Preparation of 7,8-diazaphencyclone and its use in the construction of rigid, space-separated 1,10-phenanthroline donor–acceptor systems: new ligands for metal complexation

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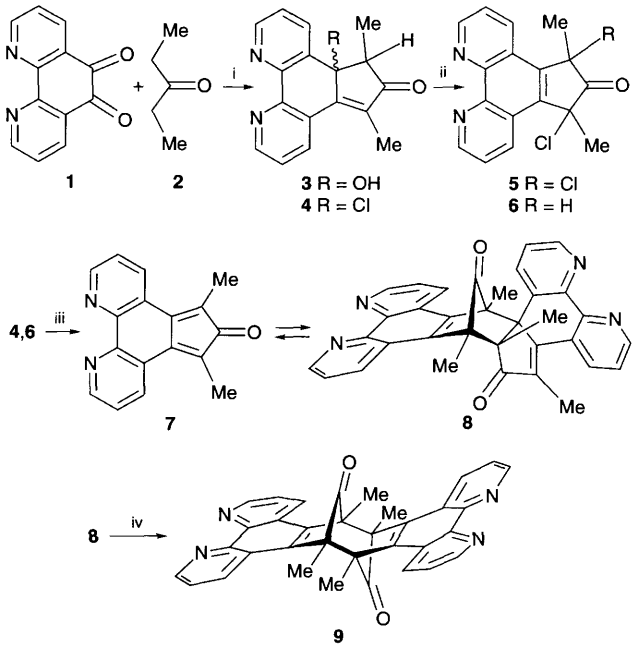
7,8-Diazaphencyclone 7 is used as a delivery reagent to fuse 1,10-phenanthroline groups onto alkenic centres of rigid spacer molecular racks (molracs); molrac alkenes containing redox-active donor–acceptor chromophores yield molrac diads whose metal complexes, *e.g.* 26, are suitable for mechanistic studies involving intramolecular electron transfer.

Polypyridyl ligands have a special role in modern studies of the properties of metal complexes, especially those related to electron transfer.[1] Previous work on intramolecular quenching processes within metal complexes containing such ligands has generally involved flexible spacers between the ligating entities and the redox-active groups.[2] Using rigid molecular racks (molracs) as spacers[3] between the ligand and the redox-functionality provides the means for a detailed assessment of spatial influences on intramolecular electron transfer.

The previously unknown 7,8-diazaphencyclone (DAPC) **7**, prepared in dimeric form **8** as outlined in Scheme 1, is used as the delivery reagent for attaching the 1,10-phenanthroline unit to the rigid molrac.

The availability of **7** as a diene was established by generating it *in situ* from its dimer **8** (but not **9**) by heating in the presence of Smith's diene **10**[4] where exclusive formation of the 1 : 1 adduct **11**‡ was observed to occur (Scheme 2). The presence of an alkenic resonance in the ^{1}H NMR of **11** at δ 6.13 showed that reaction had occurred site selectivity at the cyclobutene π centre and the stereochemistry followed from the upfield position of the ester methyl resonances which occur at δ 3.14 as a result of their proximity to the ring-current of the phenanthroline.



Scheme 1 *Reagents and conditions*: i, K_2CO_3 in MeOH, room temp., 24 h; ii, $SOCl_2$/pyridine (1 : 1); iii, NEt_3; iv, 100 °C

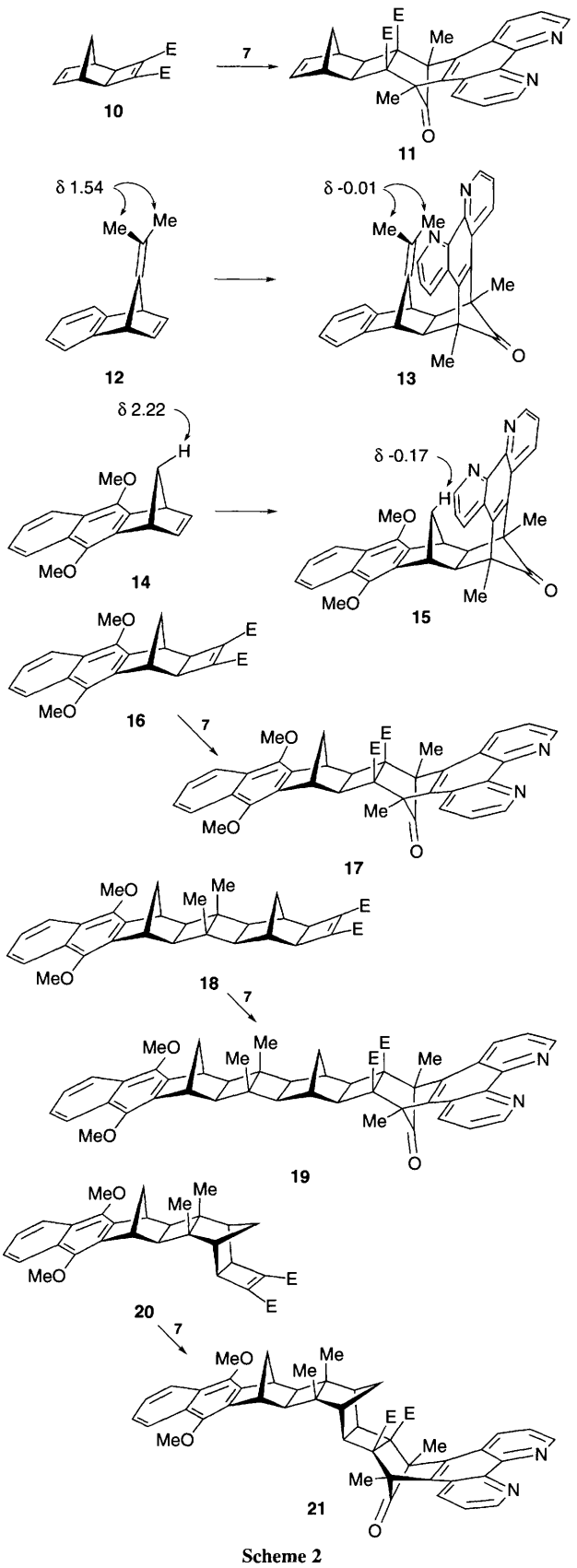
The ability of 7,8-diazaphencyclone **7** to react with benzonorbornene π-bonds was exploited in the conversion of the benzonorbornadiene **12** to the ligand **13** and of **14** to the phenanthroline **15**. The *exo,endo*-stereochemistry of these adducts is immediately apparent from the dramatic upfield shift of the isopropylidene methyl resonances (δ −0.01) in **13** and the *syn*-related bridge methylene proton (δ −0.17) in **15**.

Further members in the series of space-separated 1,10-phenanthrolines containing the dimethoxynaphthalene chromophore, *e.g.* **17**, **19** and **21** were prepared in 48–75% yields by reaction of 6,7-diazaphencyclone **7** with the corresponding molrac cyclobutenes **16**,[5] **18**[5] and **20**.[5] Spectral characteristics (^{1}H, ^{13}C NMR, *m/z*) support these structural assignments. In particular, the upfield chemical shifts of the ester methyl resonances (δ 3.22, 3.08 and 3.10 respectively) confirm the proximity of the phenanthroline ring to the ester groups in each system.

Incorporation of a naphthoquinone group can also be achieved using this reaction protocol (Scheme 3). Thus, the known quinone **22**[6] was reacted with DMAD/Ru^0 under the Mitsudo conditions[7] to produce the cyclobutene diester **23**, which was treated with 7,8-diazaphencyclone **7** to form the pale yellow 1 : 1 cycloadduct **24** in 63% yield. ^{1}H NMR data confirmed that cycloaddition had occurred at the cyclobutene preferentially to the quinone.

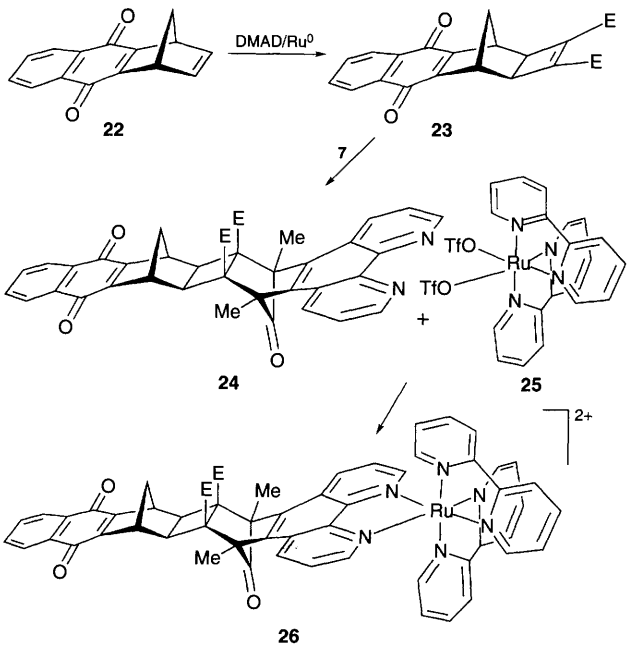
The complex [Ru(bpy)$_2$(**24**)]$^{2+}$ (**26**; bpy = 2,2′-bipyridine) was synthesised in 92% yield using an established route *via* the [Ru(bpy)$_2$(CF$_3$SO$_3$)$_2$] precursor **25**.[8] The structure of complex **26** is supported by electronic‡ and ^{1}H NMR spectroscopy (CD_3CN) where 26 non-equivalent proton resonances occur in the aromatic region due to the spatial interrelationship of the three bidentate ligands. Formation of **26** involves displacement of the triflato groups from the complex **25** (C_2 point group symmetry) by the phenanthroline ligand **24** (C_s symmetry), which yields a single product as there are no orientational consequences for its attachment. However, because of the disposition of the bipyridine rings, **24** loses its σ-plane on coordination, accounting for non-equivalence of the two halves of the phenanthroline entity and its attached components (*e.g.* the *C*-methyl substituents show separate singlets at δ 2.04 and 2.06; ester *O*-methyls at δ 3.11 and 3.36).

Cyclic voltammetric studies of **26**, {MeCN/0.1 mol dm^{-3} [$(C_4H_9)_4N$]ClO_4 solution; Pt working electrode} show two reversible redox couples, one at $E_{1/2}$ = +1045 mV (*vs.* Ag/Ag$^+$)



Scheme 2

associated with the metal centre ($Ru^{III/II}$) and the other at $E_{1/2}$ = −915 mV assigned as the first reduction of the quinone moiety ($Q^{0/1-}$). All further reductive events were totally irreversible, with characteristically sharp desorption peaks upon re-oxidation.



Scheme 3

Complex **26** does not luminesce at room temperature, presumably because of internal quenching following photo-excitation at the metal centre.

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Footnotes

† All new compounds have been characterised by spectroscopic techniques (^{1}H NMR, ^{13}C NMR) and molecular formula established by microanalysis or mass spectrometry; representative yields and mps for **7**: 50% yield; mp >350 °C. For **11**: 57% yield; mp 250–252 °C. For **13**: 83% yield; mp 273–275 °C (decomp.). For **24**: mp 198–200 °C.

‡ UV–VIS (MeCN) for **26** [λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})]: 450 (MLCT) (13500); 434(sh), (12200); 276 (59700); 252 (55100) and 194 (83400).

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