å³ was present. SQUEEZE [described in: P.V.D. Sluis and A.L. Spek, Acta Cryst., A46 (1990) 194] was applied and it determined that the void contained approximately 7 electrons indicating a very small amount of diffuse solvent. Molecular graphics is prepared with OLEX2 Software [20].

- [18] Empirical formula: $C_{38}H_{42}Br_2N_4O_6Pd$; Formula weight: 916.98; Temperature: 153 (2) K; Wavelength: 0.71073 Å; Crystal system: Monoclinic; Space group: P2(1)/c; Unit cell dimensions: a = 21.295(4) Å, b = 11.711(2) Å, c = 32.873(7) Å, $\alpha = 90^{\circ}$, $\beta = 102.80(3)^{\circ}$, $\gamma = 90^{\circ}$; Volume: 7994(3) Å³; Z: 8; Calculated density: 1.524 Mg/ m³; Absorption coefficient: 2.512 mm⁻¹; F(000): 3696; Crystal size: $0.34 \times 0.12 \times 0.04$ mm; Theta range for data collection: 2.25 to 25.05°; Limiting indices: $-25 \le h \le 22$, $-10 \le k \le 13$, $-39 \le l \le 39$; Reflections collected/unique: 44107/13678 [R(int) = 0.0893]; Completeness to theta: 25.05 (96.7%); Absorption correction: REQAB (multi-scan); Max. and min. transmission: 0.9062 and 0.4822; Refinement method: Full-matrix least-squares on F²; Data/restraints/parameters: 13678/0/931, Goodness-of-fit on F²: 1.019; Final R indices [1-2 σ (1)]; R1 = 0.0809, wR2 = 0.2029; R indices (all data): R1 = 0.1290, wR2 = 0.2352; Largest diff. peak and hole: 2.602 (0.05 Å from Pd1) and -0.993 e.A⁻³.
- [19] The aryl bromide (1.5 mmol), benzothiazole (1.0 mmol), K₃PO₄ (2 mmol) and Pd catalyst (1.5 mol%) were dissolved in N-methyl-2-pyrrolidone (NMP) (3 mL) in a small Schlenk tube under an argon atmosphere. The reaction mixture was stirred in an oil bath at 130 °C for 20–24 h. The reaction mixture was cooled to room temperature and ethyl acetate/water was added. The organic phase was dried over anhydrous MgSO₄ and filtered. Solvent was removed under reduced pressure and concentrated in vacuum to give the crude product. The crude product was purified by column chromatography on silica gel (60–120 mesh) using ethyl acetate:n-hexane (1:5) as eluent to afford the 2-substituted benzothiazoles. Purity of compounds is checked by NMR and yields are based on benzothiazole. Conversion and ratios were monitored by gas chromatography and gas chromatography-mass spectrometry.
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