

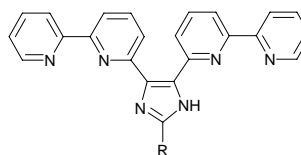
## Graphical Abstract

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### Syntheses of new binucleating heterocyclic ligands

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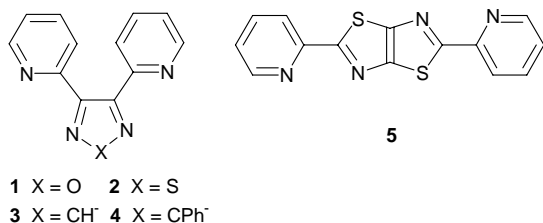
# Syntheses of new binucleating heterocyclic ligands

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**Abstract**— The syntheses of five new mixed azine-azole binucleating ligands are described. © 2007 Elsevier Science. All rights reserved

We have long been interested in the synthesis and study of new bridging heterocyclic ligands and their use in coordination and metallocsupramolecular chemistry.<sup>1</sup> For example, we have recently reported investigations of binuclear metal complexes of ligands such as **1-5** (Scheme 1).<sup>2</sup> Within this context, we showed that the binuclear ruthenium(II) complexes of ligands **1-4** exhibit unusually strong metal-metal interactions, seemingly mediated by the existence of the central azole ring.<sup>2a,2c</sup> In order to probe the origin of this intriguing phenomenon, we have prepared a number of structurally related ligands, the syntheses of which we now report.

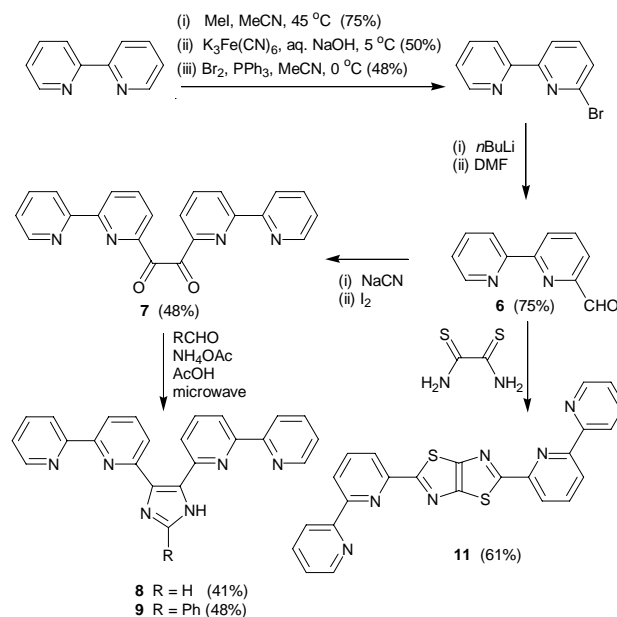


**Scheme 1.** Previously reported binucleating ligands.

In view of the intense current interest in the use of tridentate ligands related to 2,2',6',2''-terpyridine,<sup>3</sup> we decided to prepared analogues of **3** and **4** with tridentate binding domains. A key synthon for such compounds is 2,2'-bipyridine-6-carboxaldehyde **6**, which has previously been prepared by methylation of 2,2'-bipyridine and selenium dioxide oxidation,<sup>4</sup> and by Swern oxidation of the hydroxymethyl derivative.<sup>5</sup> We have found that this compound is more conveniently prepared by the sequence shown in Scheme 2. Thus 2,2'-bipyridine was converted to the 6-bromo-derivative by a methylation, oxidation, bromination sequence<sup>6</sup> and then converted into **6** by lithium

halogen exchange followed by formylation with DMF.<sup>7</sup> Subsequent benzoin condensation afforded the pyridoin, as its enediol tautomer, which was readily oxidised to the pyridil **7**.<sup>4b</sup>

Using an extension of the methodology used to prepare ligands **3** and **4**, the diketone **7** was reacted with formaldehyde (provided by hexamethylenetetramine) and benzaldehyde in the presence of excess ammonium acetate under microwave irradiation to provide the new ligands **8** and **9**, respectively.<sup>8,9</sup> This microwave procedure<sup>10</sup> avoided the formation of byproducts containing a fused imidazolo[1,5-*a*]pyridine ring system.<sup>11</sup> These ligands contain tridentate binding domains arranged in an “angular” fashion.<sup>12</sup> As was previously observed with ligands **3** and **4**,<sup>2c</sup> the <sup>1</sup>H NMR spectra of these compounds showed significant broadening of the signals of the pyridine protons due to a slow exchange on the NMR timescale of the tautomeric imidazole hydrogens resulting from intramolecular hydrogen bonding to the pyridine ring.

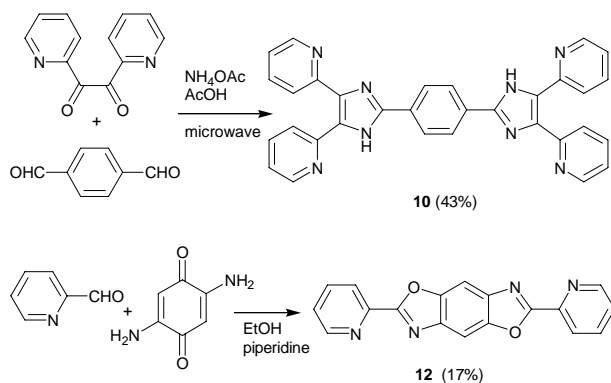


**Scheme 2.** Preparations of doubly tridentate ligands.

**Keywords:** N-ligand, Pyridine, Imidazole, Tridentate ligand

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We next considered the possibility of extending this ligand design strategy to the preparation of a potentially tetranucleating ligand. Thus, we reacted terephthalaldehyde with 2,2'-pyridil, under similar reaction conditions, which pleasingly furnished the new ligand **10** in 43% yield (Scheme 3).<sup>13</sup> Once again the signals for the pyridine ring protons were broadened due to slow prototropic tautomerism of the imidazole NH. Double deprotonation of this ligand would potentially lead to exciting new tetranuclear metal complexes, the possibility of which is under current investigation.



**Scheme 3.** Preparations of ligands **10** and **12**.

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- (a) Onggo, D.; Craig, D. C.; Rae, A. D.; Goodwin, H. A. *Aust. J. Chem.* **1991**, *44*, 331-341. (b) Heitzler, F. R.; Neuberger, M.; Zehnder, M.; Constable, E. C. *Liebigs Ann./Recueil* **1997**, 297-301.
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- Selected data for **8**: grey powder, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.75 (2H, br d, H6''); 8.33 (4H, br m, H3'/H3'');
- Based upon the interesting results we obtained from the doubly-bidentate ligand **5**, containing the unusual thiazolo[5,4-*d*]thiazole fused heterocyclic ring system,<sup>2b</sup> we also sought to extend this ligand design strategy towards a doubly tridentate analogue. Thus, reaction of **6** with rubenic acid led to the new ligand **11** in 61% yield (Scheme 2).<sup>14</sup> This ligand contains two tridentate binding domains arranged in a "stepped-parallel" manner.<sup>12</sup>
- Finally, in order to explore the possibility of tuning the metal-metal interactions in complexes of ligands such as **5**, we considered the option of introducing a benzene ring between the fused rings. This proved easier to do with the oxygen, rather than sulfur, analogue and, by reacting 2,5-diaminobenzoquinone<sup>15</sup> with pyridine-2-carbaldehyde, we obtained the new "stepped-parallel"<sup>12</sup> ligand **12**, albeit in only 17% yield (Scheme 3).<sup>16,17</sup>
- All five new ligands showed spectroscopic and characterisation data in accord with the proposed structures. Studies are currently underway employing these ligands as synthons in coordination and metallosupramolecular chemistry.
- Acknowledgements:** We thank the University of Canterbury and the Royal Society of New Zealand Marsden Fund for generous funding.
- 7.84 (1H, s, H2); 7.78 (4H, br m, H4'/H4''); 7.34 (4H, br m, H5'/H5''). ESMS: Calc. C<sub>23</sub>H<sub>17</sub>N<sub>6</sub> (MH<sup>+</sup>) 377.1515, Found 377.1759.
- Selected data for **9**: colourless powder, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.71 (2H, d, J = 5 Hz, H6''); 8.31 (4H, br d, J = 8 Hz, H3'/H3''); 8.10 (2H, d, J = 8 Hz, Hortho); 7.78 (4H, br s, H4'/H4''); 7.50 (2H, t, J = 8 Hz, Hmeta); 7.42 (1H, t, J = 8 Hz, Hpara); 7.32 (4H, br t, H5'/H5''). ESMS: Calc. C<sub>29</sub>H<sub>21</sub>N<sub>6</sub> (MH<sup>+</sup>) 453.1828, Found 453.2196.
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- Selected data for **10**: orange powder, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 11.08 (2H, br s, NH); 8.60 (4H, br d, H6''); 8.37 (4H, br d, H3''); 8.07 (4H, s, H2,3,5,6); 7.75 (4H, br t, H4''); 7.20 (4H, br d, H5'). ESMS: Calc. C<sub>32</sub>H<sub>23</sub>N<sub>8</sub> (MH<sup>+</sup>) 519.2046, Found 519.2036.
- Selected data for **11**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.72 (2H, d, J = 5 Hz, H6''); 8.61 (2H, d, J = 8 Hz, H3''); 8.52 (2H, d, J = 8 Hz, H5'); 8.24 (2H, d, J = 8 Hz, H3'); 7.97 (2H, t, J = 8 Hz, H4'); 7.93 (2H, t, J = 8 Hz, H4''); 7.38 (2H, dd, J = 8, 5 Hz, H5''). ESMS: Calc. C<sub>24</sub>H<sub>15</sub>N<sub>6</sub>S<sub>2</sub> (MH<sup>+</sup>) 451.0800, Found 451.1549.
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- Selected data for **12**: yellow powder, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.86 (2H, d, J = 5 Hz, H6'); 8.40 (2H, d, J = 8 Hz, H3'); 8.09 (2H, s, H3,6); 7.94 (2H, t, J = 8 Hz, H4'); 7.50 (2H, dd, J = 8, 5 Hz, H5'). ESMS: Calc. C<sub>18</sub>H<sub>11</sub>N<sub>4</sub>O<sub>2</sub> (MH<sup>+</sup>) 315.0882, Found 315.1482.
- The binuclear bis(2,2'-bipyridine)ruthenium(II) complex of this ligand does not show any observable metal-metal interaction, based on cyclic voltammetric electrochemical measurement

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