



# Silver(I) and palladium(II) complexes of new pentamethylene-functionalized bis-imidazolium dication ligands and its application in Heck and Suzuki–Miyaura coupling reaction



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## ABSTRACT

Two new pentamethylene-functionalized bis-imidazolium dication ligands  $L^1$  and  $L^2$  ( $L^1 = 1,5$ -bis(4-(imidazolium-1-yl-phenol)pentane dibromide;  $L^2 = 1,5$ -bis(1-vinylimidazolium-1-yl)pentane dibromide) bearing IP (4-(imidazol-1-yl)phenol) and VI (1-vinylimidazole)-functionality have been prepared via the reaction of 1,5-dibromopentane with a substituted imidazole derivative. The bis-imidazolium dication ligands  $L^1$  and  $L^2$  on reaction with  $Ag_2O$  in DCM:MeOH, followed by anion substitution with  $AgBF_4$  led to the formation of silver(I) complexes  $[Ag_2(\mu C(CH_2)_5Cp)_2][BF_4]_2$  ( $\mu C(CH_2)_5Cp = 1,5$ -bis(4-(imidazolium-1-yl-phenol)pentane (1) and  $[Ag_2(\mu C(CH_2)_5Cv)_2][BF_4]_2$  ( $\mu C(CH_2)_5Cv = 1,5$ -bis(1-vinylimidazolium-1-yl)pentane (2). Transmetalation of the bis-NHC ligand from  $[Ag_2(\mu C(CH_2)_5Cp)_2][BF_4]_2$  and  $[Ag_2(\mu C(CH_2)_5Cv)_2][BF_4]_2$  by palladium(II) salt  $[PdCl_2(CH_3CN)_2]$  in DMSO gave  $[PdCl(\mu C(CH_2)_5Cp)(CH_3CN)]BF_4$  (3) and  $[PdCl(\mu C(CH_2)_5Cv)(CH_3CN)]BF_4$  (4), respectively. The new ligands as well as their silver(I) and palladium(II) complexes have been characterized by elemental analysis, electronic, IR,  $^1H$  and  $^{13}C$  NMR, and FAB-MS spectroscopy. The molecular structure of the representative ligand  $L^1$  has been determined by single crystal X-ray analysis. The palladium<sup>II</sup> NHC complexes 3 and 4 exhibited good activity in a model Heck and Suzuki–Miyaura coupling reaction.

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## 1. Introduction

N-heterocyclic carbenes (NHCs) are nowadays ubiquitous ligands in organometallic chemistry as well as catalysis due to their unique properties. 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, several research groups have synthesized a large number of NHC-based catalysts for a wide variety of reactions, and many reviews covering different aspects such as preparation [11–14], stability [15], stereoelectronic properties [16–18], coordination strategies

[13–20], and catalytic applications [21–28] 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, methylene, ethylene, propylene, butylene, m-xylylene, o-xylylene and pentamethylene functionalities have been explored by several groups, yielding various pincer complexes containing various alkyl/aryl groups [29–38]. These ligands are highly “tunable” and active precatalysts for C–C coupling reactions and exhibit excellent thermal stability and resistance to degradation reactions [29,32,33,35,39,25]. Ag(I) (NHC) complexes have been shown to be facile reagents for the transmetalation of a variety of functionalized NHC ligands to Pd(II) [40–45]. They are readily accessed through the reaction of an imidazolium salt with  $Ag_2O$  by the method of Wang and Lin [46]. In recent years the number of crystallographically characterized Pd<sup>II</sup> (NHC) complexes has increased considerably with a rich structural diversity revealed, especially when halide ions are present in the compound [47–49]. Because of our interests in the development of Ag and Pd complexes based on NHCs [50], herein, we present the syntheses, spectral characterization of two new pentamethylene-functionalized

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bis-imidazolium dication ligands ( $L^1 = 1,5$ -bis(4-(imidazolium-1-yl)-phenol)pentane dibromide and  $L^2 = 1,5$ -bis(1-vinylimidazolium-1-yl)pentane dibromide) bearing IP (4-(imidazol-1-yl)phenol) and VI (1-vinylimidazole)-functionality and their silver(I) and Pd(II) complexes. We, also report the comparative catalytic activities of Pd(II) bis-NHC complexes in the Heck and Suzuki–Miyaura coupling reaction.

## 2. Experimental

### 2.1. Materials and physical measurements

All the synthetic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques. The solvents were dried and distilled before use following the standard procedures [51]. 1,5-dibromopentane (Aldrich), 4-(imidazol-1-yl)-phenol (IP) (Aldrich), 1-vinylimidazole (Aldrich),  $[PdCl_2(CH_3CN)_2]$  (Aldrich) was used as received.

Elemental analysis was performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N is within  $\pm 0.4\%$  of calculated values. IR(KBr) was recorded using Perkin–Elmer FT-IR spectrophotometer. Electronic spectra were obtained on a Perkin Elmer Lambda-35 spectrometer. 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. The  $^1H$  and  $^{13}C$  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 (*J*) 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. Syntheses of ligands

#### 2.2.1. 1,5-bis(4-(imidazol-1-yl)phenol-imidazolium-1-yl)pentane dibromide ( $L^1$ )

4-(Imidazol-1-yl)phenol (5.029 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 yellow solid was filtered on a glass frit, washed with  $Et_2O$  (20 mL), and dried *in vacuo*, yielding  $L^1$  (4.853 g, 60%) as a yellow powder that was handled and stored in a vacuum desiccator. *Anal. Calc.* For  $C_{23}H_{26}N_4O_2Br_2$ : C, 50.15; H, 4.72; N, 10.17. Found: C, 50.43; H, 4.88; N, 10.34. IR( $cm^{-1}$ , KBr):  $\nu = 3450, 2930, 2857, 1640, 1520, 1472, 1384, 1255, 1165, 1030, 998, 740, 720, 697, 540$ .  $^1H$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 9.71(s, 2H), 7.55 (m, 6H, 8.4 Hz), 7.14 (m, 8H, 8.1 Hz), 4.04–4.74 (m, 2H, 8.2 Hz), 3.00–3.23 (m, 2H, 7.3 Hz), 1.99–2.15 (m, 2H, 6.6 Hz), 1.19–1.54 (m, 2H, 6.6 Hz), 0.81–0.91 (m, 2H, 7.3 Hz).  $^{13}C$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 154.82, 131.71, 131.60, 128.55, 128.33, 127.97, 127.84, 127.47, 127.39, 126.72, 125.43, 116.56, 74.23, 72.39, 70.32, 67.89, 65.93, 31.67, 29.44, 29.15, 28.66, 27.44, 23.47, 22.73, 22.42, 13.87. FAB-MS (*m/z*): 550(550), [M] (100%); 390(390),  $[M]^{2+}-Br_2$  (30%).

#### 2.2.2. 1,5-bis(1-vinyl-imidazolium-1-yl)pentane dibromide ( $L^2$ )

1-Vinylimidazole (2.955 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  $L^2$  (3.937 g, 60%) as a white powder that was handled and stored in a vacuum desiccator. *Anal. Calc.* For  $C_{15}H_{22}N_4Br_2$ : C, 43.06; H, 5.26; N, 13.39. Found: C, 43.16; H, 5.48; N, 13.57. IR( $cm^{-1}$ , KBr):  $\nu = 3300, 2920, 2856, 1640, 1540, 1471, 1380, 1250, 1160, 1040, 990, 745, 726, 696, 541$ .  $^1H$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 7.67 (s, 2H), 7.55

(s, 2H), 7.24–7.38 (m, 4H, 8.5 Hz), 5.38–5.90 (dd, 4H, 3.0 Hz), 4.71 (d, 2H, 4.2 Hz), 3.44–3.95 (m, 2H, 4.2 Hz), 2.53–2.68 (quintet, 2H, 6.8 Hz), 1.33 (m, 2H, 43.9 Hz).  $^{13}C$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 136.24, 130.41, 129.04, 125.77, 118.86, 101.21, 51.12, 32.59, 29.94, 27.86, 23.32, 15.76. FAB-MS (*m/z*): 418(418), [M] (80%); 258 (258),  $[M]^{2+}-Br_2$  (80%).

### 2.3. Syntheses of complexes

#### 2.3.1. $[Ag_2(\mu C(CH_2)_5C_p)_2][BF_4]_2$ ( $\mu C(CH_2)_5C_p = 1,5$ -bis(4-(imidazolium-1-yl)-phenol) pentane (**1**))

$L^1$  (0.550 g, 1 mmol) was dissolved in 5:1 DCM–MeOH (60 mL) and  $Ag_2O$  (0.232 g, 1 mmol) added. The resulting suspension was stirred at room temperature for 6 h, yielding a gray precipitate and colorless solution. The supernatant was separated and stripped *in vacuo* and the sticky white residue washed with MeOH ( $5 \times 5$  mL). The resultant white powder was dried *in vacuo* but rapidly discolored, giving **1** (0.349 g, 30%) as a dark cream powder that showed no further signs of decomposition at room temperature. *Anal. Calc.* for  $C_{46}H_{48}N_8Br_4O_4B_2F_8Ag_2$ : C, 47.42; H, 4.12; N, 9.62; O, 5.49. Found: C, 47.64; H, 4.41; N, 9.81; O, 5.64. IR( $cm^{-1}$ , KBr):  $\nu = 3420, 3090, 2924, 2230, 1605, 1546, 1511, 1458, 1251, 1183, 1117, 1054, 1025, 833, 732, 624, 554$ .  $^1H$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 9.85 (s, 4H), 7.50 (m, 12H, 8.1 Hz), 7.30 (m, 12H, 7.8 Hz), 4.12–4.84 (m, 4H, 6.4 Hz), 3.01–3.35 (m, 4H, 4.8 Hz), 1.98–2.23 (m, 4H, 7.2 Hz), 1.20–1.58 (m, 4H, 3.6 Hz), 0.85–0.95 (m, 4H, 8.1 Hz).  $^{13}C$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 156.42, 132.01, 131.40, 128.50, 128.23, 127.47, 127.34, 127.17, 127.09, 126.22, 125.53, 116.66, 74.58, 72.40, 70.44, 67.99, 65.98, 31.66, 29.48, 29.12, 28.61, 27.40, 23.43, 22.63, 22.32, 13.88. UV–Vis {DMSO,  $\lambda_{max}$  nm ( $\epsilon/M^{-1}cm^{-1}$ ): 285(5275), 365 (8346)}. FABMS (*m/z*): 1163 (1164), (M) (40%), 990 (990),  $(M^{2+})$  (50%).

#### 2.3.2. $[Ag_2(\nu C(CH_2)_5C_v)_2][BF_4]_2$ ( $\nu C(CH_2)_5C_v = 1,5$ -bis(1-vinylimidazolium-1-yl)pentane (**2**))

$L^2$  (0.418 g, 1 mmol) was dissolved in 5:1 DCM–MeOH (60 mL) and  $Ag_2O$  (0.232 g, 1 mmol) added. The resulting suspension was stirred at room temperature for 6 h, yielding a white precipitate with colorless solution. The solution was evaporated and the sticky white residue washed with MeOH ( $5 \times 5$  mL). The resultant white powder was dried *in vacuo*, giving **2** (0.270 g, 30%) as a creamy powder that showed no further signs of decomposition at room temperature. *Anal. Calc.* for  $C_{30}H_{40}N_8B_2F_8Ag_2$ : C, 40.00; H, 4.44; N, 12.44. Found: C, 39.98; H, 4.65; N, 12.58. IR( $cm^{-1}$ , KBr):  $\nu = 3047, 2921, 2852, 1604, 1583, 1477, 1432, 1309, 1251, 1180, 1054, 1024, 995, 744, 500, 429$ .  $^1H$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 7.78 (s, 4H), 7.59 (s, 4H), 7.28–7.44 (m, 8H, 8.4 Hz), 5.31–5.98 (dd, 8H, 3.6 Hz), 4.72 (d, 4H, 5.2 Hz), 3.48–4.01 (m, 4H, 6.4 Hz), 2.51–2.78 (quintet, 4H, 4.8 Hz), 1.31 (m, 4H, 8.4 Hz).  $^{13}C$  NMR ( $\delta$  ppm, 400 MHz,  $CDCl_3$ , 298 K): 136.64, 130.11, 129.18, 125.86, 119.01, 101.56, 51.25, 32.88, 29.94, 27.66, 23.54, 15.88. UV–Vis {DMSO,  $\lambda_{max}$  nm ( $\epsilon/M^{-1}cm^{-1}$ ): 280(8981), 355(8097)}. FABMS (*m/z*): 900(900), (M) (80%), 726(726),  $(M^{2+})$  (80%).

#### 2.3.3. $[PdCl(\mu C(CH_2)_5C_p)(CH_3CN)]BF_4$ (**3**)

**1** (0.2863 g, 0.246 mmol) was dissolved in DMSO (4 mL) at room temperature and  $[PdCl_2(MeCN)_2]$  (0.0650 g, 0.251 mmol) added. The resulting yellow solution lightened and became turbid over a period of 10 min. After 1 h, the reaction was filtered and the filtrate stripped *in vacuo*. The residue was taken up in MeCN (3 mL), centrifuged to remove  $AgCl$ , and concentrated to one-third volume. The crude product was precipitated by the addition of  $Et_2O$  (5 mL), washed with  $Et_2O$  ( $2 \times 5$  mL), then extracted into MeCN (2 mL). Diffusion of  $Et_2O$  into this extract gave **3** (0.263 g, 40%) as pale yellow solid. *Anal. Calc.* for  $C_{25}H_{27}N_5O_2ClBF_4Pd$ : C,

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