

0040-4039(95)02146-9

## Synthesis of a Ligand Imposing Tetrahedral Coordination Based on 1,10-Phenanthroline

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**Abstract:** Synthesis of a ligand imposing tetrahedral coordination: 1,10-phenanthroline-2,9-bis(phenyl-2-acetic acid) is prepared via palladium catalysed cross-coupling of an aromatic halide and an ortho-substituted aryl stannane.

Ligands that impose a defined geometric donor array may result in the selective binding of certain metal cations. Zinc (II) unlike nickel (II), copper (II) and iron (III) has a complete  $d^{10}$  electronic configuration, hence there are no CFSE effects and it is not subject to any preferred binding geometry, while the other metals mentioned are subject to this effect and have preferred binding geometries (octahedral/square planar, square planar and octahedral respectively). A tetrahedral donor set may coordinate to zinc in preference to nickel (II), copper (II) and iron (III), i.e. against the Irving-Williams sequence<sup>1</sup>. Once zinc selectivity has been achieved the ligand may be used in the selective hydrometallurgic recovery of zinc<sup>2</sup>. Such tetrahedral binding may be imposed by an  $L_2X_2$  donor set (Fig. 1). Using a rigid  $L_2$  backbone (e.g. 1,10-phenanthroline) the possibility of other coordinating geometries is minimized. Both neocuproine and substituted 2,9-diphenyl-1,10-phenanthrolines have been shown to bind copper (I)<sup>3</sup> and other metals<sup>4</sup> (zinc and silver) in a tetrahedral manner. With this in mind, the target ligand **1** has been synthesised. The phenyl rings prefer to be perpendicular to the phenanthroline moiety allowing the carboxylate donors to bind from either side of the  $N_2$  plane.

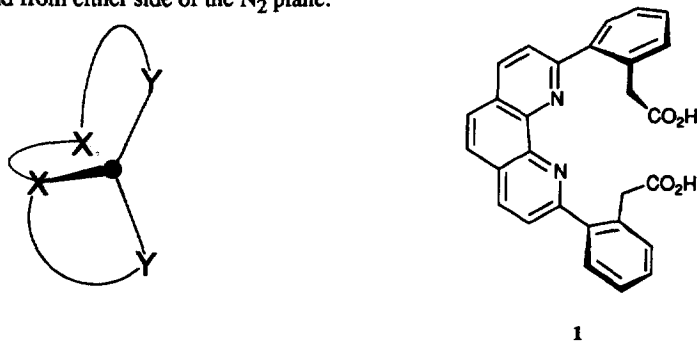
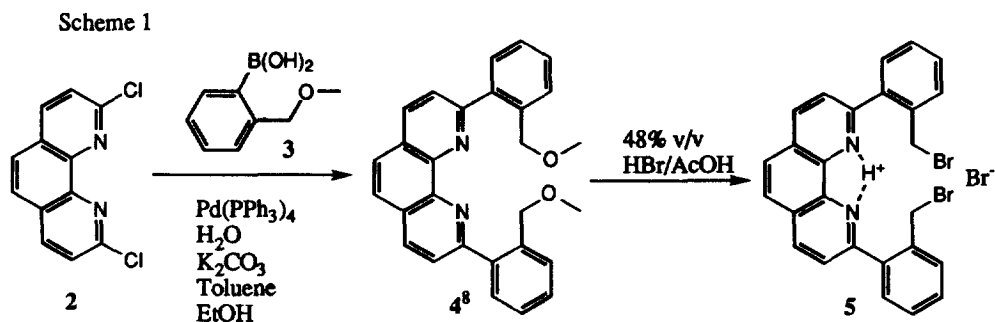
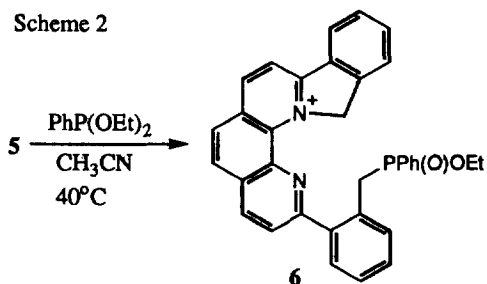


Figure 1. Diagrammatic representation of  $L_2X_2$  binding geometry.

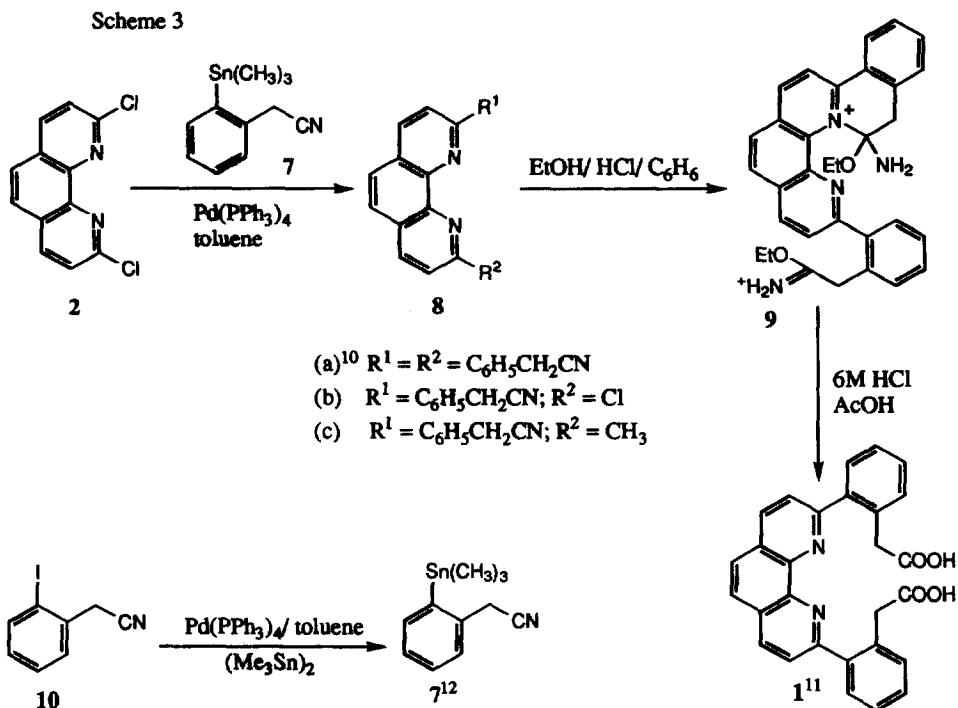
Following the patent literature<sup>5</sup>, (Scheme 1), a Suzuki cross coupling reaction between 2,9-dichloro-1,10-phenanthroline<sup>6</sup> **2** and (2-methoxymethylphenyl)boronic acid<sup>7</sup> **3** gave the required benzylic ether **4** in a higher yield than previously reported (82% against 47%).



Treatment of 4 with a solution of 48% v/v HBr/acetic acid at room temperature resulted in both demethylation and benzylic bromination. The product 5 was isolated as the protonated salt by precipitation into ether. Reaction with nucleophiles (e.g.  $\text{CN}^-$  and  $\text{PhP}(\text{OEt})_2$ ) only resulted in mono-addition with intramolecular cyclization always occurring at the other benzylic site, to yield a cationic N-alkylated product (e.g. 6, MS  $m/z = 525$ ) (Scheme 2).



An alternative route (Scheme 3) involves palladium catalysed cross coupling<sup>9</sup>. 2-(Trimethylstannyl)-benzeneacetonitrile 7 was prepared from iodophenylacetonitrile 10 and hexamethylditin in toluene using tetrakis(triphenylphosphine) palladium (0) as the catalyst. The stannane 7 was purified by column chromatography on silica (86% yield) and coupled to 2,9-dichloro-1,10-phenanthroline 2 using the palladium catalyst in toluene. Together with the desired product 8a (20%), 2-(2-methylnitrilephenyl)-9-chloro-1,10-phenanthroline 8b (35%) and 2-(2-methylnitrilephenyl)-9-methyl-1,10-phenanthroline 8c (10%) were isolated following silica chromatography. The cross-coupling reaction required a much longer reaction time (72h) than stannane formation. As well as aromatic transfer from the stannane intermediate a methyl group had also been transferred. These observations suggest that the second phenyl coupling was slower than the first addition. Direct hydrolysis of the dinitrile 8a with 6M HCl gave a mixture from which the desired product could not be isolated. Reaction of the dinitrile 8a with an excess of dry ethanol and HCl in benzene at 40°C precipitated the cyclic cationic imidate ester 9 (MS  $m/z = 504$ ). The imidate ester was hydrolysed with 50/50 v/v 6M HCl/acetic acid at 100°C to give the desired dicarboxylic acid 1.



Preliminary complexation studies (ESMS) indicated that a neutral ML complex was formed in an aqueous methanolic solution between the ligand 1 and divalent zinc or copper ions. Competitive 2:1 ligand/metal complex formation was observed (i.e. an N<sub>4</sub> donor set in the 2:1 complex). This pattern of behaviour was also observed with a proton NMR titration of the ligand with zinc. It can be concluded that the carboxylate donor is insufficiently avid for zinc binding and work is in progress to improve the affinity of the anionic donor for zinc.

#### ACKNOWLEDGMENTS

We thank EPSRC and Zeneca Specialities for support under the CASE scheme.

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8.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 3.37 (6H, s, CH<sub>3</sub>), 5.00 (4H, s, CH<sub>2</sub>), 7.46 (4H, m, phenyl Ar), 7.71 (4H, m, phenyl Ar), 7.79 (2H, s, phen H5 and H6), 7.91 (2H, d, phen H4 and H7), 8.29 (2H, d, phen H3 and H8);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 85.14 (CH<sub>3</sub>), 72.72 (CH<sub>2</sub>), 123.5, 126.1, 127.2, 127.3, 128.5, 128.6, 130.4, 136.3, 137.1, 139.9, 145.5, 160.0;  $m/z$  (DCI, NH<sub>3</sub>) 421 (M<sup>+</sup>+1);  $\nu_{\text{max}}$  (KBr disc)/cm<sup>-1</sup> 2918, 2868, 2820 (CH), 1477, 1089, 850, 771, 745. Found C, 77.63; H, 5.64; N, 6.76%. C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>·2/3(H<sub>2</sub>O) requires C, 77.76; H, 5.90; N, 6.86%.
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10.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 4.54 (4H, s, CH<sub>2</sub>), 7.26-7.50 (8H, m, phenyl-H), 7.90 (2H, s, phen H5 and H6), 7.91 (2H, d, phen H3 and H8), 8.42 (2H, d, phen H4 and H7);  $m/z$  (DCI, NH<sub>3</sub>) 411 (M<sup>+</sup>+1);  $\nu_{\text{max}}$  (KBr disc)/cm<sup>-1</sup> 3051, 2925 (CH), 2239 (CN), 1478, 1433, 857, 745; (DCI, accurate mass); found 411.1610 (M<sup>+</sup>+1) and calculated for C<sub>28</sub>H<sub>18</sub>N<sub>4</sub>+H<sup>+</sup> 411.1610.
11.  $\delta_{\text{H}}$  (CD<sub>3</sub>OD) 3.94 (4H, s, CH<sub>2</sub>), 7.54-7.64 (8H, m, phenyl-H), 8.24 (2H, d, H4 and H7), 8.31 (2H, s, H5 and H6), 8.95 (2H, d, H3 and H8);  $m/z$  (ESMS) 449 (M<sup>+</sup>+1);  $\nu_{\text{max}}$  (KBr disc)/cm<sup>-1</sup> 3422 (OH), 1718 (CO), 1186, 1120.
12.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 0.39 (9H, t, CH<sub>3</sub>, J = 27.4 Hz), 3.74 (2H, s, CH<sub>2</sub>), 7.36-7.48 (4H, m, Ar);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) -8.39 (CH<sub>3</sub>), 26.23 (CH<sub>2</sub>), 118.0 (CN), 127.4, 128.1, 129.3, 136.8, 141.8;  $m/z$  (EI<sup>+</sup>) 266 (M<sup>+</sup>+1-CH<sub>3</sub>), 236;  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 3055, 2980, 2913 (CH), 2249 (CN), 1416, 773, 752, 529.

(Received in UK 25 October 1995; revised 8 November 1995; accepted 10 November 1995)