

PREPARATION OF 1,1,3,3-TETRAMETHYLCYCLOBUTANE-BRIDGED LIGANDS FOR THE STUDY OF ENERGY- AND ELECTRON- TRANSFER REACTIONS

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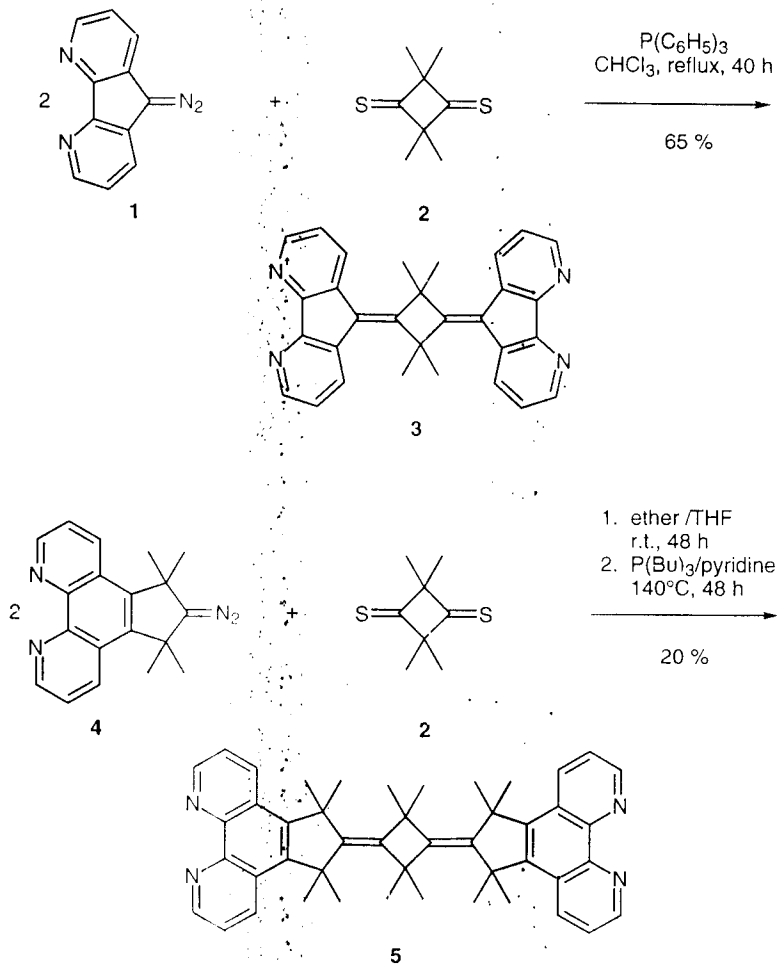
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ABSTRACT

The synthesis and characterisation of two new bis-chelating bridging ligands, with a 1,1,3,3-tetramethylcyclobutane spacer unit and two 4,5-diazafluorene or 1,10-phenanthroline chelating units respectively, are described.

Rigid rod-like bridging ligands are key substances for the study of photoinduced intramolecular energy- and electron-transfer processes in the field of supramolecular chemistry.¹⁻³ The light- and/or redox-active units are in many cases $[M(N\text{N})_3]^{n+}$, where M is a metal ion of the second or third transition row (in particular, Ru(II) and Os(II)) and N N is a bidentate bpy- or phen-type ligand (bpy : 2,2'-bipyridine, phen : 1,10-phenanthroline).⁴ Recent results indicate that long-lived charge transfer states can be achieved using rigid, adamantane-bridged bis-chelating ligands.⁵

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Scheme 1

We have designed two new bridging ligands **3** and **5** based either on two 4,5-diazafluorene or two 1,1,3,3-tetramethyl-1,3-dihydro-7,8-diaza-cyclopenta[1]-phenanthrene units respectively, connected by a 1,1,3,3-tetramethylcyclobutane spacer.

The bridging ligands are rigid and lead to binuclear complexes where the two metal-centers and the spacer lie in a plane. The synthetic routes are depicted

in Scheme 1. The synthesis of the 1,1,3,3-tetramethylcyclobutane moiety (**2**) was performed according to the method of Elam and Davis.⁶ The synthesis of the 4,5-diazafluorene- and the 1,1,3,3-tetramethyl-1,3-dihydro-7,8-diaza-cyclopenta-[1]phenanthrene diazo compounds have previously been described.⁷ The method for the preparation of the bridging ligand was a two-fold extrusion process described by Barton,⁸ specially developed for the preparation of sterically demanding olefines. The thioketone intermediate was condensed with **1** and **4** respectively, to the corresponding thiadiazoline, which was treated with phosphines to afford the desired bridging ligands **3** and **5**.

In conclusion, we have prepared two new bis-chelating bridging ligands, which are capable of forming rigid, rod-like, binuclear metal complexes.

EXPERIMENTAL

¹H-NMR (300 MHz) and ¹³C-NMR (75.4 MHz) spectra were recorded with a Varian Gemini 300 instrument using solvent as the internal standard. Chemical shifts are reported in ppm on the δ scale. Mass spectral data were obtained with a VG Instruments 7070E mass spectrometer equipped with a FAB inlet system. Elemental analysis were carried out by Mikrolabor, Ciba-Geigy, Marly. All reagents and solvents were commercial samples obtained Fluka Chemie AG or Aldrich chemical company and unless otherwise stated used as supplied.

Tetrametyl-1,3-cyclobutane-bis-4,5-diazafluorenylidene **3** :

To a 5 ml 2-necked pear shaped flask equipped with a magnetic stirring bar were added **1** (194 mg, 1.00 mmol), **2** (86 mg, 0.50 mmol) and Chloroform (4ml). The brown solution was heated at reflux for 15 h under an argon atmosphere. After

2 h a brown precipitation was observed. To the cooled brown suspension, triphenyl phosphine (350 mg, 1.33 mmol) was added. The reaction mixture was refluxed under argon atmosphere for a further 24 h. After cooling the suspension was filtered, washed with a small amount of CHCl_3 and the white solid dried in vacuum 143 mg (**3**, 0.33 mmol, 65%).

MS (FAB) : $m/z = 441 (M^+ + 1)$

$^1\text{H-NMR}$ (CDCl_3) : δ, J (Hz) = 2.17 (s, 12H), 7.39 (dd, 2H, $^3J=7.9$, $^3J=4.9$), 8.27 (d, 2H, $^3J=7.9$), 8.75 (d, 2H, $^3J=4.6$).

$^{13}\text{C-NMR}$ (CDCl_3) : $\delta = 24.6, 50.1, 122.6, 124.4, 130.9, 132.7, 149.5, 157.3, 167.5$.

Anal. calcd. for $\text{C}_{30}\text{H}_{24}\text{N}_4 \cdot 1/3 \text{H}_2\text{O}$ C, 80.69; H, 5.57; N, 12.55 Found : C, 80.63; H, 5.43; N, 12.42.

Tetramethyl-1,3-cyclobutane-bis-1,1,3,3-tetramethyl-1,3-dihydro-7,8-diazacyclopenta[1]phenanthren-2-ylidene 5 :

In a 10 ml 2-necked pear shaped flask equipped with a magnetic stirring bar and a septum **2** (86 mg, 0.5 mmol) was dissolved in dry diethyl ether (3 ml) under argon atmosphere. A solution of **4** (300 mg, 1.0 mmol) in dry THF was added through the septum. After a few minutes a white precipitate was formed. After 48 h 5 ml of diethyl ether was added to complete the precipitation of the thiadiazoline. The suspension was filtered, washed with additional ether (10 ml) and dried *in vacuo*. In a 10 ml pear shaped flask the white solid was suspended in anhyd. pyridine (5 ml) and tributyl phosphine (2.5 ml) and heated at 140°C for 48 h under an argon atmosphere. After cooling hexane (20 ml) was added to the white suspension. The mixture was filtered, washed with hexane (10 ml) and dried *in vacuo* to give a white solid 67 mg (**5**, 0.1 mmol, 20%).

MS (FAB) : $m/z = 657 (M^+ + 1)$

$^1\text{H-NMR}$ (CDCl_3) : δ, J (Hz) = 2.05 (s, 24H), 2.07 (s, 24H), 7.64 (dd, 2H, $^3\text{J}=8.5$, $^3\text{J}=4.4$), 8.68 (dd, 2H, $^3\text{J}=8.5$, $^4\text{J}=2.0$), 9.15 (dd, 2H, $^3\text{J}=4.4$, $^4\text{J}=2.0$).

$^{13}\text{C-NMR}$ (CDCl_3) : δ = 30.8, 32.9, 49.8, 52.9, 122.1, 124.4, 133.4, 134.0, 141.5, 148.4, 150.4, 151.6

Anal. calcd. for $\text{C}_{46}\text{H}_{48}\text{N}_4 \cdot 1/3 \text{H}_2\text{O}$ C, 83.35; H, 7.40; N, 8.45 Found : C, 83.33; H, 7.48; N, 8.30.

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