

SUPPLEMENTARY MATERIAL BELONGING TO THE PAPER

Stereoselectivity in the formation of tris-diimine complexes of Fe(II), Ru(II), and Os(II) with a C_2 -symmetric chiral derivative of 2,2'-bipyridine

by

Dušan Drahoňovský, Ulrich Knof, Laurence Jungo, Thomas Belser, Antonia Neels, Gaël Charles Labat, Helen Stoeckli-Evans and Alex von Zelewsky

Synthetic procedure for the ligand (-)-L

(see Scheme 3)

1st part.

Butane-2,3-dione (**I**) (100 ml, 1.17 mol) was placed into a 500-ml flask, and bromine (37 ml, 0.68 mol) was added very slowly (about 30 minutes) from a dropping funnel. The mixture was stirred vigorously during the addition and kept the temperature over a range from 20°C to 30°C. A gentle stream of Argon was passed through the reaction mixture for next hour to remove HBr. The excess of butane-2,3-dione (**I**) was distilled off at 70°C under reduced pressure of a water pump. The remains were distilled at 115°C to give the 1-bromobutane-2,3-dione (**II**) (53.12 g, 47%) as a yellow oil.²⁴ The product (**II**) was used in the next step without further purification.

2nd part.

To a mixture of the product (**II**) (53.12 g, 0.32 mol) and water (200 ml) in a 500-ml flask, a hydroxylamine solution (24 ml, 50% H₂O sol., 0.41 mol) was added slowly from a dropping funnel. The mixture was stirred during the addition and kept the temperature at about 5°C (ice bath). The pH of the mixture was adapted (with sodium hydroxide solution) to be about 4, and the resulting mixture was allowed to stand for 30 minutes at room temperature. White precipitation was filtered off, dissolved in CH₂Cl₂, and the solution was dried over Na₂SO₄. The solvent was evaporated to give the product (**III**) (24.86 g, 44%) as a white powder.²⁴ This product (**III**) was used in the next step without further purification.

3rd part.

To a solution of pyridine (14 ml, 0.17 mol) in dry ether (200 ml), a solution of the 1-bromobutane-2,3-dione-3-oxime (**III**) (24.86 g, 0.14 mol) in dry ether (200 ml) was added slowly from a dropping funnel. The mixture was stirred during the addition and kept the temperature at about 5°C (ice bath). After 3 hours, a portion of pyridine (5 ml) was added, and the mixture was allowed to stand at room temperature for 2 days. Crystalline solid was filtered off and dried in Desiccator over CaCl₂ to yield the product (**IV**) (32.01 g, 88%) as a colourless hygroscopic crystals.⁵ The pyridinium salt (**IV**) was used in the next step without further purification.

4th part.

A mixture of the pyridinium salt (**IV**) (32 g, 0.123 mol), (-)-myrtenal (18.48 g, 0.123 mol), and dry ammonium acetate (9.5 g) in formamide (200 ml) was stirred at room temperature for 7 days. After, the mixture was diluted with water (100 ml), extracted with ether (5 x 70 ml), and collected organic phase was washed with water (3 x 50 ml) and dried over Na₂SO₄. The solvent was evaporated to give the crude product (**V**) (28.76 g, 98%) as a brown sticky stuff.⁵ This raw product (**V**) was used in the next step without further purification.

5th part.

The product (**V**) (28.76 g, 0.12 mol) was refluxed with HCl solution (30 ml, 37% H₂O sol.) for 8 hours. After, the mixture was allowed to cool to room temperature, neutralized with NaOH and Na₂CO₃ up to pH = 8, extracted with ether (5 x 70 ml), and collected organic phase was washed with water (3 x 50 ml) and dried over Na₂SO₄. The resulting solution was filtered through Silicagel-pad, the solvent was evaporated to yield the product (**VI**) (19.5 g, 75%) as a yellow oil.⁵ This product (**VI**) was used in the next step without further purification.

6th part.

To a boiling solution of the product (**VI**) (19.5 g, 90 mmol) in pyridine (21 ml), a solution of iodine (22.5 g, 90 mmol) in pyridine (70 ml) was added slowly from dropping funnel. After 3 hours, the mixture was allowed to cool to room temperature, and stored over night in the refrigerator. Crystalline solid was filtered off, washed with ether, and dried under vacuo to give the product (**VII**) (29.7 g, 78%) as a colourless hygroscopic crystals.⁵ This pyridinium salt (**VII**) was used in the next final step without further purification.

7th part.

A mixture of the pyridinium salt (**VII**) (29.7 g, 68.3 mmol), (-)-myrtenal (10.5 g, 68.3 mmol), and dry ammonium acetate (20 g) in formamide (500 ml) was stirred at room temperature for 7 days. After, the mixture was diluted with water (250 ml), extracted with hexane (10 x 50 ml), and collected organic phase was washed with water (2 x 50 ml) and dried over Na₂SO₄. The solvent was evaporated to give the raw product, which was crystallized from acetone to yield the pure product – ligand (-)-**L** (12 g, 51%) as a pale brown-yellow crystals. ¹H NMR (300.075 MHz, CDCl₃): 0.63 (s, 3H-12, *endo* CH₃), 1.23 (d, 1H-9, *endo* CH₂, *J* = 10.0 Hz), 1.42 (s, 3H-13, *exo* CH₃), 2.31 (m, 1H-8, CH), 2.70 (ddd, 1H-9, *exo* CH₂, *J* = 10.0 Hz, *J* = 5.7 Hz, *J* = 5.7 Hz), 2.85 (dd, 1H-10, CH, *J* = 5.7 Hz, *J* = 5.7 Hz), 3.04 (m, 2H-7, CH₂), 7.25 (s, 1H-3, aromatic CH), 8.12 (s, 1H-6, aromatic CH) in agreement with the literature.^{7, 8}