## Synthesis of novel linear exo-bidentate bispyridine ligands and their complexes with silver(1) tetrafluoroborate

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Novel *exo*-bidentate ligands containing two  $\gamma$ -pyridyl fragments and their complexes with silver(I) tetrafluoroborate were synthesized.

Key words: supramolecular chemistry, pyridine, 4-substituted anilines, 1,4-phenylenediamine, cross-coupling, silver tetrafluoroborate, organic ligands.

The supramolecular chemistry of polymeric systems based on organic ligands and nontransition metal salts is under intense development. Ligands containing two  $\gamma$ -pyridyl residues linked to the ethylidene or arylidene fragment become the most important building blocks for supramolecular systems.<sup>1</sup> Such exo-bidentate pyridine ligands as *trans*-1,2-bis(4-pyridyl)ethylene<sup>2</sup> (stilbazole) and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene<sup>3</sup> react with silver(I) tetrafluoroborate and nickel(II) nitrate to form polymeric compounds  $(MLX_n)_m$  and  $(ML_2X_n)_m$ , respectively, where M is the complex-forming metal, L is the organic ligand, and X is the anion. At the same time, complex compounds containing exo-dipyridyl ligands with the arylenediethylene bridging group remain virtually unstudied.4

We synthesized 1,4-bis[2-(4-pyridyl)ethenyl]benzene (1) and its azomethine analogs 2 and 3 (Scheme 1). Compound 1 was prepared using a standard procedure. Compounds 2 and 3 were synthesized for the first time. Compound 2 was synthesized by the condensation of *p*-phenylenediamine with two equivalents of pyridine-4-carbaldehyde in toluene. Compound 3 was synthesized by the condensation of 4-bromaniline with pyrididine-4-carbaldehyde followed by cross-coupling of imine 4 that formed with 4-vinylpyridine in the presence of bis(triphenylphosphine)palladium dichloride. The structures of these compounds were confirmed by the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic and elemental analysis data.

Compounds 1, 2, and 3 were used as ligands in the reaction with silver(1) tetrafluoroborate to afford complexes 5-7, whose composition corresponds to the  $AgBF_4 \cdot L$  formula according to the elemental analysis data. The IR spectra of complexes 5-7 exhibit an absorption band at 1050 cm<sup>-1</sup> corresponding to the tetrafluoroborate anion. The powder X-ray diffraction analysis of the complexes indicated that all of them were crystalline with

CHO 2 3

**Reagents and conditions:** *i*. 4-vinylpyridine, Et<sub>2</sub>N [Pd(PPh<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>, 100 °C; *ii. p*-phenylenediamine, piperidine, toluene, boiling; iii. 4-bromaniline, piperidine, toluene, boiling; iv. 4-vinylpyridine, Et<sub>3</sub>N, [Pd(PPh<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>.

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Scheme 1

similar main reflection sets. This suggests that the compounds possess similar unit cell systems.

Thus, the novel *exo*-bidentate ligands containing two  $\gamma$ -pyridyl fragments and their complexes with AgBF<sub>4</sub> were synthesized.

## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra ( $\delta$ , ppm, *J*/Hz) were recorded on a Varian VXR-400 instrument with working frequencies of 400 and 100 MHz, respectively, at 28 °C in CDCl<sub>3</sub>. IR spectra (v/cm<sup>-1</sup>) were recorded on a UR-20 instrument in Nujol. X-ray diffraction analysis was carried out on a Dron-3M diffractometer ( $\lambda$ (Cu-K $\alpha$ ) = 1.5418 Å,  $\theta$ /2 $\theta$  scan mode: 5.5–65 with the 0.05 increment), and  $d_n$  reflections were presented (1000 · *I*/*I*<sub>max</sub>). Melting points of substances were determined in an open capillary and were uncorrected. All reagents were commercial (Acros<sup>®</sup>, Lancaster<sup>®</sup>) and used without additional purification.

**1,4-Bis**[*(E)*-**2-(4-pyridyl)ethenyl]benzene (1)** was synthesized using a described procedure<sup>5</sup> in 62% yield with m.p. 250 °C. <sup>1</sup>H NMR,  $\delta$ : 7.05 (d, 2 H, CH=C<u>H</u>—Ar, *J* = 16.3 Hz); 7.29 (d, 2 H, Py—C<u>H</u>=CH, *J* = 16.3 Hz); 7.37 (d, 4 H, Py(3), Py(5), *J* = 6.2 Hz); 7.55 (s, 4 H, Ar(2), Ar(3), Ar(5), Ar(6)); 8.58 (d, 4 H, Py(2), Py(6), *J* = 6.2 Hz). <sup>13</sup>C NMR,  $\delta$ : 120.9, 127.1, 128.8, 129.3, 130.4, 135.3, 144.3, 150.3. IR, cm<sup>-1</sup>: 1620—1600 (br, C=C, C=N).

**Condensation of anilines with 4-pyridinecarbaldehyde (general procedure).** A mixture of aldehyde (20 mmol) and aniline (20 mmol) in toluene (50 mL) containing piperidine (0.1 mL) was boiled for 2 h with a Dean—Stark trap. The solvent was evaporated, and the residue was recrystallized from 2-propanol or ethanol.

*N,N*'-Bis[*(E*)-4-pyridylmethylidene]-1,4-phenylenediamine (2). The yield was 92%, m.p. 165 °C (from 2-propanol). <sup>1</sup>H NMR,  $\delta$ : 7.04 (d, 4 H, Py(3), Py(5), *J* = 5.5 Hz); 8.02 (s, 4 H, Ar(2), Ar(3), Ar(5), Ar(6)); 8.44 (s, 2 H,  $-C\underline{H}=N-$ ); 8.56 (d, 4 H, Py(2), Py(6), *J* = 5.5 Hz). <sup>13</sup>C NMR,  $\delta$ : 121.8, 123.7, 134.7, 150.8, 151.2, 156.5. IR, cm<sup>-1</sup>: 1630 (C=C), 1600 (C=N), 1580 (Py). Found (%): C, 75.26; H, 5.01; N, 19.39. C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>. Calculated (%): C, 75.51; H, 4.93; N, 19.57.

*N*-[(*E*)-4-Pyridylmethylidene]-4-[(*E*)-2-(4-pyridyl)ethenyl]aniline (3) was synthesized similarly to compound 1 in 70% yield with m.p. 193 °C. <sup>1</sup>H NMR (protons of the 4-pyridylcarbimine fragment are marked by stroke),  $\delta$ : 7.00 (d, 1 H, Ar-C<u>H</u>=CH, *J* = 16.4 Hz); 7.26 (d, 2 H, Ar(2), Ar(6), *J* = 7.2 Hz); 7.29 (d, 1 H, CH=C<u>H</u>-Py, *J* = 16.4 Hz); 7.36 (d, 2 H, Ar(3), Ar(5), *J* = 7.2 Hz); 7.57 (d, 2 H, Py(3), Py(5), *J* = 6.0 Hz), 7.74 (d, 2 H, Py(3'), Py(5'), *J* = 6.0 Hz); 8.46 (s, 1 H, -C<u>H</u>=N-); 8.57 (d, 2 H, Py(2), Py(6), *J* = 6.0 Hz); 8.67 (d, 2 H, Py(2'), Py(6'), *J* = 6.0 Hz). <sup>13</sup>C NMR,  $\delta$ : 120.7, 121.5, 122.2, 126.0, 131.8, 132.5, 135.6, 142.5, 144.4, 150.1, 150.5, 150.9, 157.8. IR, cm<sup>-1</sup>: 1615 (C=C), 1590 (C=N). Found (%): C, 78.31; H, 5.53; N, 12.52. C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>. Calculated (%): C, 79.98; H, 5.30; N, 14.73.

*N*-[(*E*)-4-Pyridylmethylidene]-4-bromaniline (4). The yield was 81%, m.p. 74 °C (*cf.* Ref. 6: m.p. 81 °C). <sup>1</sup>H NMR,  $\delta$ : 7.10 (d, 2 H, Ar(3), Ar(5), *J* = 8.5 Hz); 7.51 (d, 2 H, Ar(2), Ar(6), *J* = 8.5 Hz); 7.71 (d, 2 H, Py(3), Py(5), *J* = 6.0 Hz); 8.40 (s, 1 H,

--C<u>H</u>=N-); 8.75 (d, 2 H, Py(2), Py(6), *J* = 6.0 Hz). <sup>13</sup>C NMR, δ: 120.5, 122.2, 122.6, 132.3, 142.4, 149.7, 150.6, 158.2.

Synthesis of complexes 5–7 (general procedure). The complexes were synthesized according to a described procedure<sup>2</sup> using a slow diffusion of solutions of the ligand (2 equiv.) in anhydrous methylene chloride and silver(1) tetrafluoroborate (1 equiv.) in dry acetonitrile. The finely crystalline precipitate that formed was filtered off, thoroughly washed with a fivefold excess of methylene chloride and acetonitrile to remove possible admixtures of the initial reactants, and dried *in vacuo* with weak heating.

**Complex of 1,4-bis**[*(E)*-2-(4-pyridyl)ethenyl]benzene with AgBF<sub>4</sub> (5). The reaction of compound 1 (0.568 g, 2 mmol) with AgBF<sub>4</sub> (0.192 g, 1 mmol) afforded a yellow powder (150 mg, 32%) with m.p. 353 °C (decomp.). IR, cm<sup>-1</sup>: 1615 (br, C=C, C=N), 1050 (br, BF<sub>4</sub>). Found (%): C, 50.40; H, 3.36; N, 5.86. C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>·AgBF<sub>4</sub>. Calculated (%): C, 50.15; H, 3.37; N, 5.85. X-ray diffraction pattern: 9.0416 (563), 4.5387 (1000), 3.3650 (486).

Complex of N,N'-bis[(E)-4-pyridylmethylidene]-1,4-phenylenediamine with AgBF<sub>4</sub> (6). The reaction of compound 2 (0.568 g, 2 mmol) with AgBF<sub>4</sub> (0.192 g, 1 mmol) afforded a yellow powder (130 mg, 29%) with m.p. 381 °C (decomp.). IR, cm<sup>-1</sup>: 1615 (br, C=N); 1050 (br, BF<sub>4</sub>). Found (%): C, 44.62; H, 2.78; N, 11.48. C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>·AgBF<sub>4</sub>. Calculated (%): C, 44.95; H, 2.93; N, 11.65. X-ray diffraction pattern: 9.0484 (475), 4.5064 (1000), 3.3648 (350).

Complex of *N*-[(*E*)-4-pyridylmethylidene]-4-[(*E*)-2-(4-pyridyl)ethenyl]aniline with AgBF<sub>4</sub> (7). The reaction of compound 3 (0.568 g, 2 mmol) with AgBF<sub>4</sub> (0.192 g, 1 mmol) afforded a dark yellow powder (130 mg, 29%) with m.p. 376 °C (decomp.). IR, cm<sup>-1</sup>: 1615, 1590 (C=C, C=N), 1050 (br, BF<sub>4</sub>). Found (%): C, 48.02; H, 3.15; N, 9.21. C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>·AgBF<sub>4</sub>. Calculated (%): C, 47.54; H, 3.13; N, 8.75. X-ray diffraction pattern: 9.2979 (760), 4.5062 (1000), 3.3837 (686).

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