

## A Family of Immobilizable Chiral Bis(pinenebipyridine) Ligands

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Dedicated to Prof. Alex von Zelewsky for his 77<sup>th</sup> birthday

**Abstract:** New enantiopure ligands containing two (–)-5,6-pinenebipyridine units connected by a bridge situated in position 6' of the bipyridines have been prepared. The chemically addressable groups of the bridging (hydroxyl or keto) can be covalently bound to various supports in order to heterogenize the ligand.

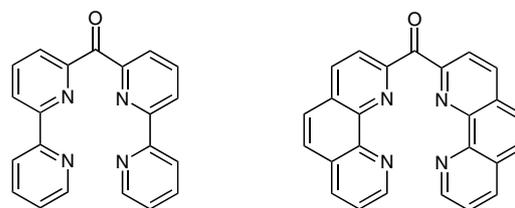
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Since the first report on 4,5- and 5,6-pinenebipyridine building blocks<sup>1</sup> 20 years ago, the enantiopure, pinene-containing oligopyridines and their derivatives have undergone an impetuous development.<sup>2</sup> The chiral pool used for the syntheses is  $\alpha$ -pinene, which has the rather unusual advantage of existing in nature in both enantiomeric forms. These ligands form with various d or f metal ions mono- and polynuclear complexes including self-assembled, supramolecular structures (i.e., helicates,<sup>3</sup> cages<sup>4</sup>). The ligand chirality predetermines the chirality of the metal centers ( $\Lambda$  or  $\Delta$ )<sup>5</sup> and of the helical assembly (P or M), leading to enantiopure compounds with interesting physicochemical properties<sup>6</sup> [light emission,<sup>7</sup> structural (stereo)dynamics,<sup>8</sup> chiral recognition,<sup>9</sup> etc.]. However, one of the most important applications is their use as enantioselective catalysts<sup>10</sup> for a wide range of chemical transformations: (ep)oxidation,<sup>11</sup> cyclopropanation,<sup>12</sup> allylic substitution,<sup>13</sup> hydrogenation,<sup>14</sup> trimethylsilylcyana- tion,<sup>15</sup> and allylation<sup>9b</sup> of benzaldehydes, as well as addition of diethylzinc to benzaldehyde.<sup>16</sup>

Herein, we describe the synthesis of a pinene-type bisbipyridine platform having as backbone bis(2,2'-bipyrid-6'-yl)ketone (**L1**).

In fact **L1**<sup>17</sup>, and its phenanthroline homologue **L2**<sup>18</sup> (Figure 1), as well as some of their derivatives,<sup>19</sup> have attracted considerable interest in the past few years. They have been shown to have an excellent ability to form complexes with structural distortions from the ideal octahedral geometry, high reactivity, and thus an improved catalytic

activity.<sup>19</sup> Moreover, **L1** with Cu<sup>II</sup> ions forms coordination polymers with the largest identifiable oligomer of 47 units.<sup>20</sup> One can therefore assume that **L3**, **L4**, and **L5** can (self)assemble with metal cations yielding enantiopure structures or MOF's having different possible applications, including catalysis.



bis(2,2'-bipyrid-6'-yl) ketone (**L1**) bis(1,10-phenanthrolin-2-yl) ketone (**L2**)

**Figure 1** Keto-bridged nonchiral bisbipyridine ligands

Another very important feature of these frameworks is the presence of a chemically 'addressable' linkable spacer (ketone, alcohol) between the bipyridine units. Ongoing projects in our group involve covalent attachment of these ligands to magnetic nanoparticles. Due to the high surface-to-volume ratio of such nano supports, the catalyst is expected to preserve an activity close to the homogeneous state while at the same time being recoverable as a heterogeneous one, simply by applying an external magnetic field.<sup>21</sup>

The best synthetic strategy for the keto-bridged ligand **L4** consists of seven synthetic steps (Scheme 1) and involves two new intermediates (**4** and **6**).

Monolithiation of 2,6-dibromopyridine as starting material was carried out according to a known procedure using BuLi and dichloromethane as a solvent, which was found to give a better selectivity<sup>22</sup> in comparison with THF or diethyl ether. Protection of the resulting 2-acetyl-6-bromopyridine (**1**) and subsequent carbonyl-bridge formation, as well as deprotection of **3** to yield triketone **5** were achieved according to established methods.<sup>23</sup> Kröhnke annulation<sup>24</sup> was used for the formation of the pinene-containing pyridine rings. The yield of this step, starting from **5** as a substrate, was very low and the required workup and purification procedures were very tedious. Hence, a

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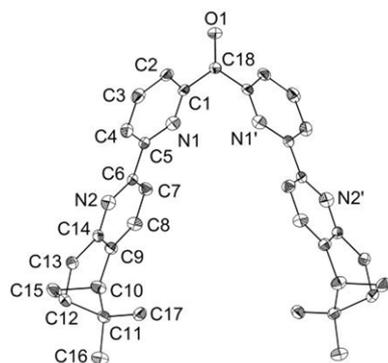
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An alternative pathway for the preparation of the key intermediate **6** is by protecting the sterically hindered diaryl keto group of **3** either with 2-chloroethanol in the presence of a weak base, or with ethylene glycol in acidic media.<sup>26</sup> Subsequently the sterically less hindered dioxolane rings protecting the acetyl groups of **4** were selectively hydrolyzed using mild acidic conditions, yielding the desired intermediate **6**. Kröhnke annulation using this substrate was found to give bisbipyridine ligand **L3** in good yields with no detectable side products. The keto-bridged bisbipyridine **L4** was obtained quantitatively by refluxing **L3** in concentrated hydrochloric acid. The reduction of **L4** to the corresponding alcohol **L5** has been achieved in quantitative yield by using NaBH<sub>4</sub>.

The molecular structures of compounds **2–4** and **7** as well as of new compounds **L3** and **L4** (Figure 2), were confirmed by single-crystal X-ray diffraction (see experimental part and Supporting Information). In most cases the protective dioxolane groups are disordered with the methylene carbon atoms localized in two different positions with approximately equal probability. The usual *trans* conformation of the bipyridine rings is observed.



**Figure 2** ORTEP representation (30% probability) and atom numbering scheme for **L4** (hydrogen atoms omitted for clarity)

Preliminary results show that ligand **L4** can be covalently attached to amino-functionalized magnetite nanoparticles while ligand **L5** can be linked, via a Williamson-type reaction, to alkyl halide functionalized magnetite nanoparticles. Such enantiopure ligands that can be immobilized on nano supports open new perspectives for ‘greener’ enantioselective processes in which very specific catalysts can be recovered and reused.<sup>27</sup>

Compounds **3**, **5**,<sup>23</sup> and **7**<sup>26</sup> were prepared using literature procedures. Crystals suitable for single-crystal X-ray diffraction were obtained by cooling sat. Et<sub>2</sub>O solutions for **2–4**, or by slow evaporation of solvent from CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O solutions for **7**, **L3**, and **L4**. <sup>13</sup>C NMR spectra are given in the Supporting Information. Crystallographic data for compounds **2–4**, **7**, **L3**, and **L4** have been deposited at the Cambridge Crystallography Data Centre, with CCDC numbers 949803–949808.

#### Synthesis of Compound 2

To a solution of 2,6-dibromopyridine (26.53 g, 112 mmol) in anhyd CH<sub>2</sub>Cl<sub>2</sub> (400 mL) *n*-BuLi in hexane (70 mL, 1.6 M, 112 mmol) was

added dropwise (1 h) at –78 °C. Stirring was continued at –78 °C for one more hour and then *N,N*-dimethylacetamide (10.41 mL, 9.75 g, 112 mmol) was slowly added. The temperature was kept at –78 °C for 30 min and then allowed to warm up to –50 °C, after which H<sub>2</sub>O (20 mL) was added, and the mixture was left under stirring overnight. H<sub>2</sub>O (300 mL) was added, and the organic layer was separated. The aqueous phase was further extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL), the organic extracts dried were over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed. The resulting dark brown oil was refluxed with ethylene glycol (50 mL) and TsOH·H<sub>2</sub>O (2.5 g, 13.1 mmol) in benzene using a Dean–Stark trap for 24 h, after which the mixture was poured into sat. Na<sub>2</sub>CO<sub>3</sub> solution. The organic layer was separated, and the aqueous phase was extracted with toluene (3 × 50 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated, and the dark brown oil obtained was distilled (100 °C, 10<sup>–3</sup> mbar). Colorless crystals of compound **2** were obtained upon cooling an Et<sub>2</sub>O solution; yield 22.2 g (81.2%). The compound was identified by its <sup>1</sup>H NMR spectrum.<sup>23</sup>

#### Synthesis of Compound 4

Compound **3** (8.5 g, 23.8 mmol), ethylene glycol (238 mmol), and H<sub>2</sub>SO<sub>4</sub> (0.5 mL) were refluxed in benzene using a Dean–Stark trap for 1 week after which 10% Na<sub>2</sub>CO<sub>3</sub> solution was added, and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Removing the solvent from the previously dried (MgSO<sub>4</sub>) solution gave a pale yellow solid, which was thoroughly washed with Et<sub>2</sub>O yielding a colorless solid; yield 8.1 g (84.8%)

Anal. Calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>: C, 62.99; H, 6.04; N, 7.00. Found: C, 63.0; H, 6.4; N 6.6; MS (ESI<sup>+</sup>): *m/z* (%) = 401.1 (100) [M + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.56 (s, 6 H, H9), 3.90 (m, 8 H, H10,11), 4.18 (s, 4 H, H10), 7.41 (dd, 2 H, H4, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz), 7.70 (m, 4 H, H2,3).

#### Synthesis of Compound 6

Compound **4** (0.74 g, 1.8 mmol) was stirred in a mixture of acetone (20 mL) and 1 M HCl (20 mL) for 24 h. A sat. Na<sub>2</sub>CO<sub>3</sub> solution (50 mL) was added to the reaction mixture, and the resulting solution was extracted with Et<sub>2</sub>O (3 × 50 mL). The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated to obtain compound **6** as yellow-orange oil; yield 0.58 g (100%).

Anal. Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.2; H, 5.3; N 8.9; MS (ESI<sup>+</sup>): *m/z* (%) = 313.0 (100) [M + H]<sup>+</sup>, 335.0 (12) [M + Na]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.56 (s, 6 H, H9), 4.27 (s, 4 H, H7), 7.96 (m, 6 H, H2,3,4).

#### Synthesis of Ligand L3

Compound **6** (1.88 g, 6 mmol) and I<sub>2</sub> (3.05 g, 12.0 mmol) were refluxed in pyridine (10 mL) for 5 h under inert atmosphere. The mixture was cooled, and the pyridine was evaporated under reduced pressure. NH<sub>4</sub>OAc (18 g, 233.5 mmol) and AcOH (12 mL) were added to this brown solid, and the resulting suspension was heated (100 °C) under stirring for 30 min and then allowed to cool down (50 °C). Subsequently, pinocarvone (2.19 g, 14.5 mmol) was injected, and the reaction flask was heated at 100 °C and stirred at this temperature for 12 h under inert atmosphere. The resulting solution was basified (pH 10) using a 4 M KOH solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 × 50 mL). After drying over Na<sub>2</sub>SO<sub>4</sub>, removal of CH<sub>2</sub>Cl<sub>2</sub> gave a brown solid, which was washed with MeOH, eluted through a short column using Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub> (1:1), and finally washed with acetone to yield the **L3** as a colorless solid; yield 2.17 g (63%).

Anal. Calcd for C<sub>37</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>: C, 77.87; H, 6.71; N, 9.82. Found: C, 78.1; H, 7.0; N 9.6; MS (ESI<sup>+</sup>): *m/z* (%) = 286.2 (100) [M + 2H]<sup>2+</sup>, 571.2 (17) [M + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.62 (s, 6 H, H16), 1.26 (d, 2 H, H15a, <sup>3</sup>J<sub>HH</sub> = 9.4 Hz), 1.39 (s, 6 H, H17), 2.36 (m, 2 H, H12), 2.66 (m, 2 H, H15b), 2.75 (t, 2 H, H10, <sup>3</sup>J<sub>HH</sub> = 5.6 Hz), 3.14 (s, 4 H, H13), 4.26 [s, 4 H, –O(CH<sub>2</sub>)<sub>2</sub>O–], 7.20 (2 H, H8, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 7.81 (m, 4 H, H2,3), 7.95 (d, 2 H, H7, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 8.30 (dd, 2 H, H4, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.9 Hz).

**Synthesis of Ligand L4**

**L3** (0.42 g, 0.74 mmol) was refluxed in HCl (32%, 10 mL) for 3 h and then basified to pH 10 with NaOH (4 M in H<sub>2</sub>O) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). Drying over Na<sub>2</sub>SO<sub>4</sub> and removal of CH<sub>2</sub>Cl<sub>2</sub> yielded almost quantitatively **L4** as a pale brown solid.

Anal. Calcd for C<sub>35</sub>H<sub>34</sub>N<sub>4</sub>O: C, 79.82; H, 6.51; N, 10.64. Found: C, 79.5; H, 6.8; N 10.4. MS (ESI<sup>+</sup>): *m/z* (%) = 527.2 (100) [M + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.66 (s, 6 H, H16), 1.30 (d, 2 H, H15a, <sup>3</sup>J<sub>HH</sub> = 9.5 Hz), 1.41 (s, 6 H, H17), 2.40 (m, 2 H, H12), 2.69 (m, 2 H, H15b), 2.78 (t, 2 H, H10, <sup>3</sup>J<sub>HH</sub> = 5.6 Hz), 3.18 (s, 4 H, H13), 7.22 (2 H, H8, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 8.00 (m, 4 H, H3,7), 8.10 (dd, 2 H, H2, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz), 8.61 (dd, 2 H, H4, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz).

**Synthesis of Ligand L5**

**L4** (0.40 g, 0.76 mmol) was suspended in EtOH (25 mL), and NaBH<sub>4</sub> (0.06 g, 1.6 mmol) was added under stirring to the resulting suspension. Stirring was continued for 1 h after which H<sub>2</sub>O (25 mL) and CH<sub>2</sub>Cl<sub>2</sub> (25 mL) were added. The organic layer was separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 20 mL). After drying the combined extracts over Na<sub>2</sub>SO<sub>4</sub>, removal of CH<sub>2</sub>Cl<sub>2</sub> yielded almost quantitatively **L5** as a colorless solid.

Anal. Calcd for C<sub>35</sub>H<sub>36</sub>N<sub>4</sub>O: C, 79.51; H, 6.86; N, 10.60. Found: C, 79.2; H, 6.9; N 10.5; MS (ESI<sup>+</sup>): *m/z* (%) = 265.2 (100) [M + 2H]<sup>2+</sup>, 529.2 (19) [M + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.69 (s, 6 H, H16), 1.31 (d, 2 H, H15a, <sup>3</sup>J<sub>HH</sub> = 9.6 Hz), 1.43 (s, 6 H, H17), 2.40 (m, 2 H, H12), 2.72 (m, 2 H, H15b), 2.83 (t, 2 H, H10, <sup>3</sup>J<sub>HH</sub> = 5.6 Hz), 3.18 (s, 4 H, H13), 6.03 (s, 1 H, H18), 6.13 (OH), 7.37d (2 H, H8, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 7.56 (d, 2 H, H2, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 7.74 (t, 2 H, H7, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 8.19 (d, 2 H, H7, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 8.29 (d, 2 H, H4, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz).

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**Supporting Information** for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synlett>.

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