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# New pentamethylene-bridged bis-imidazolium dication ligands and its palladium(II) complexes: Synthesis, characterization, and catalysis

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# ABSTRACT

Two new pentamethylene-bridged bis-imidazolium dication ligands (L<sup>1</sup> = 1,5-bis(1-(4-cyanophenyl)imidazolium-1-yl)pentane dibromide) and L<sup>2</sup> = 1,5-bis(1-(4-methoxyphenyl)-imidazolium-1-yl)pentane dibromide) bearing CPI (1-(4-cyanophenyl)-imidazole) and MPI (1-(4-methoxyphenyl)-1*H*-imidazole)functionality have been prepared *via* the reaction of 1,5-dibromopentane with a substituted imidazole derivative. The imidazolium ligand L<sup>1</sup> and L<sup>2</sup> on reaction with [PdBr<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>] led to the formation of neutral bis-imidazolium dication palladium(II) complexes [L<sup>1</sup>] [PdBr<sub>4</sub>] **[1**] (L<sup>1</sup> = 1,5-bis(1-(4-cyanophenylimidazolium-1-yl)pentane) and [L<sup>2</sup>] [PdBr<sub>4</sub>] **[2**] (L<sup>2</sup> = 1,5-bis(1-(4-methoxyphenyl) imidazolium-1-yl)pentane), respectively. The new ligands as well as their palladium(II) complexes, has been characterized by elemental analysis, electronic, IR, <sup>1</sup>H and <sup>13</sup>C NMR, FAB-MS and ESI-MS spectroscopy. The molecular structure of the representative complex [L<sup>2</sup>] [PdBr<sub>4</sub>] **[2**] have been determined by single crystal X-ray analysis. Complex **2** exhibits the strong intra- and inter-molecular C-H…X (X = Br, O,  $\pi$ ) weak interactions, which plays an important role in stabilizing the crystal packing. Furthermore, the C-H…O interactions in **2** lead to a single-helical motif. The complexes **1** and **2** exhibited good activity in a model Suzuki-Miyaura coupling reaction.

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# 1. Introduction

*N*-heterocyclic carbenes (NHCs) are an extremely useful and versatile class of ligands for catalyst design. After the pioneering reports by Öfele and Wanzlick [1,2], and the early studies by Lappert [3–8] on the coordination to late transition-metal complexes, NHC chemistry remained quiescent for more than twenty years, until Arduengo pointed out the idea that NHCs could be stable enough for crystallographic characterization [9]. In 1995, Herrmann took the story a step forward, with the use of NHCs in the preparation of the first NHC-based homogeneous catalysts [10]. Since then, many research groups have provided a large number of NHC-based catalysts for a wide variety of reactions, and many reviews covering aspects such as preparation [11–13], stability [14], stereoelectronic properties [15–17], coordination strategies [13,18,19], and catalytic applications [20–26] have been entirely devoted to this type of ligand. The concept of two NHC

groups separated by various spacer such as pyridine, benzene, amido, ether, and pentamethylene functionalities have been explored by several groups, yielding Pd(II) pincer complexes containing various alkyl/aryl groups [27-35]. These ligands are highly "tunable" and active precatalysts for C-C coupling reactions and exhibit excellent thermal stability and resistance to degradation reactions [27,30,31,33,36,24]. Ag(I) (NHC) complexes have been shown to be facile reagents for the transmetalation of a variety of functionalized NHC ligands to Pd(II) [37-42]. They are readily accessed through the reaction of an imidazolium salt with Ag<sub>2</sub>O by the method of Wang and Lin [43]. In recent years the number of crystallographically characterized Pd(II) (NHC) complexes has increased considerably with a rich structural diversity revealed, especially when halide ions are present in the compound [44–46]. Keeping these facts in mind, herein, we present synthetic, spectral characterization of two new pentamethylene-bridged bis-imidazolium dication ligands ( $L^1 = 1,5$ -bis(1-(4-cyanophenyl)imidazolium-1-yl)pentane dibromide) and  $L^2 = 1.5$ -bis(1-(4methoxyphenyl)-imidazolium-1-yl)pentane dibromide) bearing CPI (1-(4-cyanophenyl)-imidazole) and MPI (1-(4-methoxyphenyl)-1H-imidazole)-functionality which are potential precursors to



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novel, bi-functional NHCs. We, also report their palladium(II) complexes (1 and **2**) and their comparative catalytic activities in the Suzuki–Miyaura coupling reaction.

# 2. Experimental

### 2.1. Materials and physical measurements

All reactions were performed under an atmosphere of dry dinitrogen or argon using standard Schlenk techniques. Solvents were dried and distilled before use following the standard literature procedures. 1,5-dibromopentane (Aldrich), 1-(4-methoxyphenyl)-1*H*imidazole (MPI) (Aldrich), was used as received. All other reagents were used as received.  $[PdBr_2(C_6H_5CN)_2]$  [47] and 1-(4-cyanophenyl)-imidazole) (CPI) were prepared and purified following the literature procedure [48].

Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N is within ±0.4% of calculated values. IR(KBr) and electronic spectra were recorded using Perkin-Elmer FT-IR spectrophotometer and Perkin Elmer Lambda-35 spectrometer, respectively. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature with m-nitrobenzyl alcohol as the matrix. ESI-MS data were recorded using a waters micromass LCT Mass Spectrometer/Data system. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL DELTA2 spectrometer at 400 MHz using TMS as an internal standard. The chemical shift values are recorded on the  $\delta$  scale and the coupling constants (1) are in Hz. GCMS studies were done with the Shimadzu-2010 instrument containing a DB-5/RtX-5MS-30Mt column of 0.25 mm internal diameter.

## 2.2. Pentamethylene-functionalised bis-imidazolium salts

# 2.2.1. 1,5-Bis(1-(4-cyanophenyl)-imidazolium-1-yl)pentane dibromide $(L^1)$

1-(4-Cyanophenyl)-imidazole) (5.306 g, 31.4 mmol) was added to 1,5-dibromopentane (2.0 mL, 14.7 mmol) in THF (60 mL) and refluxed for 24 h. The resultant white solid was filtered on a glass frit, washed with  $Et_2O$  (20 mL), and dried in vacuo, yielding L<sup>1</sup> (14.26 g, 80%) as a white powder that was handled and stored in a vacuum dessicator. Anal. Calc. For C<sub>25</sub>H<sub>24</sub>N<sub>6</sub>Br<sub>2</sub>: C, 52.82; H, 4.23; N, 14.79. Found: C, 53.10; H, 4.36; N, 14.94%. IR(cm<sup>-1</sup>, nujol):v = 3320, 2927, 2230, 1606, 1508, 1402, 1247, 1016, 848, 749, 568. <sup>1</sup>H NMR (δ ppm, 400 MHz, CDCl<sub>3</sub>, 298 K): 9.30 (s, 2H), 8.50 (s, 1H), 7.90 (d, 2H, 6.9 Hz), 7.80 (d of t, 2H, 2.4 Hz), 7.77 (d, 1H, 9.0 Hz), 7.71(d of t, 2H, 2.4 Hz) 7.48(d, 2H, 6.0 Hz), 7.41(d, 2H, 7.5 Hz), 4.20(t, 4H, 7.5 Hz), 1.80(quintet, 4H, 7.4 Hz), 1.20(br quintet, 2H, 6.0 Hz). <sup>13</sup>C NMR (δ ppm, 400 MHz, CDCl<sub>3</sub>, 298 K): 136.16, 132.05, 129.30, 127.46, 124.00, 124.30, 123.61, 122.56, 115.64, 49.4, 35.21, 28.71, 22.61. FAB-MS m/z 568 (569), [M] (20%); 488 (488), [M]<sup>+</sup>-Br (50%); 408 (407),  $[M]^{2+}$ -Br<sub>2</sub> (20%).

# 2.2.2. 1,5-Bis(1-(4-methoxyphenyl)-imidazolium-1-yl)pentane dibromide $(L^2)$

1-(4-Methoxyphenyl)-1*H*-imidazole (5.469 g, 31.4 mmol) was added to 1,5-dibromopentane (2.0 mL, 14.7 mmol) in THF (60 mL) and refluxed for 24 h. The resultant white solid was filtered on a glass frit, washed with Et<sub>2</sub>O (20 mL), and dried in vacuo, yielding L<sup>2</sup> (10.88 g, 60%) as a white powder that was handled and stored in a vacuum dessicator. Anal. Calc. For C<sub>25</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Br<sub>2</sub>: C, 51.90; H, 5.19; N, 9.69. Found: C, 52.20; H, 5.41; N, 9.85%. IR(cm<sup>-1</sup>, nujol): v = 3419, 3054, 2924, 1608, 1518, 1481, 1435, 1308, 1250, 1185, 1091, 1024, 841, 748, 722, 696, 541, 517. <sup>1</sup>H NMR ( $\delta$  ppm,

400 MHz, CDCl<sub>3</sub>, 298 K): 9.20 (s, 2H), 7.80 (d of t, 2H, 1.8 Hz), 7.73(d of t, 2H, 1.8 Hz) 7.38–7.43 (m, 8H, 7.1 Hz), 4.18(t, 4H, 7.2 Hz), 3.49(s, 6H), 1.82(quintet, 4H, 7.4 Hz), 1.21(br quintet, 2H, 7.0 Hz). <sup>13</sup>C NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298 K): 136.20, 132.39, 129.29, 127.46, 124.69, 123.92, 122.97, 54.26, 49.48, 35.14, 28.92, 22.58. FAB–MS *m/z* 578(577), [M](40%); 498(498), [M]<sup>+</sup>-Br(90%); 418(418), [M]<sup>2+</sup>-Br<sub>2</sub>(20%).

### 2.3. Bis-imidazolium dication palladium(II) complexes

# 2.3.1. [L<sup>1</sup>] [PdBr4] (**1**)

L<sup>1</sup>(0.568 g, 1 mmol) was dissolved in 1:1 DCM–MeOH (30 mL) and  $[PdBr_2(C_6H_5CN)_2]$  (0.472 g, 1 mmol) added. The resulting yellow suspension was refluxed with stirring at room temperature for 24 h. The solvent was removed in vacuo and the residue washed with Et<sub>2</sub>O (5 ml) giving 1 as a pale yellow solid. Yield: (0.603 g, 80%). Anal. Calc. for C<sub>25</sub>H<sub>24</sub>N<sub>6</sub>Br<sub>4</sub>Pd: C, 39.78; H, 3.18; N, 11.14. Found: C, 40.08; H, 3.45; N, 11.38%. IR(cm<sup>-1</sup>, nujol): *v* = 3420, 3090, 2924, 2230, 1605, 1546, 1511, 1458, 1251, 1183, 1117, 1066, 1025, 833, 732, 624, 554. <sup>1</sup>H NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298 K): 9.10 (s, 2H), 8.40 (s, 1H), 7.85 (d, 2H, 6.8 Hz), 7.81 (d of t, 2H, 3.6 Hz), 7.76 (d, 1H, 6.0 Hz), 7.70(d of t, 2H, 5.4 Hz) 7.47(d, 2H, 6.9 Hz), 7.40(d, 2H, 6.4 Hz), 4.23(t, 4H, 8.0 Hz), 1.81(quintet, 4H, 8.4 Hz), 1.25(br quintet, 2H, 7.5 Hz).  $^{13}$ C NMR ( $\delta$ ppm, 400 MHz, CDCl<sub>3</sub>, 298 K): 136.20, 132.00, 129.50, 127.60, 124.10, 124.40, 123.60, 122.80, 113.11, 49.20, 35.40, 28.75, 22.60. UV–VIS {DMSO,  $\lambda_{max}$  nm ( $\epsilon/M^{-1}$  cm<sup>-1</sup>)}: 261(4725), 280(2421), 354(5346). ESI-MS (m/z): 408.9 (M<sup>+</sup>).

#### 2.3.2. $[L^2]$ [PdBr<sub>4</sub>] (**2**)

L<sup>2</sup>(0.578 g, 1 mmol) was dissolved in 1:1 DCM–MeOH (30 mL) and  $[PdBr_2(C_6H_5CN)_2]$  (0.472 g, 1 mmol) added. The resulting red suspension was refluxed with stirring at room temperature for 24 h. The solvent was removed in vacuo and the residue washed with  $Et_2O(5 \text{ ml})$  giving 2 as a orange red solid. The solid mass thus obtained was extracted with MeCN and filtered, and the filtrate was layered with diethyl ether and left for slow crystallization. After a couple of days a brown block crystals were obtained. It was filtered out, washed several times with diethyl ether, and dried under vacuo. Yield: (0.633 g, 75%). Anal. Calc. for C<sub>25</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Br<sub>4</sub>Pd: C, 35.54; H, 3.55; N, 6.64. Found: C, 35.78; H, 3.65; N, 6.78%. IR(cm<sup>-1</sup>, nujol): v = 3434, 3047, 2921, 2852, 1604, 1583, 1477, 1432, 1309, 1251, 1180, 1094, 1024, 995, 744, 500, 429. <sup>1</sup>H NMR (δ ppm, 400 MHz, CDCl<sub>3</sub>, 298 K): 9.30 (s, 2H), 7.77 (d of t, 2H, 6.0 Hz), 7.72(d of t, 2H, 3.6 Hz) 7.39-7.45 (m, 8H, 7.5 Hz), 4.20(t, 4H, 8.0 Hz), 3.48(s, 6H), 1.81(quintet, 4H, 6.4 Hz), 1.20(br quintet, 2H, 7.5 Hz). <sup>13</sup>C NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298 K): 136.30, 132.40, 129.30, 127.45, 124.68, 123.90, 123.10, 54.30, 49.20, 35.18, 28.98, 22.62. UV-VIS {DMSO,  $\lambda_{max}$  nm ( $\epsilon$ /  $M^{-1} cm^{-1}$ ): 261(8020), 271(4981), 355(7099). ESI-MS (*m*/*z*): 418.8 (M<sup>+</sup>).

# 2.4. X-ray crystallographic study

X-ray data for 2 was collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programs [49]. Denzo-Scalepack software packages were used for data collection and data integration for 2. Structure solution and refinement were carried out using the SHEIXL97-Program [50]. The nonhydrogen atoms were refined with anisotropy thermal parameters. All the hydrogen atoms were treated using appropriate riding models. The computer programme PLATON was used for analyzing the interaction and stacking distances [51,52].



Scheme 2. Synthesis of 1 and 2.

#### 2.5. Catalysis

 $K_2CO_3$  (0.553 g, 4.0 mmol) was added to a 100 ml three-necked flask with a stirring bar and the flask was dried under vacuum and then filled with nitrogen, aryl halide or 4-halotolune (0.342 g, 2.0 mmol) and phenylboronic acid (0.244 g, 2.0 mmol) in DMF (10 mL). Then 0.1 mol% palladium complex in DMF was added *via* a syringe under nitrogen atmosphere. The mixture was stirred at 120 °C for the indicated reaction time. The mixture was cooled and the precipitate was removed by filtration and the product was extracted from the filtrate with diethyl ether. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After evaporation, the obtained residue was purified by silica-gel column

L1(R=CN)

L<sup>2</sup>(R=OCH<sub>2</sub>)

chromatography to give the coupling product. Product identities were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR and GC–MS.

[1] (R=CN)

[2](R=OCH3)

# 3. Results and discussion

#### 3.1. Synthesis

# 3.1.1. Pentamethylene-bridged bis-imidazolium salts

Methodology similar to that used for the preparation of the ether-functionalised bis-imidazolium salt analogues [34] was employed to prepare pentamethylene-bridged- functionalised bis-imidazolium salts. Reaction of 1,5-dibromopentane with



Fig. 1. Projection view of 2 shown with 50% ellipsoids; hydrogen atoms are omitted for clarity.

Table 1					
Crystallographic	data	for	<b>2</b> at	150(2)	) K

	1
Empirical formula	C <sub>25</sub> H <sub>30</sub> Br <sub>4</sub> N <sub>4</sub> O <sub>2</sub> Pd
Formula weight	844.57
Colour and habit	Brown, Block
Crystal size/mm	$0.30 \times 0.30 \times 0.18~mm$
Crystal system, space group	monoclinic, P 2 <sub>1</sub> /c
a (Å)	11.0445(3)
b (Å)	10.1972(2)
<i>c</i> (Å)	25.9445(7)
β(°)	101.428(1)
γ (°)	90
$V(Å^3)$	2864.02(12)
$Z_{\rm r} D_{\rm c} ({\rm mg}{\rm m}^{-3})$	4, 1.959
$\mu (\mathrm{mm}^{-1})$	6.258
T/K	150(2) K
λ (Mo Kα) (Å)	0.71073
Number of reflections/unique	40937/6510
Number of refined parameter	327
R factor $[I > 2\sigma(I)]$	0.0547
$wR_2 [I > 2\sigma(I)]$	0.1390
R factor (all data)	0.1083
$wR_2$ (all data)	0.1619
Goodness-of-fit (GoF)	1.043

1

1-(4-cyanophenyl)-imidazole)/1-(4-methoxyphenyl)-1*H*-imidazole in refluxing THF gave bis-imidazolium salts  $L^1$  and  $L^2$  as white powder in good yields, as shown in Scheme 1.

Bis-imidazolium salts  $L^1$  and  $L^2$  were characterized by elemental analysis, electronic, IR, <sup>1</sup>H and <sup>13</sup>C NMR and FAB–MS spectroscopy. Analytical data of  $L^1$ , and  $L^2$  corroborated well with their respective formulations (see F-1 to F-4, Supporting material). A comparison of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the CPI and MPIfunctionalised bis-imidazolium salts shows that variation of the functional group has a negligible effect on the chemical shifts of the imidazolium ring protons.

## 3.1.2. Bis-imidazolium dication Pd(II) complexes

Bis-imidazolium salts  $L^1$  and  $L^2$  were reacted with  $[PdBr_2(C_6H_5CN)_2]$  in 1:1 stoichiometric ratio in a mixture of methanol and dichloromethane (1:1 v/v) under refluxing followed by stirring at RT for 3 h, which afforded neutral, bis-imidazolium dication palladium complexes  $[L^1]$  [PdBr<sub>4</sub>] [1] ( $L^1 = 1,5$ -bis(1-(4-cyanophenylimidazolium-1-yl)pentane) and  $[L^2]$  [PdBr<sub>4</sub>] [2] ( $L^2 = 1,5$ bis(1-(4-methoxyphenyl) imidazolium-1-yl)pentane) in reasonable yields (75, 80%) as shown in Scheme 2.

1 and 2 were isolated as air-stable, non-hygroscopic solids and soluble in dichloromethane, chloroform, methanol, dimethylformamide, and dimethylsulphoxide but insoluble in petroleum ether and diethyl ether. Analytical data of 1 and 2 corroborated well with their respective formulations. Information about composition of the complexes was also obtained from ESI-MS spectra of the complexes (recorded in the Section 2). The position of various peaks and overall fragmentation pattern in the ESI-MS spectra of the respective complexes conformed well to their respective formulations. More information about the structure and bonding in the complexes has been deduced from the spectral studies.

Infrared spectrum of 1 in nujol displayed sharp and intense bands around 2230 cm<sup>-1</sup> corresponding to v(C $\equiv$ N). Two characteristic frequencies observed at 1251 cm<sup>-1</sup> and 1024 cm<sup>-1</sup> in 2 corresponds to the asymmetric and symmetric stretching frequencies of C–O–C of MPI. The vibrations corresponding to v(C $\equiv$ N) in 1 and 2 which appeared at ~1600 cm<sup>-1</sup> are because of the imidazole moiety.

The purity and composition of both the ligands  $L^1$  and  $L^2$ , and their complexes have been checked by NMR spectroscopy. Both the ligands and their complexes display sharp <sup>1</sup>H NMR signals

Table 2	2
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Selected non-hydrogen atom geometries for 2 at 150(2) K.

	1
Distances (Å)	
Pd-Br(3)	2.4100(10)
Pd-Br(4)	2.4144(9)
Pd-Br(2)	2.4176(9)
Pd-Br(1)	2.4445(9)
O(1)-C(1)	1.452(9)
O(1)-C(2)	1.383(9)
N(1)-C(10)	1.334(9)
N(1)-C(8)	1.394(9)
N(2)-C(9)	1.380(9)
N(2)-C(10)	1.328(9)
N(2)-C(11)	1.464(9)
N(3)-C(15)	1.464(9)
C(11)-C(12)	1.488(12)
C(12)-C(13)	1.511(12)
C(13)-C(14)	1.544(12)
C(14) - C(15)	1.505(11)
N(3)–C(16)	1.394(9)
N(3)-C(18)	1.326(9)
N(4) - C(18)	1.326(9)
N(4) - C(17)	1.384(9)
O(2) - C(22)	1.366(9)
O(2) - C(25)	1.408(10)
Angles (°)	
Br(3)-Pd-Br(2)	175.29(4)
Br(4)-Pd-Br(1)	176.82(4)
C(12)-C(13)-C(14)	111.2(7)
C(15)-C(14)-C(13)	109.7(7)
N(3)-C(15)-C(14)	111.6(7)
N(2)-C(11)-C(12)	112.7(7)
C(11)-C(12)-C(13)	113.8(8)
C(18) - N(3) - C(15)	128.3(6)
C(10)-N(2)-C(11)	125.4(6)
C(16) - N(3) - C(15)	123.5(6)
C(9)-N(2)-C(11)	125.5(7)
C(18) - N(3) - C(16)	108.1(6)
C(10) - N(2) - C(9)	109.0(6)
N(3) - C(18) - N(4)	109.5(6)
N(2) - C(10) - N(1)	109.4(6)
C(18) - N(4) - C(17)	107.5(6)
C(10) - N(1) - C(8)	107.8(6)
C(17) = N(4) = C(19)	125.9(6)
C(10) = N(1) = C(5)	126.4(6)
C(18) = N(4) = C(19)	120.0(0)
C(8) = N(1) = C(5)	125.9(0)
C(10) - C(17) - N(4)	108.4(7)
C(9) = C(8) = N(1)	107.2(6)
C(0) - C(0) - N(2) C(17) C(16) N(2)	106.7(0)
C(17) - C(10) - N(3)	100.5(7)
Torsion angles (°)	
C(12)-C(13)-C(14)-C(15)	-175.91
C(13)-C(14)-C(15)-N3	-83.46
C(13)-C(12)-C(11)-N2	59.82
C(14)-C(15)-N3-C(18)	109.30
C(12)-C(11)-N2-C(10)	80.06
$C_3N_2/C_3N_{2'}$ interplanar dihedral ( $\theta$ , °)	
θ	48.94

which integrate well to the corresponding hydrogens. Further, it was observed that the signals associated with various protons and carbons of the complexes displayed little change on coordination in comparison to the bis-imidazolium salts.

The electronic absorption spectra of the complexes 1 and 2 display bands at 260–280 and 354–355 nm. The higher energy band corresponds to the intra-ligand transition, whilst the lower energy band can be assigned to MLCT transition.

#### 3.2. Molecular structure determination

The molecular structure for 2 with atom-labels is shown in Fig. 1. Details concerning the data collection, solution and refine-

Hydrogen	bond	parameters	for	<b>2</b> a	at 1	50(	2)	K
nyarogen	bond	purumeters	101			50(	-,	

D-H…A-X	d H…A Å	D D…A Å	$\theta$ D–H····A°
Complex 2			
$C(9)-H(9)\cdots Br(4)^{a}$	2.87	3.7893	162
$C(10)-H(10)\cdots Br(1)^{b}$	2.79	3.6295	149
$C(11)-H(11A)-Br(2)^{b}$	2.89	3.7669	148
$C(16)-H(16)-Br(1)^{c}$	2.84	3.6617	146
$C(16)-H(16)-Br(2)^{c}$	2.81	3.5248	133
$C(17)-H(17)-Br(4)^{d}$	2.81	3.4782	128
C(18)-H(18)Br(1) <sup>a</sup>	2.88	3.5318	127
C(18)–H(18)…Br(3) <sup>a</sup>	2.68	3.5789	157
C(21)-H(21)Br(3) <sup>e</sup>	2.74	3.6806	168

Symmetry equivalents.

<sup>a</sup> 1 - x, 1/2 + y, 1/2 - z.

<sup>b</sup> 1-x, -1/2 + y, 1/2 - z.

 $c_{1+x, y, z}$ 

<sup>d</sup> 2 - x, 1/2 + y, 1/2 - z.

 $e^{-x}, 1/2 - y, -1/2 + z.$ 

ment are enlisted in Table 1 and non-hydrogen atom geometries and hydrogen bond parameters are tabulated in Tables 2 and 3, respectively. The asymmetric unit contains one 1,5-bis(1-(4methoxyphenyl)imidazolium-1-yl) pentane dication and one  $[PdBr_4]^{2-}$  anion, with the palladium atom on a center of symmetry. The molecular structure shows that the imidazolium unit is not directly attached to the metal. The square planar environment of Pd is completed by four Br atoms. The Pd-Br bond distances are 2.4100(10) to 2.4445(9) Å which are comparable with those found for other  $[PdBr_4]^{2-}$  containing compounds [53,54]. The angles around Pd are close to 90° and suggest that the hydrogen-bonding interaction with the 1,5-bis(1-(4-methoxyphenyl)imidazolium-1vl) pentane dication causes little distortion on the  $[PdBr_4]^{2-}$  anion. The bond lengths and angles within the  $C_3N_2$  rings of 2 are comparable to those found in the complex  $[Ag_2(MeC(CH_2)_5C)_2][AgBr_2]_2$  $(M_eC(CH_2)_5C) = C,C'-1,5-bis(3-methylimidazolin-2-yliden-1-yl)$  pentane) [34] and in other related complexes [27–35]. The two  $C_3N_2$ rings in 2 differ significantly only in the C(12)-C(11)-N(2)-C(10)and C(14)-C(15)-N(3)-C(18) torsions for each section, being relatively rotated about the C(11)–N(2) and C(15)–N(3) bond and dispersed to either side of the alkyl linkage. The C(sp<sup>3</sup>)–O bond distances in 2 are 1.408(10)-1.452(9) Å, respectively. The ligand 4-methoxyphenylimidazole has lost planarity upon coordination with pentamethylene linkage. One phenyl group of the 4-methoxyphenylimidazole is not coplanar with imidazole ring and is tilted with respect to the imidazole ring plane at an angle of 30.36° in 2, while the other ring is remains essentially coplanar (tilt angle 2.65°); crystal packing, rather than electronic factors, are presumably the origin of this difference.

Crystal packing in 2 is stabilised by inter- and intra-molecular C–H…X (X = Br, O,  $\pi$ ) weak interactions. An interesting feature of the crystal packing in **1** is a single helical motif (Fig. 2) resulting from C-H...O interactions having contact distances of 2.61 Å [55]. The C-H-Br contact distances in the crystal packing are in the range of 2.68–2.88 Å and the associated angles having range from 127 to 168° (see F-5, Supporting material). These are within the range for analogous distances reported in the literature [56]. Additionally, the contact distances for intra-molecular C–H $\cdots$   $\pi$  interactions are in the range of 2.64–2.89 Å (see F-6. Supporting material) [57]. The crystal packing of 2 closely resembles that of related tetrahalometallate derivatives of simple pyridinium cations [53,58-60]. The distinctive feature is therefore the chains of the cations building up a lamellar structure with single-layer type of organization (Fig. 3). This results in the propagation of alternate cation and anion layers along the [010] direction.

# 3.3. Catalytic tests

The complexes 1 and 2 were tested as catalysts in the model Suzuki-Miyaura reaction of selected aryl halides with phenylboronic acid (Table 4). Complex 2 exhibited higher catalytic activity than the complex 1; that is, the reaction of aryl halides with phenylboronic acid in the presence of 0.1 mol% of Pd complex (1, and 2) in DMF at 120 °C for 12 h gave 65% to 100% yield of the Suzuki-Miyaura coupling product, corresponding to TON of 100-169. The results presented in Table 4 are in agreement with the earlier observation by Trzeciak et al. on Pd(II) anionic, square planar complexes of the type  $[IL]_2[PdX_4]$  (where IL = imidazolium cations, X = Cl, Br) in the Suzuki-Miyaura reaction in alcohols at 40 °C [61]. The higher product yield obtained with palladium precursor 2 containing the methoxy functionalised imidazolium cation may be explained by the stabilizing effect of methoxy moiety on the palladium active form. In all the Suzuki-Miyaura reactions under study, with Pd-catalyst precursors 1 and 2, colloidal nanoparticles



Fig. 2. Single helical structure in 2 resulting from C-H...O interaction: (a) wire-frame model, and (b) space-filled model.



Fig. 3. Polyhedral representation of 2 viewed down the [010] direction.

#### Table 4

Results of the Suzuki-Miyaura cross-coupling reactions of aryl halides with phenylboronic acid using complex 1 and 2.ª



<sup>a</sup> All reactions were carried out using 2.0 mmol aryl halide, 2.0 mmol phenylboronic acid, 4.0 mmol K<sub>2</sub>CO<sub>3</sub>, 0.1 mol% Pd complex and 10 ml DMF at 120 °C for 12 h.

<sup>b</sup> Isolated yield.

<sup>c</sup> Mol(product)/mol(Pd).

of Pd(0) were formed. Their formation was confirmed by the change of the colour of Pd(II) solution to almost black at the end of reaction.

# 4. Conclusion

In this work, we have presented two new pentamethylenebridged bis imidazolium dication ligands and their Pd(II) complexes. We have also demonstrated that both 1 and 2 exhibit good catalytic activity in the Suzuki–Miyaura reaction at 120 °C. From the catalytic studies it is evident that by judicious selection of the functional groups especially the +R groups at the *para* position of the benzene ring of 1-Phenyl-1*H*-imidazole, one can tune the catalytic responses of these compounds and their coordination complexes. Also, the ligands under investigation can be a useful source for the preparation of *N*-heterocyclic carbenes complexes. The utilization of these ligands as potential NHCs will be the target of our future investigations.

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#### **Appendix A. Supplementary material**

CCDC 795256 contains the supplementary crystallographic data for this paper. 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.ica.2011. 10.065.

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