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Silver(I) and palladium(II) complexes of new pentamethylenefunctionalized 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 L¹ and L² (L¹ = 1,5-bis(4-(imidazolium-1-yl-phenol)pentane dibromide; L² = 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 L¹ and L² on reaction with Ag₂O in DCM:MeOH, followed by anion substitution with AgBF₄ led to the formation of silver(I) complexes [Ag₂(_PC(CH₂)₅C_P)₂][BF₄]₂ (_PC(CH₂)₅C_P = 1,5-bis(4-(imidazolium-1-yl-phenol) pentane (1) and [Ag₂(_VC(CH₂)₅C_V)₂][BF₄]₂ (_VC(CH₂)₅C_V = 1,5-bis(1-vinylimidazolium-1-yl)pentane (2). Transmetalation of the bis-NHC ligand from [Ag₂(_PC(CH₂)₅C_P)₂][BF₄]₂ and [Ag₂(_VC(CH₂)₅C_V)₂][BF₄]₂ by palladium(II) salt [PdCl₂(CH₂CN)₂] in DMSO gave [PdCl(_PC(CH₂)₅C_P) (CH₃CN)]BF₄ (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 ¹³C NMR, and FAB-MS spectroscopy. The molecular structure of the representative ligand L¹ has been determined by single crystal X-ray analysis. The palladium^{II} 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 Ag₂O by the method of Wang and Lin [46]. 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 [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-vinylimida-zolium-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), [PdCl₂(CH₃CN)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 ±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 ¹³C 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 δ 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 1,5dibromopentane (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 dessicator. Anal. Calc. For C23H26N4O2Br2: C, 50.15; H, 4.72; N, 10.17. Found: C, 50.43; H, 4.88; N, 10.34. IR(cm⁻¹ KBr):v = 3450, 2930, 2857, 1640, 1520, 1472, 1384, 1255, 1165, 1030, 998, 740, 720, 697, 540. ¹H NMR (δ ppm, 400 MHz, CDCl₃, 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). ¹³C NMR (δ ppm, 400 MHz, CDCl₃, 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), $[M]^{2+}$ -Br₂ (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 Et₂O (20 mL), and dried in vacuo, yielding L² (3.937 g, 60%) as a white powder that was handled and stored in a vacuum dessicator. *Anal.* Calc. For C₁₅H₂₂N₄Br₂: C, 43.06; H, 5.26; N, 13.39. Found: C, 43.16; H, 5.48; N, 13.57. IR(cm⁻¹, KBr): ν = 3300, 2920, 2856, 1640, 1540, 1471, 1380, 1250, 1160, 1040, 990, 745, 726, 696, 541. ¹H NMR (δ ppm, 400 MHz, CDCl₃, 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). ¹³C NMR (δ ppm, 400 MHz, CDCl₃, 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⁺–Br₂ (80%).

2.3. Syntheses of complexes

2.3.1. $[Ag_2(_PC(CH_2)_5C_P)_2][BF_4]_2 (_PC(CH_2)_5C_P = 1,5-bis(4-(imidazolium-1-yl-phenol) pentane (1)$

L¹ (0.550 g, 1 mmol) was dissolved in 5:1 DCM-MeOH (60 mL) and Ag₂O (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 $(5 \times 5 \text{ mL})$. 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 C₄₆H₄₈N₈Br₄O₄B₂F₈Ag₂: 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):v = 3420, 3090, 2924, 2230, 1605, 1546, 1511, 1458, 1251, 1183, 1117, 1054, 1025, 833, 732, 624, 554. ¹H NMR (δ ppm, 400 MHz, CDCl₃, 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). ¹³C NMR(δ ppm, 400 MHz, CDCl₃, 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, λ_{max} nm (ε/M^{-1} cm⁻¹)}: 285(5275), 365 (8346). FABMS (m/z): 1163 (1164), (M) (40%), 990 (990), (M^{2+}) (50%).

2.3.2. $[Ag_2(_VC(CH_2)_5C_V)_2][BF_4]_2(_VC(CH_2)_5C_V = 1,5-bis(1-vinylimidazolium-1-yl)pentane (2)$

L² (0.418 g, 1 mmol) was dissolved in 5:1 DCM-MeOH (60 mL) and Ag₂O (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 C₃₀H₄₀N₈B₂F₈Ag₂: C, 40.00; H, 4.44; N, 12.44. Found: C, 39.98; H, 4.65; N, 12.58. IR(cm⁻¹, KBr): *v* = 3047, 2921, 2852, 1604, 1583, 1477, 1432, 1309, 1251, 1180, 1054, 1024, 995, 744, 500, 429. ¹H NMR (δ ppm, 400 MHz, CDCl₃, 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). ¹³C NMR(δ ppm, 400 MHz, CDCl₃, 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, λ_{max} nm (ϵ/M^{-1} cm⁻¹)}: 280(8981), 355(8097). FABMS (*m*/*z*): 900(900), (M) (80%), 726(726), (M²⁺) (80%).

2.3.3. $[PdCl(_PC(CH_2)_5C_P)(CH_3CN)]BF_4$ (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 Et₂O (5 mL), washed with Et₂O (2 × 5 mL), then extracted into MeCN (2 mL). Diffusion of Et₂O into this extract gave **3** (0.263 g, 40%) as pale yellow solid. *Anal.* Calc. for C₂₅H₂₇N₅O₂ClBF₄Pd: C,

45.59; H, 4.10; N, 10.64. Found: C, 45.80; H, 4.35; N, 10.88. IR (cm⁻¹, KBr): ν = 3420, 3090, 2924, 2327, 2301, 1605, 1546, 1511, 1458, 1251, 1183, 1117, 1054, 1025, 833, 732, 624, 554. ¹H NMR (δ ppm, 400 MHz, CDCl₃, 298 K): 9.78 (s, 2H), 7.40 (m, 6H, 6.8 Hz), 7.10 (m, 6H, 8.8 Hz), 4.34–4.88 (m, 2H, 5.2 Hz), 2.98–3.22 (m, 2H, 4.8 Hz), 2.35(s, 3H), 1.98–2.05 (m, 2H, 6.8 Hz), 1.15–1.50 (m, 2H, 7.6 Hz), 0.88–1.05 (m, 2H, 6.3 Hz). ¹³C NMR(δ ppm, 400 MHz, CDCl₃, 298 K): 155.82, 132.01, 128.65, 128.22, 127.67, 126.32, 125.13, 118.11, 74.03, 72.09, 70.11, 67.32, 65.63, 31.01, 29.14, 29.01, 28.06, 27.04, 23.37, 22.43, 22.02, 13.07, 1.6. UV–VIS {DMSO, λ_{max} nm (ϵ /M⁻¹ cm⁻¹)}: 280(5421), 358(8346). FABMS (m/z): 571(571), (M⁺) (80%), 535(535), (M⁺–Cl) (50%).

2.3.4. $[PdCl(_VC(CH_2)_5C_V)(CH_3CN)]BF_4$ (4)

2 (0.221 g. 0.246 mmol) was dissolved in DMSO (4 mL) at room temperature and [PdCl₂(MeCN)₂] (0.0650 g, 0.251 mmol) added. The resulting vellow 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 Et₂O (5 mL), washed with Et_2O (2 \times 5 mL), then extracted into MeCN (2 mL). Diffusion of Et_2O into this extract gave **4** (0.220 g, 42%) as pale yellow solid. Anal. Calc. for C₁₇H₂₃N₅F₄BClPd: C, 38.78; H, 4.37; N, 13.30. Found: C, 38.88; H, 4.45; N, 13.38. IR(cm⁻¹, KBr): *v* = 3434, 3047, 2921, 2852, 2332, 2305, 1604, 1583, 1477, 1432, 1309, 1251, 1180, 1054, 1024, 995, 744, 500, 429. $^1{\rm H}$ NMR (δ ppm, 400 MHz, CDCl₃, 298 K): 7.60 (s, 2H), 7.50 (s, 2H), 7.20-7.48 (m, 4H, 6.4 Hz), 5.39-5.88 (dd, 4H, 6.0 Hz), 4.75 (d, 2H, 5.2 Hz), 3.46-3.91 (m, 2H, 7.2 Hz), 2.45-2.69 (quintet, 2H, 8.8 Hz), 2.09 (s, 3H), 1.33 (m, 2H, 8.8 Hz). ¹³C NMR (δ ppm, 400 MHz, CDCl₃, 298 K): 135.94, 130.21, 129.22, 125.76, 118.86, 101.21, 51.22, 32.49, 29.88, 27.46, 23.11, 15.46, 1.2. UV–Vis {DMSO, λ_{max} nm (ϵ / M⁻¹ cm⁻¹)}: 286(7981), 362(8099). FABMS (*m*/*z*): 440(439), (M⁺) (100%), 403 (403), (M⁺-Cl) (20%).

2.4. X-ray crystallographic study

X-ray data for L¹ was collected on a Bruker APEX II CCD diffractometer at 100(2) K using Mo K α radiation (λ = 0.71073 Å). Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programs [52]. ApexII, and SAINT software packages were used for data collection and data integration for L¹. Structure solution and refinement were carried out using the SHELXL97-Program [53]. The non-hydrogen 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 [54,55].

2.5. General procedure for Mizoroki-Heck reaction

 K_2CO_3 (553 mg, 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 (2.0 mmol) and n-butylacrylate or styrene (2.0 mmol) in DMF (10 mL). Then 0.1 mol% palladium complexes in DMF were added through syringe under nitrogen atmosphere. The mixture was stirred at 120 °C for the indicated reaction time. After the completion of the reaction, the mixture was cooled, 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 Na₂SO₄ and filtered. After evaporation, the obtained residue was purified by silica-gel column chromatography to give the Mizoroki–Heck product. Product identities were confirmed by ¹H and ¹³C NMR and GC–MS.

2.6. General procedure for Suzuki coupling reaction

 K_2CO_3 (553 mg, 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 (2.0 mmol) and phenylboronic acid (244.0 mg, 2.0 mmol) in DMF (10 mL). Then 0.1 mol% palladium complexes in DMF were 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 Na₂SO₄ and filtered. After evaporation, the obtained residue was purified by silica-gel column chromatography to give the coupling product. Product identities were confirmed by ¹H and ¹³C NMR and GC–MS.

3. Results and discussion

3.1. Synthesis

3.1.1. Pentamethylene-functionalized bis-imidazolium dication ligands Methodology similar to that used for the preparation of the alkyl-functionalised bis-imidazolium salt analogues [36] was employed to prepare pentamethylene-functionalized bis-imidazolium dication ligands. Reaction of 1,5-dibromopentane with 4-(imidazolium-1-yl-phenol/1-vinylimidazole in refluxing THF gave bis-imidazolium dication ligands L¹ and L² as white powder in good yields (Scheme 1).

Bis-imidazolium dication ligands L¹ and L² were characterized by elemental analysis, IR, ¹H & ¹³C NMR and FAB-MS spectroscopy. Analytical data of L¹, and L² corroborated well with their respective formulations (See **F-1** to **F-6**, Supporting material). A comparison of the ¹H and ¹³C NMR spectra of the IP and VI-functionalised bis-imidazolium dication ligands shows that variation of the functional group has a negligible effect on the chemical shifts of the imidazolium ring protons.

3.1.2. Ag (I) and Pd(II) complexes

Bis-imidazolium dication ligands L¹ and L² were reacted with Ag₂O in 1:1 stoichiometric ratio in a mixture of methanol and dichloromethane (1:5 v/v) under stirring for 6 h followed by anion substitution with AgBF₄ gave silver(I) complexes [Ag₂(_PC(CH₂)₅C_P)₂][BF₄]₂ (_PC(CH₂)₅C_P = 1,5-bis(4-(imidazolium-1-yl-phenol) pentane [**1**] and [Ag₂(_{VI}C(CH₂)₅C_{VI})₂][BF₄]₂ (_vC(CH₂)₅C_V = 1,5-bis(1-vinylimidazolium-1-yl)pentane [**2**] in reasonable yields (30%) as shown in Scheme 2.

Attempts for the syntheses of Pd(II) complexes of the bis-carbene ligands L^1 and L^2 *via* reaction of imidazolium salts L^1 and L^2 with [PdCl₂(CH₃CN)₂] gave a mixture of poorly soluble Pd^{II}(NHC) complexes that could not be satisfactorily separated by chromatography on silica. NHC ligand transmetalation from Ag(I) to Pd(II) has proved useful method for the synthesis of palladium(II) complexes [PdCl(_PC(CH₂)₅C_P)(CH₃CN)]BF₄ [**3**] and [PdCl(_VC(CH₂)₅C_V)(CH₃CN)] BF₄ [**4**], respectively in reasonable yields (40–42%) as shown in Scheme 3.

3.2. Characterization

All the complexes were isolated as air-stable, non-hygroscopic solids and soluble in dichloromethane, chloroform, methanol, dimethylformamide, and dimethylsulfoxide but insoluble in petroleum ether and diethyl ether. Analytical data of **1–4** corroborated well with their respective formulations. Information about composition of the complexes was also obtained from FAB-MS spectra of the complexes (recorded in the Section 2). The position of various





Scheme 2. Synthesis of silver(I) complexes 1 and 2.



Scheme 3. Synthesis of palladium(II) complexes 3 and 4.

peaks and overall fragmentation pattern in the FAB-MS spectra of the respective complexes confirmed well to their respective formulations (See F-7 to F-10, Supporting material). More information about the structure and bonding in the complexes has been deduced from the spectral studies. Poor quality of crystals of the complexes 1–4 has restricted us to provide any structural support at this stage.

Infrared spectrum of 1 and 3 in KBr displayed broad band around 3450 cm⁻¹ corresponding to v(OH). The band observed at 1630–1640 cm⁻¹ in **2** and **4** corresponds to olefinic C = C stretching that is usually found in the region of 1680–1630 cm⁻¹. The characteristic bands for $v(C \equiv N)$ in **3** and **4** appears at 2327–2332 cm⁻¹. The vibrations corresponding to v(C=N) in all the complexes which appeared at \sim 1590–1600 cm⁻¹ are because of the imidazole moiety. All the complexes exhibit intense bands at 1054 cm⁻¹ which is due to presence of counterion BF₄. 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 ¹H and ¹³C NMR signals which integrate well to the corresponding hydrogens and carbons. 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 all the complexes 1-4 display bands at 280-286 and 355-365 nm. The higher energy band corresponds to the intraligand π - π ^{*} transition, whilst the lower energy band can be assigned to MLCT transition.

One X-ray structure emerged in the current study. The refinement details of L^1 are summarized in Table 1, and selected bond

| Table | 1 | | | |
|--------|------------|------|-----|------------------|
| Crysta | llographic | data | for | L ¹ . |

| Empirical formula FW | C ₂₃ H ₂₆ Br ₂ N ₄ O ₂ 550.30 |
|---|---|
| Crystal system | Orthorhombic |
| Space group | Pccn |
| a (Å) | 12.5824(7) |
| b (Å) | 13.0703(8) |
| <i>c</i> (Å) | 17.6434(10) |
| α (°) | 90.00 |
| β (°) | 90.00 |
| γ (°) | 90.00 |
| V (Å ³) | 2901.6(3) |
| Ζ | 4 |
| D_{calc} (g cm ⁻³) | 1.260 |
| μ (mm ⁻¹) | 2.816 |
| T (K) | 100(2) |
| R ₁ all | 0.1037 |
| $R_1 \left[I > 2\sigma(I) \right]$ | 0.0754 |
| wR ₂ | 0.2258 |
| $wR_2 [I > 2\sigma(I)]$ | 0.2020 |
| Goodness-of-fit (GOF) on F^2 | 1.038 |
| | |

lengths and angles are presented in Table 2. L¹ crystallise in the orthorhombic space group *Pccn*, with one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit in each case. The X-ray structure of L¹ is depicted in Fig. 1. The bond lengths and angles within the C_3N_2 rings of L¹ are comparable to those found in the complex $[Ag_2(MeC(CH_2)_5C)_2][AgBr_2]_2$ (MeC (CH₂)₅C) = C,C'-1,5-bis(3-methylimidazolin-2-yliden-1-yl)pentane) [36] and in other related complexes [29–37]. The two C_3N_2 rings in

| Table 2 | |
|--|----|
| Selected bond lengths (Å), and bond angles (°) for L | 1. |

| O(1)-C(1) | 1.358(6) |
|--|----------|
| N(1)-C(7) | 1.322(6) |
| N(1)-C(9) | 1.378(6) |
| N(1)-C(4) | 1.437(6) |
| N(2)-C(7) | 1.315(6) |
| N(2)-C(8) | 1.379(6) |
| N(2)-C(10) | 1.478(6) |
| C(10)-C(11) | 1.505(7) |
| C(11)-C(12) | 1.528(6) |
| $C(12)-C(11)^{\#1}$ | 1.528(6) |
| C(7)-N(1)-C(9) | 108.0(4) |
| C(7)-N(1)-C(4) | 125.6(4) |
| C(9)-N(1)-C(4) | 126.4(4) |
| C(7)-N(2)-C(8) | 108.3(4) |
| C(7)-N(2)-C(10) | 125.2(4) |
| C(8)-N(2)-C(10) | 126.5(4) |
| O(1)-C(1)-C(6) | 122.6(4) |
| O(1)-C(1)-C(2) | 117.6(4) |
| N(2)-C(7)-N(1) | 109.4(4) |
| N(2)-C(10)-C(11) | 113.2(4) |
| C(10)-C(11)-C(12) | 113.8(5) |
| $C(11)^{\#1}-C(12)-C(11)$ | 112.1(6) |
| $C(10)-C(11)-C(12)-C(11)^{\#1}$ | 173.0(5) |
| N(2)-C(10)-C(11)-C(12) | 63.8(5) |
| C_3N_2 interplanar dihedral (θ ,°) | 63.24 |

Symmetry transformations used to generate equivalent atoms: #1 -x + 3/2, -y + 1/2, z.

 L^1 have similar torsions for each section, being relatively rotated about the C(10)-N(2) bond and dispersed to either side of the alkyl linkage. The C(sp²)-O bond distances in L¹ are 1.358(6) Å. The ligand 4-(imidazol-1-yl)phenol has lost planarity upon coordination with pentamethylene linkage. The phenyl group of the 4-(imidazol-1-yl) phenol is not coplanar with imidazole ring and is tilted with respect to the imidazole ring plane at an angle of 31.20°.

Crystal packing in L¹ is stabilized by inter- and intra-molecular C-H···Br weak interactions. An interesting feature of the crystal packing in L¹ is a linear chain motif (Fig. 2) resulting from C-H···Br

3.3. Catalysis

3.3.1. Catalytic activities for Heck coupling reaction

The palladium-catalyzed Heck coupling reaction has been widely employed for the preparation of aryl olefins. The Heck coupling reactions of activated, non-activated and deactivated aryl halides with vinyl compounds were examined in DMF at 120 °C by using 0.1 mol% of complex **3** and **4** as the catalyst precursors. The results are summarized in Table 3. As can be seen from Table 3, our catalysts are so active that allows the olefination reactions of activated, non-activated and deactivated aryl halides with vinyl compounds such as n-butyl acrylate or styrene proceed at 120 °C by using only 0.1 mol% of 3 or 4. The corresponding coupled products could be isolated in 40-98% yields. In the case of n-butyl acrylate, only the *trans* isomer was detected, whereas for the coupling reactions of styrene cis olefins were also observed as minor products in not more than 20% yields. For the activated bromide and iodide substrates, the palladium-NHC catalysts are even more effective than most of known palladium catalysts such as phospha-palladacycle [58-60] and Pd-phosphine-imidazolium salt systems [61]. A high yield for the Heck coupling product was obtained for activated aryl iodides or bromides (Table 3, entry 4, 5, 10, 11 and 13-16) than activated aryl chlorides (Table 3, entry 6, 12 and 17) by using complex 3 in comparison to complex 4. Extending the reaction time up to 48 h did not give better results for activated aryl chlorides. However, for non-activated iodo or bromo or chlorobenzene, the desired coupled product yield was obtained in 68-96% for 3 as compared to 64-92% yield with in complex 4 (Table 3, entry 1, 2, 3, 7, 8 and 9). The low yields obtained with aryl chloride or non-activated aryl chlorides are due to the stronger C_{sp}^2 -Cl bonds of aryl chlorides than those of the heavier congeners.



Fig. 1. Projection view of L¹ shown with 50% ellipsoids; hydrogen atoms are omitted for clarity.



Fig. 2. Linear chain motif resulting from C-H...Br interactions.

Table 3

| Results of the Heck cross-coup | ng reactions of ar | vl halides with vinvl | compounds using | complex 3 and 4 . ^a |
|--------------------------------|--------------------|-----------------------|-----------------|--|
|--------------------------------|--------------------|-----------------------|-----------------|--|



^a All reactions were carried out using 2.0 mmol activated or non-activated or decativated aryl halide, 2.0 mmol vinyl compound, 4.0 mmol K₂CO₃, 0.1 mol% Pd complex and 10 ml DMF at 120 °C for 24 h.

^b Isolated yield.

^c Yield of *cis*-product.

With the best conditions in hand, we explored substrate scope of the reaction. In particular, our target was to verify the ability of our catalysts to promote the reaction with different aryl halides. It was found that activated bromo and iodo arenes reacted smoothly and in good yields (Table 3, entry 13–16) than chloro arene (Table 3, entry 17). On the other hand, deactivated haloarenes had an adverse effect on the reactivity, resulting in moderate to poor yields of isolated product (Table 3, entry 18–23). Further

investigation of the true activation mechanism for pentamethylene-functionalized quasi-pincer carbene containing palladium(II) and its practical applications are undergoing in our laboratory.

3.3.2. Catalytic activities for Suzuki-Miyaura reaction

The catalytic activities of the palladium complexes (**3** and **4**) were studied for C–C formation reactions. Suzuki coupling

Table 4

Results of the Suzuki-Miyaura cross-coupling reactions of aryl halides with phenylboronic acid using complex 3 and 4^a.



^a All reactions were carried out using 2.0 mmol aryl halide, 2.0 mmol phenylboronic acid, 4.0 mmol K₂CO₃, 0.1 mol% Pd complex and 10 ml DMF at 120 °C for 12 h. ^b Isolated yield.

reactions have been the most versatile and important method for the synthesis of unsymmetrically substituted biaryl compounds [62–71]. The coupling reaction of selected aryl halides with phenylboronic acid in DMF with 0.001 equivalent catalysts loading using K₂CO₃ as base at 120° was studied. Both the catalysts are effective towards activated, non-activated and deactivated aryl bromides and aryl iodides. The data clearly show that complex 3 is more active than 4; that is, the reaction of aryl halides with phenylboronic acid in the presence of 0.001 equivalent of Pd complex in DMF at 120 °C for 12 h gave 52-98% yield of the Suzuki-Miyaura coupling product. The results are presented in Table 4. In general, the activities of these palladium complexes are similar to other palladium(II) catalysts based on phosphine-NHC ligands [72-76] and pyridine-NHC ligands [77-80] but greater than amido-NHC ligand [81]. The higher product yield obtained with palladium complex **3** containing the hydroxy functionalised dicarbene ligand may be explained by the stabilizing effect of hydroxy moiety on the palladium active form. With the best conditions in hand, we explored substrate scope of our catalysts towards activated, non-activated and deactivated aryl bromides and aryl iodides. It was observed that activated or non-activated aryl bromides and aryl iodides gave higher yields of isolated product (Table 4, entry 1–6) than the deactivated aryl bromides and aryl iodides (Table 4, entry 7-10).

4. Conclusion

In this paper, we have reported two new bis-imidazolium dication ligands bearing pentamethylene functionality and their silver (I) and Pd(II) complexes. We have also investigated the performance of palladium(II) complexes in the Heck and Suzuki–Miyaura coupling reaction. Complex **3** has higher catalytic activities as compared to complex **4**. From the catalytic studies it is evident that by judicious selection of the functional groups at the 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 work towards replacement of the phenol and vinyl substituents with the bulkier Mes or dipp groups is in progress in our laboratory.

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Appendix A. Supplementary material

CCDC 1042392 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 http://dx.doi.org/10. 1016/j.ica.2016.04.039.

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