Synthesis of New Rigid, Bridging Ligands for the Study of Energy and Electron-Transfer Reactions

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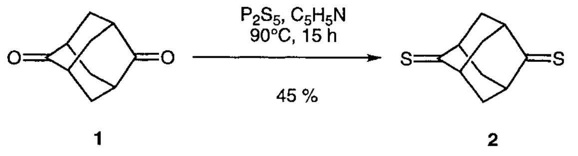
The synthesis and characterization of rigid, rod-like, bridging ligands with an adamantane spacer and two 4,5-diazafluorene, or 1,10-phenanthroline chelating units, respectively, are described.

Photoinduced energy and electron-transfer processes in supramolecular species[1-3] are currently the object of interest since they can be exploited for the construction of light-harvesting[4] devices, sensors, and charge separation devices.[5,6] The light- and/or redox-active units are in many cases M(N–N)$_3^{n+}$ complexes, where M is a metal ion of the second or third transition rows [in particular, Ru(II) and Os(II)] and N–N is a bidentate bpy- or phen-type ligand (bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline).[7] When the active units for the energy and electron-transfer process are metal complexes, the connectors or spacers have to be bridging ligands. An important point in the choice of the bridging ligands is their rigidity and the presence of a C_2-axis that allows the determination of the exact distance between the two metal centres.

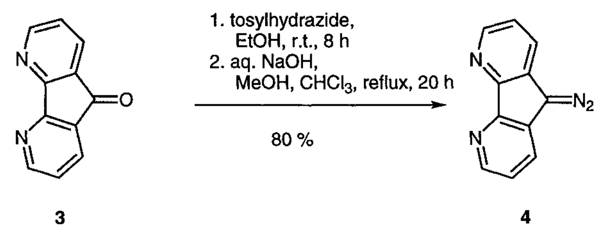
We have designed two new bis-chelating bridging ligands **11** and **12** based either on two 4,5-diazafluorene or two 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthrene units, respectively, connected by an adamantane spacer. These bridging ligands are rigid and lead to binuclear species where the two metals and the spacer lie in a row.

Here we report the preparation of the new bridging ligands. The synthetic routes are depicted in Schemes 1–4. The synthesis of the precursor adamantane spacer, adamantane-2,6-dithione (**2**), was performed according to the method of Greidanus[8] by treatment of adamantane-2,6-dione (**1**)[9] with P_2S_5/pyridine at 90 °C under an argon atmosphere (Scheme 1).



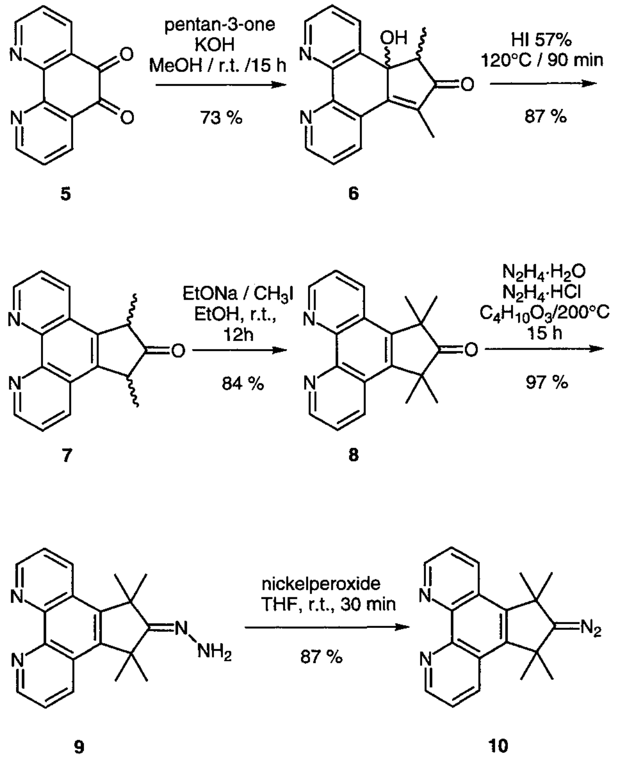
Scheme 1

9-Diazo-4,5-diazafluorene (**4**) was synthesized by treating the tosylhydrazone of 4,5-diazafluorenone (**3**)[10] with base at 70 °C in good yield[11] (Scheme 2).

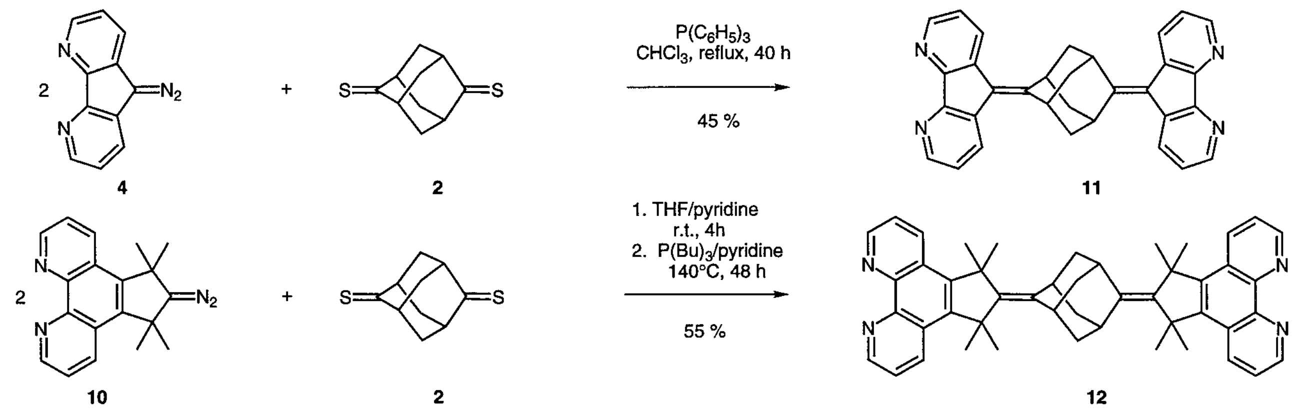


Scheme 2

The precursor 1,10-phenanthroline-5,6-dione (**5**) which was prepared according to the method of Yamada et al.[12] was condensed with pentan-3-one in a solution of KOH in methanol to give 1,11b-dihydro-11b-hydroxy-1,3-dimethyl-7,8-diazacyclopenta[1]phenanthren-2-one (**6**) as a white powder. Treatment of **6** with hydriodic acid at 120 °C yielded the ketone 1,3-dihydro-1,3-dimethyl-7,8-diazacyclopenta[1]phenanthren-2-one (**7**). Methylation of **7** in an ethanolic solution of NaOEt and methyl iodide at room temperature led to 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthrene-2-one (**8**). This was then transformed into the corresponding 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthrene-2-hydrazone (**9**). A mild oxidation of **9** with nickel peroxide gave final precursor **10** (Scheme 3).



Scheme 3



Scheme 4

The general method for the preparation of the bridging ligands was a twofold extrusion process described by Guziec[13] and Barton,[14] especially developed for the preparation of sterically hindered alkanes. Adamantane-2,6-dithione (**2**) was condensed with **4** and **10**, respectively, to the corresponding intermediate thiadiazolines which were then treated with triphenylphospine and tributylphosphine to afford the desired bridging ligands **11** and **12** in good yields (Scheme 4).

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

^{1}H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded on a Varian-Gemini 300 instrument by using the proton resonances resulting from the incomplete deuteration of the NMR solvent as internal standard. Mass spectral data were obtained using a VG Instruments 7070E mass spectrometer equipped with a FAB inlet system. Elemental analyses were carried out by the Mikrolabor, Ciba-Geigy, Marly. Compounds **1**–**12** gave satisfactory elemental analyses (C,H,N,S ± 0.5 % from the theoretical value, including 0.33 water molecule per diimine units).

All reagents and solvents were commercial samples and used as supplied unless otherwise stated.

Adamantane-2,6-dithione (2):

To a 25 mL 2-necked round-bottom flask equipped with a magnetic stirring bar were added adamantane-2,6-dione (**1**; 0.525 g, 3.20 mmol) and anhyd pyridine (10 mL, water content < 0.05 %). Under an Ar atmosphere P_2S_5 (0.356 g, 1.6 mmol) was added in portions (30 min) at 90 °C. The mixture was stirred vigorously for 15 h at this temperature; the initially yellow mixture changed to orange during this process. After cooling to r.t. the mixture was added to hexane (100 mL), the hexane layer was washed with water (3 x 100 mL), 2 N HCl (3 x 100 mL) and again twice with water (100 mL). After drying ($MgSO_4$) the solvent was removed in vacuo to give 0.535 g of crude **2**. The orange solid was purified by sublimation (1 mbar, 120 °C) to give pure **2** as orange crystals; yield: 0.282 g (45 %).

MS (EI, 70 eV): $m/z = 196 (M^+), 163 (M^+ - SH), 129 (M^+ - 2SH)$.

^{1}H NMR ($CDCl_3$): $\delta = 2.32$–2.38 (m, 8 H), 3.48–3.55 (m, 4 H).

^{13}C NMR ($CDCl_3$): $\delta = 43.1$ (CH_2), 55.4 (CH), 263.8 (C=S).

9-Diazo-4,5-diazafluorene (4):

Tosylhydrazide (2.00 g, 10.73 mmol) and 4,5-diazafluorenone (**3**; 1.00 g, 5.49 mmol) were dissolved in anhyd EtOH (100 mL) and stirred for 8 h at r.t. The resulting yellow suspension was filtered and washed with a small amount of EtOH. The solid was dissolved in a mixture of $CHCl_3$ (200 mL), MeOH (200 mL) and 2 M NaOH (100 mL). The mixture was refluxed for 20 h. The organic layer was separated, washed with water (100 mL), dried ($MgSO_4$), treated with charcoal and filtered. The reddish brown solution was concentrated by distillation to give a brown solid; yield: 0.85 g (80 %).

The compound is not stable and should be used within few days after its preparation.

MS (EI, 70 eV): $m/z = 194 (M^+), 166 (M^+ - N_2)$.

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 7.36 (dd, 2 H, $^3J = 8.0$, $^3J = 4.7$), 7.88 (dd, 2 H, $^3J = 8.0$, $^4J = 1.4$), 8.68 (dd, 2 H, $^3J = 4.7$, $^4J = 1.4$).

1,11b-Dihydro-11b-hydroxy-1,3-dimethyl-7,8-diazacyclopenta[l]-phenanthren-2-one (6):

In a 50 mL round-bottom flask equipped with a magnetic stirring bar were placed 1,10-phenanthroline-5,6-dione (**5**; 2.0 g, 9.5 mmol), pentan-3-one (1.5 mL, 14 mmol) and anhyd MeOH (10 mL). To this yellow suspension a solution of KOH (170 mg), in anhyd MeOH (10 mL) was added. Without heating, the suspension was then left to stir for 15 h in the dark. The green-yellow suspension was filtered and washed with a minimal amount of Et_2O/CH_2Cl_2 (1:1). The crude product was dissolved in $CHCl_3$ (200 mL) and the resulting green suspension filtered through Celite. The solvent from the filtrate was removed in vacuo to give a white powder; yield: 1.92 g (73 %).

MS (EI, 70 eV): $m/z = 278 (M^+)$.

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 1.57 (d, 3 H, $^3J = 7.4$), 2.06 (s, 3 H), 3.02 (q, 1 H, $^3J = 7.4$), 7.36–7.41 (m, 2 H), 7.82 (d, 1 H, $^3J = 7.8$), 8.01 (d, 1 H, $^3J = 6.8$), 8.70 (d, 1 H, $^3J = 5.0$), 8.76 (d, 1 H, $^3J = 4.7$).

1,3-Dihydro-1,3-dimethyl-7,8-diazacyclopenta[l]phenanthren-2-one (7):

Into a 250 mL round-bottom flask equipped with a magnetic stirring bar were placed **6** (5.20 g, 18.7 mmol) and 57 % HI (90 mL). The dark brown solution was heated to 120 °C for 90 min. After cooling, water (160 mL) was added, the resulting suspension was filtered and washed with water. The brown solid was suspended in 10 % $NaHSO_3$ (100 mL) and refluxed for 30 min. The yellow suspension was cooled, filtered and washed with a small amount of 10 % $NaHSO_3$. The solid was suspended in H_2O/MeOH (1:1, 150 mL) and neutralized with $NaHCO_3$. The orange solution was extracted with CH_2Cl_2 (3 x 50 mL). The organic layer was washed with water and dried ($MgSO_4$). Filtration and removal of the solvent under vacuum gave a pale yellow solid yield: 4.27 g (87 %) (*cis*/*trans*-isomer).

MS (EI, 70 eV): $m/z = 262 (M^+)$.

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 1.59 and 1.63 (d, 6 H, $^3J = 7.5$ and 7.6), 3.91 and 3.99 (q, 2 H, $^3J = 7.5$ and 7.5), 7.60–7.69 (m, 2 H), 7.36–7.41 (m, 2 H), 8.20–8.30 (m, 2 H), 9.12–9.20 (m, 2 H).

1,3-Dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[l]phenanthren-2-one (8):

To a suspension of **7** (0.50 g, 1.91 mmol) and MeI (1.2 mL, 19.0 mmol) at r.t. was added a solution of NaOEt (0.32 g, 4.70 mmol, prepared from 0.110 g of Na) in EtOH (5 mL) during 15 min. The resulting dark-red solution was stirred at r.t. After 12 h the reaction was quenched with water (30 mL) and neutralized with 1 N HCl. The mixture was extracted with CH_2Cl_2 (3 x 20 mL), the organic layer washed with water and dried ($MgSO_4$). Filtration and removal of the solvent under vacuum gave crude **8**. This crude product was dissolved in conc. HCl and the resulting yellow solution was washed with CH_2Cl_2 (3 x 20 mL). The aqueous layer was neutralized with aq NaOH and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were dried ($MgSO_4$), treated with charcoal and filtered through Celite. The solvent was evaporated under vacuum to give **8** as a beige solid; yield: 4.63 g (84 %).

MS (EI, 70 eV): $m/z = 290$ (M^+).

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 1.68 (s, 12 H), 7.65 (dd, 2 H, $^3J = 8.4$, $^3J = 4.2$), 8.53 (dd, 2 H, $^3J = 8.4$, $^4J = 1.6$), 9.15 (dd, 2 H, $^3J = 4.2$, $^4J = 1.6$).

^{13}C NMR ($CDCl_3$): δ = 25.6, 50.4, 122.7, 125.2, 132.4, 138.8, 146.7, 149.6, 224.3.

1,3-Dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[l]phenanthrene-2-hydrazone (9):

To a 100 mL round-bottom flask equipped with a magnetic stirring bar were added **8** (2.00 g, 6.90 mmol), hydrazine hydrate 100 % (10 mL, 206 mmol), hydrazine hydrochloride (5 g, 73 mmol), anhyd Na_2SO_4 (10 g) and freshly distilled diethylene glycol (50 mL). The mixture was heated to 200 °C for 15 h under an Ar atmosphere. After cooling the mixture was diluted with water (200 mL) and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with water (3 x 100 mL), dried ($MgSO_4$) and evaporated to dryness on a rotary evaporator to give a yellow solid; yield: 2.02 g (97 %).

MS (EI, 70 eV): $m/z = 304$ (M^+).

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 1.74 (s, 6 H), 1.98 (s, 6 H), 7.60–7.65 (m, 2 H), 8.54 (dd, 1 H, $^3J = 8.5$, $^4J = 1.6$), 8.63 (dd, 1 H, $^3J = 8.5$, $^4J = 1.6$), 9.14–9.17 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 23.5, 29.2, 46.4, 48.7, 122.2, 122.5, 124.4, 125.1, 132.3, 132.8, 139.9, 140.3, 146.9, 147.2, 149.1, 149.3, 166.4.

2-Diazo-1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[l]-phenanthrene (10):

To a 25 mL round-bottom flask equipped with a magnetic stirring bar was added **9** (0.230 g, 0.76 mmol), finely powdered nickel peroxide hydrate (0.460 g) and anhyd THF (15 mL). The black suspension was left to stir for 45 min at r.t. and then filtered through Celite; the plug was washed with additional THF (15 mL) to ensure the complete elution of the diazo compound. The reddish-brown filtrate was concentrated by distillation on a rotary evaporator to give a brown solid; yield: 0.199 g (87 %).

The compound is not stable and should be used within a day after its preparation.

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 1.79 (s, 12 H), 7.61 (dd, 2 H, $^3J = 8.5$, $^3J = 4.3$), 8.53 (dd, 2 H, $^3J = 8.5$, $^4J = 1.6$), 9.15 (dd, 2 H, $^3J = 4.2$, $^4J = 1.6$).

Adamantane-2,6-bis(4,5-diazafluorenylidene) (11):

To a 5 mL 2-necked pear shaped flask equipped with a magnetic stirring bar were added **4** (194 mg, 1.00 mmol), **2** (98 mg, 0.50 mmol) and $CHCl_3$ (4 mL). The brown solution was refluxed for 15 h under an Ar atmosphere. After 2 h, a brown precipitation occured. To the cooled brown suspension, was added Ph_3P (350 mg, 1.33 mmol). The mixture was refluxed under an Ar atmosphere for another 24 h. After cooling the suspension was filtered, washed with a small amount of $CHCl_3$ and the white solid dried in vacuo; yield: 103 mg (45 %).

MS (FAB): $m/z = 465$ ($M^+ + 1$).

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 2.47 (s, 8 H), 4.16 (s, 4 H), 7.30 (dd, 2 H, $^3J = 8.0$, $^3J = 4.8$), 8.22 (dd, 2 H, $^3J = 8.0$, $^4J = 1.3$), 8.68 (dd, 2 H, $^3J = 4.8$, $^4J = 1.3$).

^{13}C NMR ($CDCl_3$): δ = 35.2, 41.1, 122.4, 122.6, 131.6, 133.2, 149.0, 156.9, 159.8.

2,6-Adamantanebis(1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[l]phenanthren)-2-ylidene (12):

In a 10 mL 2-necked pear shaped flask equipped with a magnetic stirring bar and a septum, compound **2** (60 mg, 0.31 mmol) was dissolved in anhyd THF (3 mL) under an Ar atmosphere. A solution of **10** (200 mg, 0.66 mmol) in anhyd pyridine was added through the septum. After a few min a white precipitate was formed. After 4 h, THF (5 mL) was added to complete the precipitation of the thiadiazoline. The suspension was filtered, washed with additional THF (10 mL) and dried in vacuo. In a 10 mL pear shaped flask the white solid was suspended in anhyd pyridine (5 mL) and Bu_3P (2.5 mL) and heated to 140 °C for 48 h under an Ar 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; yield: 115 mg (55 %).

MS (FAB): $m/z = 681$ ($M^+ + 1$).

^{1}H NMR ($CDCl_3$): δ, J (Hz) = 1.92 (s, 24 H), 2.17 (s, 8 H), 3.45 (s, 4 H), 7.63 (dd, 2 H, $^3J = 8.5$, $^3J = 4.3$), 8.53 (dd, 2 H, $^3J = 8.5$, $^4J = 1.6$), 9.15 (dd, 2 H, $^3J = 4.3$, $^4J = 1.6$).

^{13}C NMR ($CDCl_3$): δ = 29.3, 33.4, 39.9, 48.5, 122.1, 124.7, 133.2, 139.0, 141.8, 147.2, 148.6, 150.5.

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