



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 ($L^1 = 1,5\text{-bis}(1\text{-}(4\text{-cyanophenyl})\text{-imidazolium-1-yl})\text{pentane dibromide}$) and $L^2 = 1,5\text{-bis}(1\text{-}(4\text{-methoxyphenyl})\text{-imidazolium-1-yl})\text{pentane dibromide}$) 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^1 and L^2 on reaction with $[\text{PdBr}_2(\text{C}_6\text{H}_5\text{CN})_2]$ led to the formation of neutral bis-imidazolium dication palladium(II) complexes $[\text{L}^1][\text{PdBr}_4]$ **[1]** ($L^1 = 1,5\text{-bis}(1\text{-}(4\text{-cyanophenyl})\text{-imidazolium-1-yl})\text{pentane}$) and $[\text{L}^2][\text{PdBr}_4]$ **[2]** ($L^2 = 1,5\text{-bis}(1\text{-}(4\text{-methoxyphenyl})\text{-imidazolium-1-yl})\text{pentane}$), respectively. The new ligands as well as their palladium(II) complexes, has been characterized by elemental analysis, electronic, IR, ^1H and ^{13}C NMR, FAB-MS and ESI-MS spectroscopy. The molecular structure of the representative complex $[\text{L}^2][\text{PdBr}_4]$ **[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, π) 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_2O 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 ($L^1 = 1,5\text{-bis}(1\text{-}(4\text{-cyanophenyl})\text{-imidazolium-1-yl})\text{pentane dibromide}$) and $L^2 = 1,5\text{-bis}(1\text{-}(4\text{-methoxyphenyl})\text{-imidazolium-1-yl})\text{pentane dibromide}$) bearing CPI (1-(4-cyanophenyl)-imidazole) and MPI (1-(4-methoxyphenyl)-1*H*-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)-1H-imidazole (MPI) (Aldrich), was used as received. All other reagents were used as received. $[\text{PdBr}_2(\text{C}_6\text{H}_5\text{CN})_2]$ [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 $\pm 0.4\%$ 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 ^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 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. 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^1 (14.26 g, 80%) as a white powder that was handled and stored in a vacuum dessicator. *Anal. Calc.* For $\text{C}_{25}\text{H}_{24}\text{N}_6\text{Br}_2$: C, 52.82; H, 4.23; N, 14.79. Found: C, 53.10; H, 4.36; N, 14.94%. IR(cm^{-1} , nujol): $\nu = 3320, 2927, 2230, 1606, 1508, 1402, 1247, 1016, 848, 749, 568$. ^1H NMR (δ ppm, 400 MHz, CDCl_3 , 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). ^{13}C NMR (δ ppm, 400 MHz, CDCl_3 , 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), $[\text{M}]^+$ (20%); 488 (488), $[\text{M}]^+-\text{Br}$ (50%); 408 (407), $[\text{M}]^{2+}-\text{Br}_2$ (20%).

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

1-(4-Methoxyphenyl)-1H-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_2O (20 mL), and dried in vacuo, yielding L^2 (10.88 g, 60%) as a white powder that was handled and stored in a vacuum dessicator. *Anal. Calc.* For $\text{C}_{25}\text{H}_{30}\text{N}_4\text{O}_2\text{Br}_2$: C, 51.90; H, 5.19; N, 9.69. Found: C, 52.20; H, 5.41; N, 9.85%. IR(cm^{-1} , nujol): $\nu = 3419, 3054, 2924, 1608, 1518, 1481, 1435, 1308, 1250, 1185, 1091, 1024, 841, 748, 722, 696, 541, 517$. ^1H NMR (δ ppm,

400 MHz, CDCl_3 , 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). ^{13}C NMR (δ ppm, 400 MHz, CDCl_3 , 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), $[\text{M}]^+$ (40%); 498(498), $[\text{M}]^+-\text{Br}$ (90%); 418(418), $[\text{M}]^{2+}-\text{Br}_2$ (20%).

2.3. Bis-imidazolium dication palladium(II) complexes

2.3.1. $[L^1][\text{PdBr}_4]$ (1)

L^1 (0.568 g, 1 mmol) was dissolved in 1:1 DCM–MeOH (30 mL) and $[\text{PdBr}_2(\text{C}_6\text{H}_5\text{CN})_2]$ (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_2O (5 ml) giving 1 as a pale yellow solid. Yield: (0.603 g, 80%). *Anal. Calc.* for $\text{C}_{25}\text{H}_{24}\text{N}_6\text{Br}_4\text{Pd}$: C, 39.78; H, 3.18; N, 11.14. Found: C, 40.08; H, 3.45; N, 11.38%. IR(cm^{-1} , nujol): $\nu = 3420, 3090, 2924, 2230, 1605, 1546, 1511, 1458, 1251, 1183, 1117, 1066, 1025, 833, 732, 624, 554$. ^1H NMR (δ ppm, 400 MHz, CDCl_3 , 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 (δ ppm, 400 MHz, CDCl_3 , 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, λ_{max} nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 261(4725), 280(2421), 354(5346)}. ESI–MS (m/z): 408.9 (M^+).

2.3.2. $[L^2][\text{PdBr}_4]$ (2)

L^2 (0.578 g, 1 mmol) was dissolved in 1:1 DCM–MeOH (30 mL) and $[\text{PdBr}_2(\text{C}_6\text{H}_5\text{CN})_2]$ (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 ml) giving 2 as an 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 $\text{C}_{25}\text{H}_{30}\text{N}_4\text{O}_2\text{Br}_4\text{Pd}$: C, 35.54; H, 3.55; N, 6.64. Found: C, 35.78; H, 3.65; N, 6.78%. IR(cm^{-1} , nujol): $\nu = 3434, 3047, 2921, 2852, 1604, 1583, 1477, 1432, 1309, 1251, 1180, 1094, 1024, 995, 744, 500, 429$. ^1H NMR (δ ppm, 400 MHz, CDCl_3 , 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). ^{13}C NMR (δ ppm, 400 MHz, CDCl_3 , 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, λ_{max} nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 261(8020), 271(4981), 355(7099)}. ESI–MS (m/z): 418.8 (M^+).

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 ($\lambda = 0.71073 \text{ \AA}$). 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 SHELXL97–Program [50]. 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 [51,52].

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