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Synthesis and characterization of *N*-heterocyclic carbene palladium complex and its application on direct arylation of benzoxazoles and benzothiazoles with aryl bromides

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Synthesis and characterization of *N*-heterocyclic carbene palladium complex and its application on direct arylation of benzoxazoles and benzothiazoles with aryl bromides

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A mixed-halogen *bis*(1-(4-*tert*-butylbenzyl)-3-(2,4,6-trimethylbenzyl)-1*H*-benzo[*d*]imidazol-2-ylidene) palladium(II) complex, *trans*-[Pd(Cl_{0.7}Br_{0.3})₂(C₂₈H₃₂N₂)₂], has been synthesized and characterized by elemental analysis, ¹H-NMR, ¹³C-NMR, and IR spectroscopy, and single crystal X-ray diffraction. The palladium in the mononuclear complex is four-coordinate in a square-planar configuration with two carbenes of two benzo[*d*]imidazole rings and two halides. The two halides are disordered between Br and Cl, with the Cl: Br ratio approximately 0.7:0.3. The angles C1–Pd1–Br1, 88.63(11)° and C1ⁱ–Pd1–Br1ⁱ, 91.37(11)° (i: 1–*x*, 1–*y*, 1–*z*) in the coordination sphere are very close to the ideal value of 90°. The Pd–X distance is slightly longer than other carbene derivative Pd–Cl single bond distances and slightly shorter than Pd–Br single bond distances. These results agree with the Cl/Br disorder at the halogen position. The palladium–carbene complex was tested as a catalyst in the direct arylation reaction of benzoxazoles and benzothiazoles with aryl bromides.

Keywords: Synthesis; *N*-Heterocyclic carbene; Benzoxazoles; Direct arylation; Palladium complex; Single crystal structure

1. Introduction

The first study on metal coordination chemistry of *N*-heterocyclic carbenes was reported by Öfele in 1968 [1]. *N*-heterocyclic carbenes are excellent σ -donor ligands with only slight back bonding character. This important property has drawn much attention to *N*-heterocyclic carbene derivatives. Metal complexes bearing *N*-heterocyclic carbenes

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have been employed as catalysts in a wide variety of chemical reactions such as polymerization, metathesis, hydrosilylation, and C–C coupling [2–4].

A number of simple *N*-heterocyclic carbene (NHC) palladium-based complexes have emerged as effective catalysts for a variety of cross-coupling reactions [5]. Various aryl-substituted azole compounds having imidazole, oxazole, and thiazole skeletons exhibit pharmacological activities and are also of importance in π -conjugated functional materials. Among the most useful methods to prepare such arylheterocycles is palladium catalyzed cross-coupling of either heteroaryl halides with aryl metal complexes or aryl halides with heteroaryl metal complexes [6].

Aryl benzoxazoles are important biaryl pharmacophores with low toxicities, which have exhibited a variety of biological activities, including anti-HIV, anti-inflammatory, anti-microbial, antibiotic, and anti-tumor properties [7]. Benzoxazole derivatives have attracted the attention of many research groups [8, 9] and biological activities have made them popular synthetic targets.

The direct arylation of heterocycles is of 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. The pioneering work in this field was performed by Aoyagi and co-workers [10]. A number of other researchers have focused on these arylation reactions [9–14], using different catalysts and solvents to obtain optimum direct coupling reaction conditions. Most of these were coupling reactions of heteroaryl derivatives with aryl bromides *via* C–H activation at high temperature.

Our research group has synthesized, characterized, and investigated for catalytic activity in Suzuki-Miyura and Heck reactions, *N*-heterocyclic carbene derivative ligands and their metal complexes [15–29]. Based on these findings and our continuing interest in developing more efficient and stable catalysts for direct arylation coupling reactions of benzoxazole and benzothiazoles with aryl halides, we now report the straightforward preparation of the palladium complex and its structural and spectroscopic characterization. The application of this novel palladium complex in the direct arylation of benzoxazoles and benzothiazoles with aryl bromides is also described in this work.

2. Experimental

2.1. Instrumentation

^1H and ^{13}C NMR spectra were recorded using a Varian 400 spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. ^1H and ^{13}C NMR were performed in CDCl_3 . Infrared spectra were recorded as KBr pellets in the range of 400–4000 cm^{-1} on an 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 Turkish Research Council (Ankara, Turkey) Microlab. All reactions were monitored on a Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness. Single crystal X-ray data were collected on a Rigaku AFC8S Mercury CCD

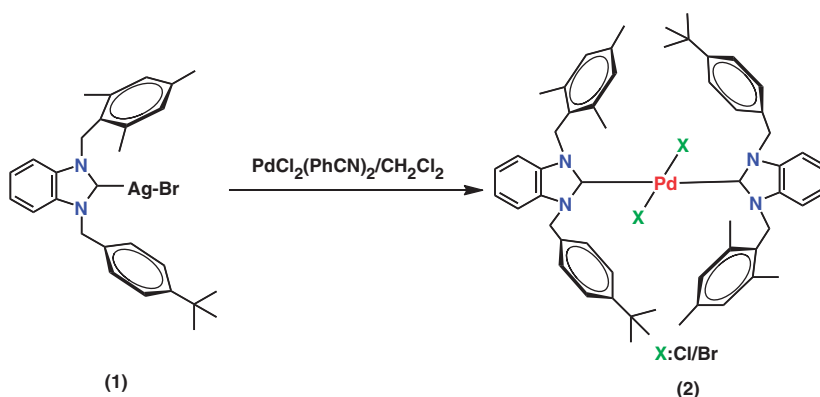
Table 1. Summary of crystallographic data and parameters of the palladium complex.

Empirical formula	C ₅₆ H ₆₄ Br _{0.56} Cl _{1.44} N ₄ Pd
Formula weight	995.53
Temperature (K)	153(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions (Å, °)	
<i>a</i>	10.636(2)
<i>b</i>	23.080(5)
<i>c</i>	11.818(2)
β	104.76(3)
<i>V</i> (Å ³)	2805.1(10)
<i>Z</i>	2
<i>D</i> _c (Mg m ⁻³)	1.179
Absorption coefficient (mm ⁻¹)	0.837
<i>F</i> (000)	1036
Crystal size (mm ³)	0.29 × 0.19 × 0.17
θ range for data collection (°)	2.47–25.05
Index ranges	−11 ≤ <i>h</i> ≤ 12; −27 ≤ <i>k</i> ≤ 27; −14 ≤ <i>l</i> ≤ 14
Reflections collected	21,294
Independent reflections (<i>R</i> _{int})	4962 (0.0447)
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/parameters	4962/293
Goodness-of-fit on <i>F</i> ²	1.115
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0572, <i>wR</i> 2 = 0.1364
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0673, <i>wR</i> 2 = 0.1470
Largest difference peak and hole (e. Å ⁻³)	1.999 and −0.736

diffractometer [30] using monochromated Mo-K α radiation. The structures were solved [30] by direct and conventional Fourier methods. Full-matrix least-squares refinement was [30] based on *F*². Apart from hydrogen all atoms were refined anisotropically; hydrogen atom coordinates were calculated at idealized positions and refined using a riding model. Further details concerning data collection and refinement are given in table 1.

2.2. Synthesis

Syntheses were carried out by using Standard Schlenk techniques under an argon atmosphere with previously dried solvents. PdCl₂(PhCN)₂ (0.38 g, 1.00 mmol) was added into dichloromethane solution containing [AgBr(NHC)] complex (**1**) (1.17 g, 1.00 mmol) in the dark and the mixture was allowed to stir for 24 h, followed by filtration giving a pale yellow clear filtrate (scheme 1). The solvent was removed in vacuum to yield a pale yellow powder. The crude product was re-crystallized from dichloromethane:diethyl ether (1:2) at room temperature. Yield: 0.87 g (90%); m.p.: 278–279°C (Dec.); FT-IR (KBr pellet, cm⁻¹): ν_{CN} 1421 cm⁻¹. Anal. Found: C, 69.4; H, 6.6; N, 5.8. Calcd for C₅₆H₆₄N₄PdBr_{0.56}Cl_{1.44}: C, 67.6; H, 6.5; N, 5.6. ¹H NMR (δ, 399.9 MHz, CDCl₃): 1.26 [s, 18H, CH₂C₆H₄C(CH₃)₃-*p*]; 2.31 [s, 12H, CH₂C₆H₂(CH₃)₃-2, 4, 6]; 2.40 [s, 6H, CH₂C₆H₂(CH₃)₃-2, 4, 6]; 6.06–6.21 [m, 8H, CH₂C₆H₂(CH₃)₃-2, 4, 6 and CH₂C₆H₄C(CH₃)₃-*p*]; 6.89 [s, 4H, CH₂C₆H₂(CH₃)₃-2, 4, 6]; 6.44–7.61 [m, 16H, NC₆H₄N and CH₂C₆H₄C(CH₃)₃-*p*]. ¹³C {H} NMR (δ, 100.5 MHz,



Scheme 1. Synthesis of the palladium complex.

CDCl₃): 21.0 and 21.1 [CH₂C₆H₂(CH₃)_{3-2,4,6}]; 31.3 [CH₂C₆H₄C(CH₃)_{3-p}]; 34.5 [CH₂C₆H₄C(CH₃)_{3-p}]; 49.9 [CH₂C₆H₂(CH₃)_{3-2,4,6}]; 52.3 [CH₂C₆H₄C(CH₃)_{3-p}]; 125.6, 129.7, 134.5, 134.8, 138.1, and 138.5 [CH₂C₆H₂(CH₃)_{3-2,4,6}]; 111.3, 111.7, 128.2, 128.4, 132.6, and 132.9 [NC₆H₄N]; 122.4, 122.8, 127.5, 127.7, 150.4 and 150.7 [CH₂C₆H₄C(CH₃)_{3-p}]; 182.1 [C_{carbene}].

2.3. General procedure for direct arylation of benzoxazoles with aryl bromides

The aryl bromide derivatives (1.5 mmol), benzoxazole, and 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 argon. The reaction mixture was stirred in an oil bath at 130°C for 48 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography (silica gel 60–120 mesh) using ethylacetate: *n*-hexane (1 : 5) as eluent to afford the pure product. The purity of the compounds was checked by NMR and yields were based on benzoxazole and benzothiazole. All reactions were monitored by gas chromatography and gas chromatography-mass spectrometry.

3. Results and discussion

During our work in the field of *N*-heterocyclic carbene derivatives and catalysts, *trans*-bis(1-(4-*tert*-butylbenzyl)-3-(2,4,6-trimethylbenzyl)-1*H*-benzo[*d*]imidazol-2-ylidene) dihalopalladium(II) (Halo: Cl/Br, 0.72/0.28), was isolated. The palladium(II) complex was synthesized by the reaction of (1-(4-*tert*-butylbenzyl)-3-(2,4,6-trimethylbenzyl)-2,3-dihydro-1*H*-benzo[*d*]imidazol-2-yl)silver(I) bromide with [PdCl₂(PhCN)₂]. The compound was purified by re-crystallization from a dichloromethane: diethylether mixture (1 : 2) and characterized by elemental analysis, ¹H NMR, ¹³C NMR, and IR

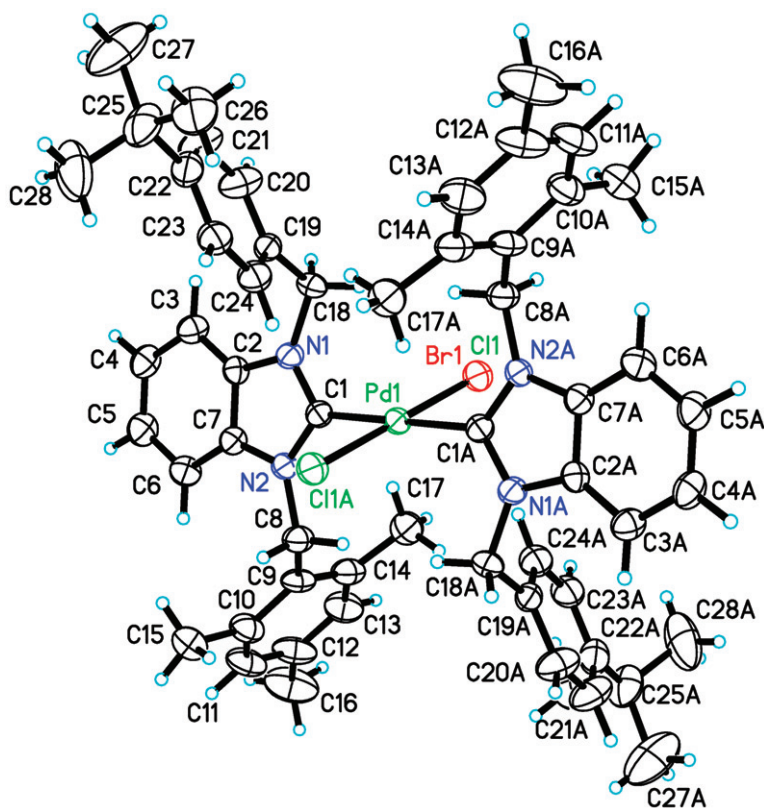


Figure 1. A perspective view of the title compound, with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

spectroscopy. The analytical and spectroscopic data are consistent with the proposed structure given in scheme 1.

The structure was confirmed by single crystal X-ray structure determination. The molecular structure of the complex with the atom-numbering scheme is depicted in figure 1. Selected bond lengths and angles are presented in table 2.

The coordination polyhedron of Pd is square-planar (the sum of the bond angles about Pd is 360.0°). The compound crystallizes with Pd on an inversion centre, with the pairs of carbene and halogeno ligands *trans*. All the angles (C1-Pd1-Br1 , $88.63(11)^\circ$ and $\text{C1}^i\text{-Pd1-Br1}^i$, $91.37(11)^\circ$ (Symmetry code: $i: 1-x, 1-y, 1-z$) in the coordination polyhedron are very close to the ideal value of 90° (table 2). The C1-Pd1-C1^i and $\text{Cl}^i\text{-Pd1-Cl1}$ angles are 180° , as required by symmetry. X-ray structure analysis reveals a 0.72:0.28 Cl:Br disorder ratio at the halogen position.

The Pd-X distances agree with the averaged values of corresponding structures retrieved from the Cambridge Structural Database [31]. The Pd-X distance in the palladium complex is slightly longer than other carbene Pd-Cl single bond distances (2.289(4) and 2.302(4) Å) [32], and slightly shorter than Pd-Br (2.4999(6) [33] and 2.4942(6) Å) [34] single bond distances. These results agree with the Cl/Br disorder at the halogen position.

Table 2. Selected geometric parameters (Å, °).

Bond lengths			
Pd1–C1	2.021(4)	N1–C2	1.394 (5)
Pd1–C1 ⁱ	2.021(4)	N1–C18	1.467 (5)
Pd1–Br1 ⁱ	2.3851(9)	N2–C1	1.361 (5)
Pd1–Cl1	2.3851(9)	N2–C7	1.395 (5)
N1–C1	1.353(5)	N2–C8	1.474 (5)
Bond angles			
C1–Pd1–C1 ⁱ	180.0	Br1 ⁱ –Pd1–Cl1	180.0
C1–Pd1–Br1 ⁱ	88.63 (11)	Cl1 ⁱ –Pd1–Cl1	180.0
C1 ⁱ –Pd1–Br1 ⁱ	91.37(11)	C1–N1–C2	111.4 (3)
C1–Pd1–Cl1 ⁱ	88.63(11)	C1–N1–C18	125.3 (3)
C1 ⁱ –Pd1–Cl1 ⁱ	91.37(11)	C1–N2–C7	110.9 (3)
Br1 ⁱ –Pd1–Cl1 ⁱ	0.00(4)	C1–N2–C8	122.9 (3)
C1–Pd1–Cl1	91.37 (11)	N1–C2–C7	105.8 (3)
C1 ⁱ –Pd1–Cl1	88.63(11)	N2–C7–C2	106.1 (3)

Symmetry code: i: 1 – x, 1 – y, 1 – z.

Table 3. Hydrogen-bond geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
C17–H17A...N2	0.96	2.57	3.247 (6)	128
C15–H15A...Cg4 ⁱⁱ	0.96	2.99	3.899 (6)	158
C15–H15C...Cg3 ⁱⁱⁱ	0.96	2.78	3.554 (7)	138

Symmetry codes: ii: x, y, 1 + z; iii: 1 – x, 1 – y, 2 – z. Cg3 and Cg4 are the centroids of the C9–C10–C11–C12–C13–C14, and C19–C20–C21–C22–C23–C24 phenyl rings, respectively.

The Pd–C_{carbene} bond length values [2.021 (4) Å] are in agreement with other Pd–carbene complexes [17, 33, 35–37] and are slightly longer than Pd–C sp³ single bond distances [17, 34].

Both benzo(*d*)imidazole rings are almost planar. The maximum deviation from planarity is 0.025(5) Å for C1. The dihedral angles between the two benzo(*d*)imidazol moieties, between the two 4-tert-butylbenzyl rings and between the two 2,4,6-trimethylbenzyl rings are 0.0°. In addition, the coordination plane forms a dihedral angle of 69.66(5)° with both of the benzo(*d*)imidazol rings.

The structure of **1** is stabilized by intramolecular C–H...N hydrogen bonds and by C–H...π interactions which link the molecules into a 3-D molecular network (table 3, figure 2). The crystal packing is shown in figure 3.

We tested the reaction parameters for direct arylation of *para*-substituted aryl bromides with benzoazoles in the presence of **1** as a catalyst. The yield of the direct arylation reaction is dependent on a variety of parameters such as base, temperature, solvent, and catalyst loading. The influence of various bases such as Cs₂CO₃, K₃PO₄, K₂CO₃, and KOBu^t was studied. Only K₃PO₄ afforded good yields of the desired product. The effect of various solvents such as NMP, DMSO, and DMF was studied and NMP gave the best results. Thus, using Pd(NHC) as catalyst, K₃PO₄ as base, and NMP as solvent the products were obtained in 54–72% yield; the optimized reaction conditions were found to be base, K₃PO₄; time: 48 h; solvent: NMP, catalyst loading, 1.5 mol%. The obtained results are summarized in table 4 with the chemical reaction and structure.

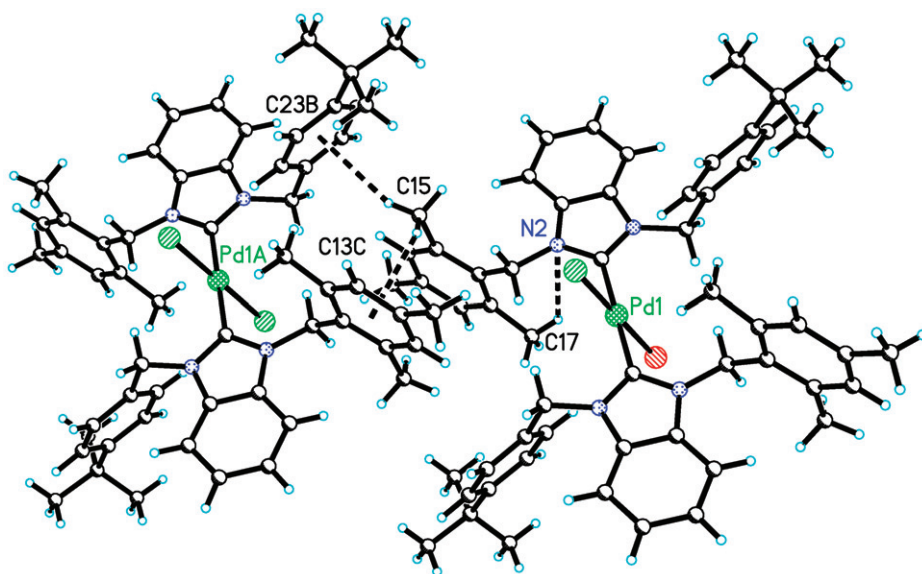


Figure 2. Short contacts for **1**. Symmetry codes: (B) $x, y, 1+z$; (C) $1-x, 1-y, 2-z$.

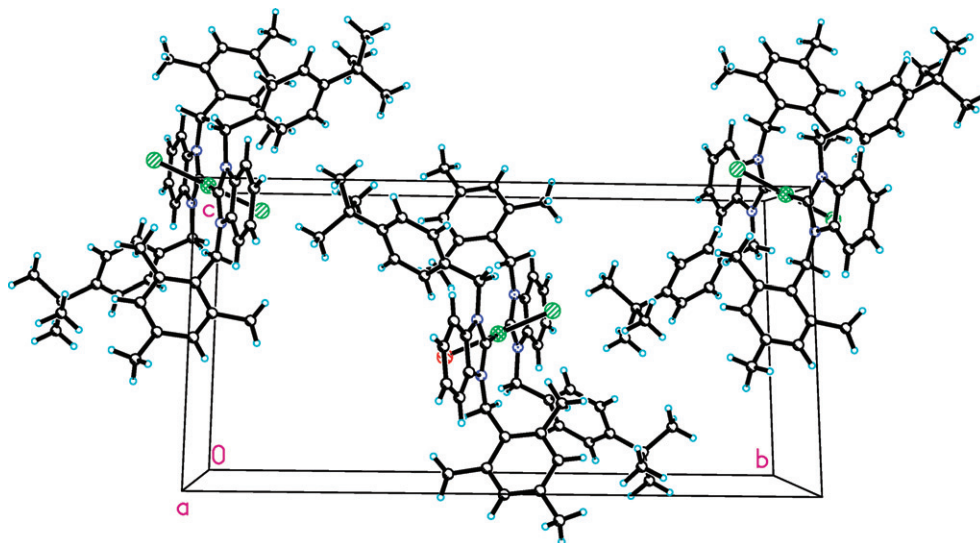


Figure 3. The crystal packing diagram for the palladium complex.

4. Conclusion

We have synthesized and characterized a mixed-halide *bis*(1-(4-*tert*-butylbenzyl)-3-(2,4,6-trimethylbenzyl)-1*H*-benzo[*d*]imidazol-2-ylidene)palladium(II) complex, *trans*-[Pd(Cl_{0.7}Br_{0.3})₂ (C₂₈H₃₂N₂)₂]. X-ray single crystal structure studies and other characterization techniques confirm the suggested structure of the palladium (II) complex. In addition, we have established that the synthesized palladium complex is an

Table 4. Pd(NHC) catalyzed C-2 arylation of benzoazoles using *para*-substituted aryl bromides^a.

Entry	Y	R	Product	Yield (%)
1	S	OMe		54
2	S	H		72
3	S	NO ₂		60
4	O	OMe		67
5	O	H		65
6	O	NO ₂		64

^a Reaction conditions: 1.5 mmol of R-C₆H₄Br, 1.0 mmol of benzoazoles, 2.0 mmol K₃PO₄, 1.5 mol % Pd catalyst, NMP (3 mL), 48 h at 130 °C; Purity of compounds was checked by NMR and yields are based on benzoazoles; All reactions were monitored by gas chromatography and gas chromatography-mass spectrometry.

efficient catalyst for the direct arylation of benzoxazoles and benzothiazoles with aryl bromide derivatives.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with quotation number CCDC-713669 for *trans*-[Pd(Cl_{0.7}Br_{0.3})₂(C₂₈H₃₂N₂)₂] and can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgement

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