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The Preparation of Rigidly-Linked 4,5-Diazafluorenes: New Molrac Bidentate Ligand Systems

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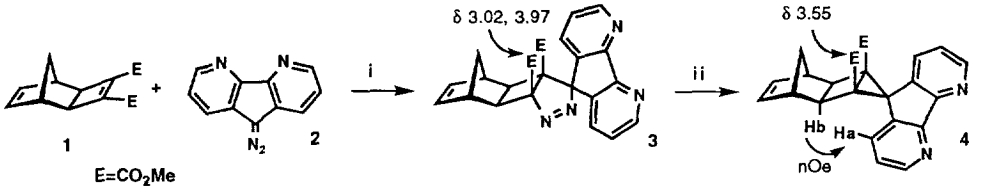
Abstract: New rigid molracs have been prepared in which terminal positions are occupied by spiro-fused 4,5-diazafluorene ligand. This is achieved *via* a thermally-induced (or high pressure) 1,3-dipolar cycloaddition of 9-diazo-4,5-diazafluorene onto the π-bond of the molrac followed by thermal (or photochemical) ejection of dinitrogen from the intermediate pyrazoline; norbornadiene alone gives a rearranged product **22** upon deazetisation.

Metal complexes formed from ligands fused to rigid scaffolds have been identified as a prerequisite for studies seeking to establish the geometric parameters of electron and energy transfer.[1] While dipyridyl pyridazine (dpp) complexes of rigid systems have been reported,[2] the fact that (mono) transition metal complexes of dpp do not retain their symmetry makes them less attractive than those involving more conventional bidentate ligands like bipyridyl (bipy), phenanthroline (phen) or diazafluorene (daf), especially where more than one ligand centre is present in the molecule. Bipy and phen ligands linked to donor/acceptor centres have been reported where the linker has been flexible.[1,3] Diad[2] and triad systems[4] based on molrac frameworks have found application in energy transfer studies, but none have incorporated bidentate ligands. In this communication we report on a simple method for producing molrac systems incorporating the daf ligating species. The orthogonal linking of daf to the molrac offers complementary geometric alignments to the coplanar geometry of dpp[5] and phen[6] ligands.



1 E=CO_2Me 2 3 4

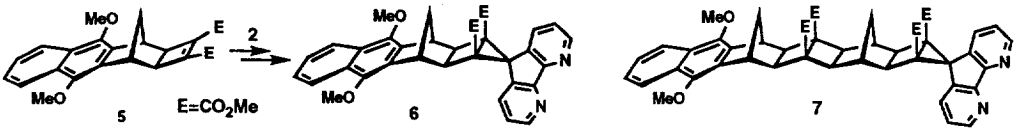
i) ambient temperature and pressure (2 weeks) or 14 kbar (3 days) ii) 110°C or photochemical (λ= 300 nm)

Scheme 1

We elected to exploit the 1,3-dipolar properties of 9-diazo-4,5-diazafluorene (DADAF) **2** for attachment of the ligand component to π-centres of the molrac, following our earlier work on the reaction of simple diazoalkanes with alicyclic olefins, eg **1**.[7] Several 9-diazofluorenes and 9-diazodiazafluorenes have been reported and their photochemistry studied in detail,[8] yet little attention has been paid to DADAF **2** where the nitrogen atoms are positioned in the α,δ-relationship required for bidentate ligation. It has been reported that

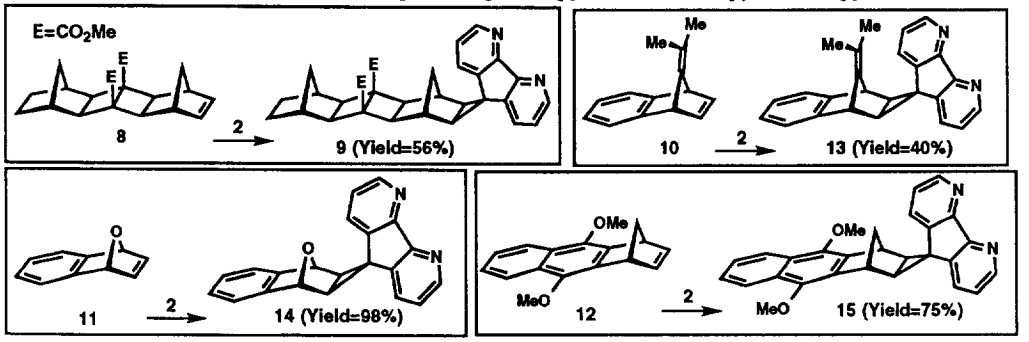
DADAF **2** reacts with olefins under photochemical conditions to form cyclopropanes, but such reactions are only efficient when the intermediate carbene can be trapped using excess olefin, often as reagent and solvent.[10] This was inappropriate for our synthetic requirements as most substrates are solids.

DADAF **2** was reacted with Smith's diene **1**[9] in benzene to assess its 1,3-dipolar reactivity and π-bond preference. ^{1}H NMR spectroscopy supported initial formation of 1:1-adduct **3** (unsymmetrical; distinct ester methyl resonances differentially shielded by the daf ring-current)[10] which was thermolysed *in situ* (toluene at reflux) to produce the symmetrical spiro diazafluorene (DAF) ligand **4** (m.p. 207-208 °C (dec.); yield 88%).[10] The presence of the olefinic resonances in the ^{1}H nmr spectrum of **3** and **4** supports exclusive reaction having occurred at the cyclobutene π-bond and the nOe observed between aromatic proton Ha and the methine protons Hb in **4** confirms the stereochemistry. Further addition of DADAF **2** to the norbornene π-bond of **4** was unsuccessful even under more forcing conditions. Reaction of **1** with **2** was also conducted under high pressure conditions (14kbar, ambient temperature, 3:1 CH_2Cl_2:hexane, 72 h) to produce the pyrazoline **3** (m.p. 115-125 °C (dec.); >90% yield); conversion to **4** could be achieved by ultraviolet irradiation (λ=300 nm; ~100% yield) in benzene or chloroform solution or thermally (above).



Scheme 2

Reaction of the known cyclobutene diester **5**[11] with DADAF **2** (Scheme 2) produced a single symmetrical product **6** (m.p. 236-236.5 °C (dec.); yield 72%)[8] following thermolysis of the addition product. The structure of **6** has been confirmed by X-ray crystal structure analysis (Fig 1).[12] This reaction is general and more extended spacer ligand/donors can been produced, eg formation of **7** (m.p. 294-295 °C (dec.); 67% yield).[12] These compounds form metal complexes, eg $[Ru(bpy)_2(\mathbf{6}\text{ or }\mathbf{7})]^{2+}$ (bpy = 2,2'-bipyridine).[13]

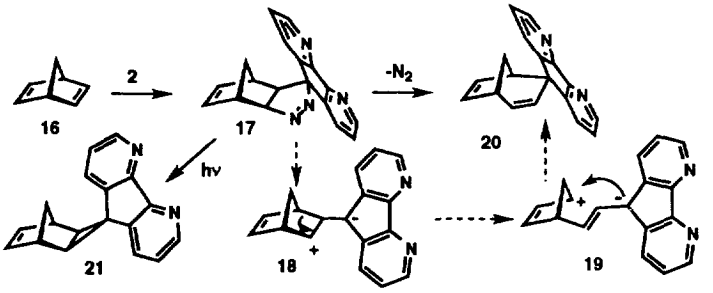


Scheme 3

DADAF **2** reacts with molrac **8**[11] to produce **9**, confirming that reaction can occur with some molrac norbornene end-groups (Scheme 3), although it is necessary to use excess DADAF **2** and to add it batchwise. Benzonorbornenes, however, are quite reactive towards DADAF **2** and that allows ready access to ligands **13-15**[10] by reaction with the appropriate benzonorbornene **10-12** and ejection of dinitrogen.

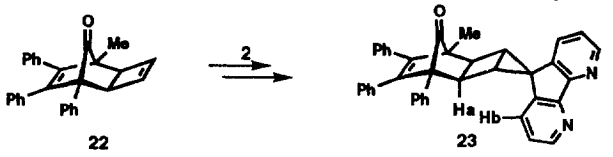
Norbornadiene **16** reacts with DADAF **2** to form a 1:1-adduct **17** which undergoes rearrangement in the thermal deazetisation step to form the spiroligand **20**[10] containing the bicyclo[3.2.1.]octadiene ring-structure.

There is precedent[14] for this rearrangement which can be mechanistically rationalised as proceeding through dipolar intermediates **18** and **19**. In contrast, photolysis of pyrazoline **17** yields the cyclopropane **21**.



Scheme 4

The ring-strain of unsubstituted cyclobutenes also makes them candidates for cycloaddition and DADAF has been shown to react inefficiently with fused cyclobutene **22**[15] to produce the DAF product **23** (m.p. 262-3 °C (dec.); 57 % yield based on recovered **22**). The stereochemistry of **23** is supported by an nOe between Ha (and its partner) on the molrac underface and Hb on the DAF heterocycle.



Scheme 5

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10. All new compounds were fully characterised by spectroscopic techniques (^{1}H NMR, ^{13}C NMR, IR, MS) and their molecular formulae established by microanalysis or high resolution mass spectrometry. Following are representative. **3:** ^{1}H NMR (300MHz, $CDCl_3$) δ 8.84 (dd; *J*=1.4, 4.8 Hz; 1H), 8.72 (dd; *J*=1.4, 4.8 Hz; 1H), 7.84 (dd; *J*=1.4, 8.1 Hz; 1H), 7.62 (dd; *J*=1.4, 8.1 Hz; 1H), 7.35 (dd; *J*=4.8, 8.1 Hz;1H), 7.23 (dd; *J*=4.8, 8.1 Hz; 1H), 6.12 (d; *J*=3.2 Hz,1H), 6.07 (d; *J*=3.2 Hz, 1H), 3.97 (s; 3H), 3.75 (s; 1H), 3.02 (s; 3H), 2.72 (s; 1H), 2.43 (d; *J*=6.8 Hz, 1H), 2.32 (d; *J*=6.8 Hz; 1H), 1.75 (d; *J*=10.1 Hz; 1H), 1.38 (d; *J*=10.1 Hz; 1H). **4:** 8.76 (dd; *J*=1.4, 4.8 Hz; 1H), 8.69 (dd; *J*=1.4, 4.8 Hz; 1H), 7.92 (dd; *J*=1.4, 8.1 Hz; 1H), 7.90 (dd; *J*=1.4, 8.1 Hz; 1H), 7.24 (dd; *J*=4.8, 8.1 Hz; 1H), 7.21 (dd; *J*=4.8, 8.1 Hz; 1H), 6.30 (brt ; *J*=1.8 Hz; 2H), 3.60 (s; 6H), 3.02 (brs; 2H), 2.79 (s; 2H), 2.50 (d; *J*=9.9 Hz; 1H), 1.55 (d; *J*=9.9 Hz; 1H). MS (*m/z*, EI): 400 (M^+), 334, 281. **6:** 8.70-8.74 (m; 2H), 8.15 (dd; *J*=3.2, 6.5 Hz; 2H), 7.93 (dd; *J*=1.4, 8.1 Hz; 1H), 7.61 (dd; *J*=1.2, 8.1 Hz; 1H), 7.51 (dd; *J*=3.2, 6.5 Hz; 2H), 7.25 (dd; *J*=4.8, 8.1 Hz; 1H), 7.10 (dd; *J*=4.8, 8.1 Hz; 1H), 4.00 (s; 6H), 3.66 (s; 6H), 3.94 (s; 2H), 3.12 (d; *J*=10.5 Hz; 1H), 3.11 (s; 2H), 2.02 (d; *J*=10.5 Hz; 1H). ^{13}C NMR (75MHz, $CDCl_3$) δ 166.0, 159.8, 157.2, 150.0, 149.9, 145.3, 136.5, 134.8, 133.7, 132.5, 132.0, 128.4, 125.8, 122.4, 122.3, 62.2, 52.3, 47.3, 45.5, 43.8, 41.6, 41.3. **7:** yield: 67%; m.p. 294-295°C **9:** yield: 56%; m.p. 234-6°C. ^{1}H NMR (300MHz, $CDCl_3$) δ 8.66 (brs; 1H), 8.64 (brs; 1H), 7.96 (dd; *J*=1.2, 8.2 Hz; 1H), 7.30 (dd; *J*=1.5, 7.9 Hz; 1H), 7.21 (dd; *J*=4.7, 8.2 Hz; 1H), 7.17 (dd; *J*=4.7, 7.9 Hz; 1H), 3.74 (s; 6H), 2.78 (s; 2H), 2.71 (s; 2H), 2.49 (s; 2H), 2.20 (brs; 2H), 2.12 (d; *J*=10.8 Hz; 1H), 2.06 (s; 2H), 1.90 (s; 2H), 1.53 (brd; *J*=7.4 Hz; 2H), 1.20-1.16 (m; 3H). **13:** yield: 40%; m.p. 240-1°C. ^{1}H NMR (300MHz, $CDCl_3$) δ 8.64 (dd; *J*=1.4, 4.7 Hz; 1H), 8.61 (dd; *J*=1.8, 4.4 Hz; 1H); 8.01 (dd; *J*=1.4, 8.0 Hz; 1H), 7.27 (dd; *J*=3.1, 5.2 Hz; 2H), 7.05-7.15 (m; 5H); 4.20 (s; 2H), 2.25 (s; 2H), 1.71 (s; 6H). **14:** yield: 98%; m.p. 298-300°C. **15:** yield: 75%; m.p. 256-9°C. ^{1}H NMR (300MHz, $CDCl_3$) δ 8.73 (dd; JJ=1.2, 4.7 Hz; 1H), 8.65 (dd; *J*=1.4, 4.6 Hz; 1H), 8.14 (dd; *J*=1.2, 8.1 Hz; 1H), 8.13 (dd; *J*=3.3, 6.3 Hz; 2H), 7.52 (dd; *J*=3.3, 6.3 Hz; 2H), 7.29 (dd; *J*=4.7, 8.1 Hz; 1H), 7.24 (dd; *J*=1.4, 7.9 Hz; 1H), 7.17 (dd; *J*=4.6, 7.9 Hz; 1H), 4.29 (s; 2H), 4.06 (s; 6H), 2.81 (d; *J*=10.3 Hz; 1H), 2.35 (s; 2H), 1.88 (d; *J*=10.3 Hz; 1H). **20:** yield: 89%; m.p. 143-6°C. ^{13}C NMR (75MHz, $CDCl_3$) δ 157.6, 157.5, 149.9, 149.7, 145.7, 144.0, 142.3, 137.0, 133.3, 133.0, 131.9, 126.6, 122.7, 122.1, 50.3, 47.9, 41.7, 38.4. MS (*m/z*, EI): 258 (M^+), 193, 180. **24:** 8.83 (dd; *J*=1.3, 4.8 Hz; 1H), 8.70 (dd; *J*=1.6, 4.5 Hz; 1H) 7.96 (dd; *J*=1.3, 7.9 Hz; 1H), 7.36 (dd; *J*=4.8, 7.9 Hz; 1H), 7.25-7.30 (m; 2H), 6.76-7.30 (m; 15H), 3.73 (dd; *J*=2.0, 4.5 Hz; 1H), 3.19 (dd; *J*=2.0, 4.5 Hz; 1H), 2.81 (dd; *J*=2.0, 4.2 Hz; 1H), 2.76 (dd; *J*=2.0, 4.2 Hz; 1H), 1.44 (s; 3H). MS (*m/z*, EI): 540 (M^+), 512, 373, 168.

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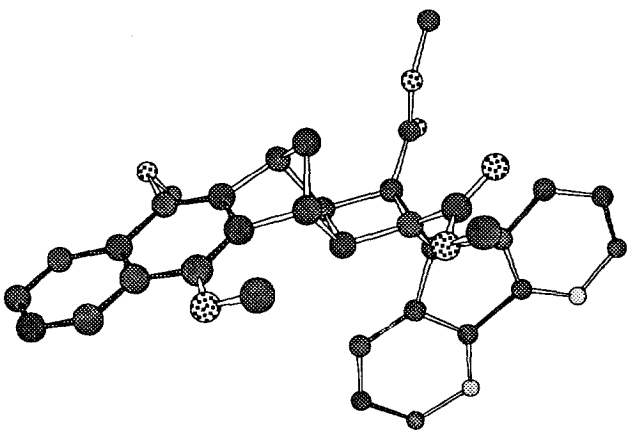

Fig 1. X-Ray structure of spiroligated molrac **6**

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