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# A $(bpy)_2Ru$-coordinated dehydro[12]annulene with exotopically fused diimine binding sites†

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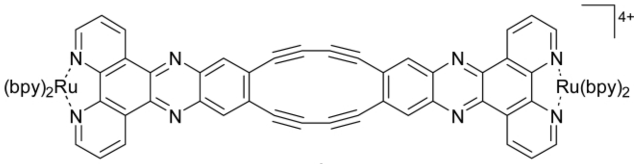
**Synthesis and electronic properties of a dinuclear $(bpy)_2Ru^{II}$ polypyridyl complex are described in which the bridging ligand consists of two dipyridophenazines fused to a formally anti-aromatic dehydro[12]annulene and where the electronic and electrochemical properties of the complex are markedly influenced by the cyclic all-carbon core.**

The linearity and rigidity of acetylene moieties render them attractive inter-connectors for polypyridine metal binding sites, as these features allow excellent control over the distance and hence over the interaction between coordinated metal centres.[1] In addition, by virtue of their extensive π-orbital network, acetylene substituents on polypyridine ligands contribute to metal-to-ligand interactions and offer additional through-bond communication pathways.[2] In recognition of these properties, poly(phenyl)acetylenes have been widely used for the construction of linear rod-like polypyridine scaffolds.[1,2] In contrast, cyclic acetylene structures of the dehydroannulene type have been less well explored as inter-connectors for diimine binding sites, although the first examples have emerged over the last five years.[3–5] The acetylenic cores of these prototypes, however, are neither rigorously rigid nor planar and hence fail to maximise possible metal-to-ligand and metal–metal interactions. We therefore set out to explore a dipyridophenazine-fused dehydro[12]annulene as a scaffold for coordinating metal fragments as we envisioned that the formally antiaromatic electron count of the cyclic core could facilitate additional charge transfer processes. The planarity of the targeted novel ligand system is ensured by obvious rotational restrictions and has been demonstrated crystallographically for more simple dibenzodehydro[12]annulene systems.[6,7] We report here the synthesis and an initial investigation of the electronic properties of the dinuclear Ru(II) complex **1**, the first representative of this class of compounds.

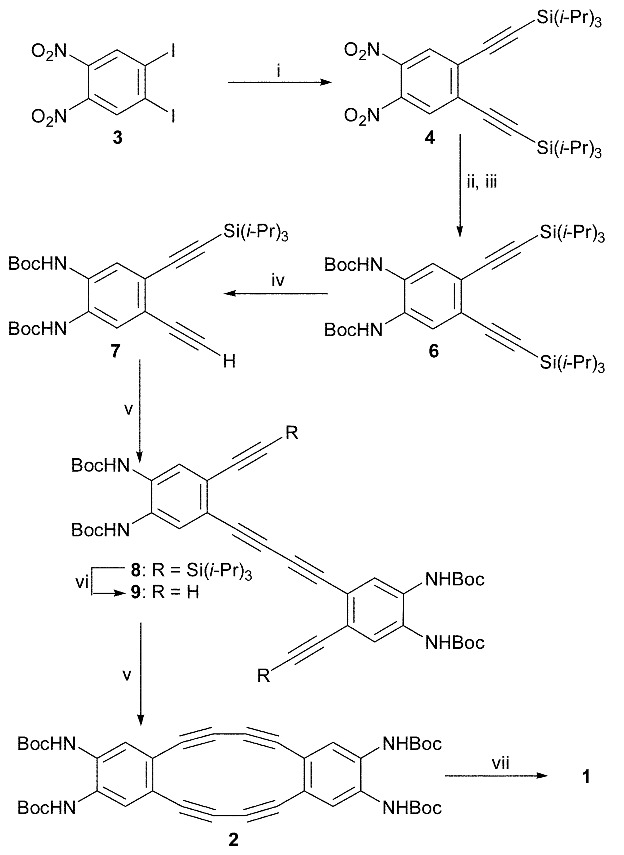



**1** $(PF_6^-)_4$

Our previous experience in the construction of ruthenium complexes with acetylenic polyimine ligands, and our difficulties in separating dehydroannulenes with varying ring sizes,[8] prompted us to pursue a synthetic approach in which dehydroannulene formation precedes metal complexation. Hence we designed the tetra-Boc-protected tetraaminodibenzooctadehydro[12]annulene **2** (Scheme 1) as a key building block. Compound **2** offers the advantage that both amine-deprotection and the subsequent implementation of the diimine binding site onto the core of **2** through condensation of the intermediate tetraamine with suitably functionalised [1,10]phenanthroline-5,6-diones are both acid-catalysed and can therefore be conducted in a single operation. Furthermore, the voluminous protecting groups in **2** should aid in avoiding solubility problems that are often encountered in the construction of large planar systems.[5,9]

1,2-Diethynyl-4,5-dinitrobenzene **4** was prepared from diiodoarene **3**[10] under cross-coupling conditions developed by Sonogashira *et al.* (Scheme 1).[11] Reduction of **4** with tin in HCl–ethanol produced the unstable diamine **5** which was immediately Boc-protected to furnish **6**. The stepwise, controlled assembly of **2** was rendered possible by a desymmetrisation of **6**, achieved under kinetic control with TBAF in THF. *Inter*molecular oxidative acetylene homocoupling of **7** furnished butadiyne **8** in 80% yield. Formation of **2** was concluded by a second, exhaustive proto-desilylation to afford **9** and by its subsequent cyclisation *via intra*molecular oxidative acetylene coupling.‡

The functionalised benzodehydroannulene **2** was isolated as a yellow, hygroscopic solid that, due to extensive aggregation, was




**Scheme 1** *Reagents and conditions*: i, $(^iPr)_3SiC\equiv CH$, $[Pd(PPh_3)_2Cl_2]$ (5 mol%), CuI (2 mol%), $Et_3N$, 80 °C, 3 h, 70%; ii, Sn, HCl (conc.)–EtOH, 70 °C, 15 min, 57%; iii, $Boc_2O$, $(^iPr)_2EtN$, THF, 3 d, Δ, 94%; iv, $Bu_4NF$, THF, 0 °C, 30 min, 50% (73% based on recovered starting material); v, $Cu(OAc)_2$, CuCl, pyridine, MeOH, 60 °C, 4 h, 80% for **8**, 72% for **2**; vi, $Bu_4NF$, THF, rt, 90 min, 96%; vii, **10**, TFA, $CH_3CN$, 70 °C, 24 h, 21%.

† Electronic supplementary information (ESI) available: Analytical data for the ruthenium complexes. See http://www.rsc.org/suppdata/cc/b3/b313788k/

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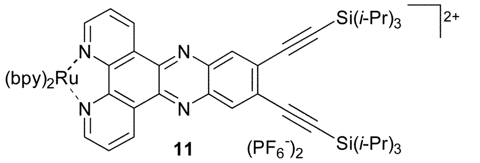
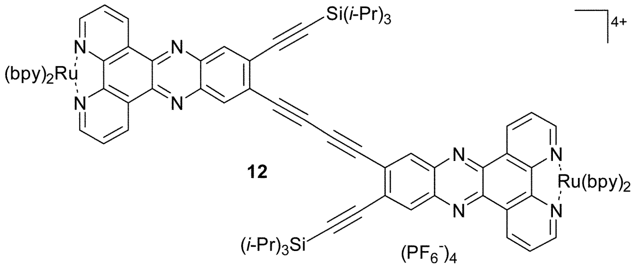
difficult to redissolve in common organic solvents. The $^1$H NMR spectrum of **2** reveals a single aryl-proton resonance at $\delta$ = 7.16, which is shifted to higher magnetic field strengths relative to the corresponding two signals of **8** (resonating at $\delta$ = 7.73 and $\delta$ = 7.67, respectively; all measurements in $CDCl_3$) due to the presence of the paratropic dehydroannulene core in the former compound. Subjecting **2** to a solution of $[(bpy)_2Ru(phenanthroline\text{-}5,6\text{-}dione)]^{2+}(PF_6^-)_2$ **10**[12] in acetonitrile in the presence of trifluoroacetic acid furnished the desired dinuclear $Ru^{II}$ complex **1** as a dark red hygroscopic solid in 21% yield.†

For an evaluation of the electrochemical and photophysical properties of **1**, the mono- and dinuclear $[(bpy)_2Ru^{II}(dipyridophenazine)]$ complexes **11** and **12** were prepared for comparison using methods similar to those depicted in Scheme 1.†




The electrochemical properties of **1**, **11** and **12** were investigated by cyclic voltammetry.† The redox potential of the $Ru^{II}/Ru^{III}$ couple at +1.25 V ($CH_3CN$, *vs.* SCE, $Fc^{+/0}$ at 0.31 V) and the reductions of the ancillary bpy-ligands (around −1.47 V) are largely invariant of the nature of the dipyridophenazine ligands in all three complexes. Differences occur, however, in the reduction potential directly associated with the acetylenic heterocycles. While the dipyridophenazine ligand in mononuclear **11** is reduced at −0.89 V, the first and second reductions of the dehydroannulene complex **1** occur more readily at −0.72 V and −0.87 V, respectively. The butadiynyl-linked dinuclear complex **12** also features two dipyridophenazine reductions, but at slightly more negative potentials (−0.79 V and −0.91 V). It is thus clear that the electron affinity of the dehydroannulene in **1** is significantly higher than that of non-cyclic alkynyl dipyridophenazines. In comparison, the reductions in **1** proceed at a potential similar to that required for the first reduction of fullerene $C_{60}$ ($CH_2Cl_2$, 1.02 V *vs.* $Fc^{+/0}$), which is known as a good electron acceptor.[13]

The UV/Vis absorption spectra of **1**, **11** and **12** are typical for $Ru^{II}$ polypyridine complexes in the sense that they are dominated by ligand-centred $\pi \rightarrow \pi^*$ transitions around 300 nm and by MLCT bands in the region beyond 400 nm (Fig. 1).[14] There are, however, remarkable differences between the spectrum of **1** and those of **11** and **12**. For example, the spectrum of **1** shows a distinct absorption maximum at 369 nm, which we assign to transitions located mainly on the quinoxalinodehydro[12]annulene subunit. In addition, the MLCT bands of **1** are bathochromically shifted relative to those of **11** and **12** and are split into two maxima at 433 and 459 nm, respectively, perhaps indicative of electronic interactions between the phenanthroline moieties and the dehydroannulene framework. Preliminary luminescence measurements show that the emission maximum of **1** at 772 nm is shifted bathochromically compared to that of **11** and **12** by 14 and 6 nm, respectively. The excited state lifetime of **1** is with 28 ns (at rt in $CH_3CN$) significantly shorter than that of the "linear" model complexes **11** (88 ns) and **12** (52 ns) suggesting that the intramolecular quenching process in **1** is accelerated by the presence of the bridging dehydroannulene. The nature of this process is the focus of ongoing investigations.

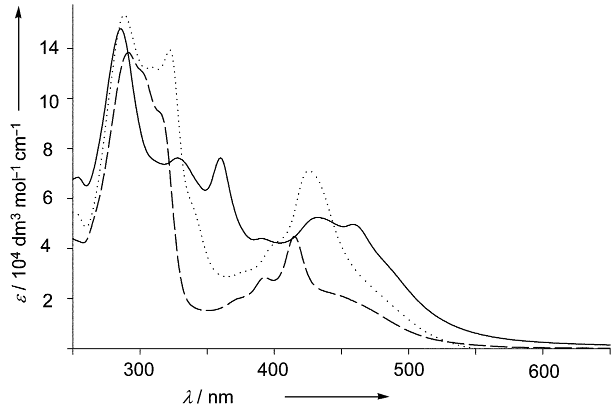



**Fig. 1** Electronic absorption spectra of **1** (—), **11** (**---**) and **12** (···) in acetonitrile at 25 °C.

In this work, we have described the synthesis of the dinuclear ruthenium complex of the first rigid dehydroannulene with exotopically-fused metal binding sites *via* an acid-catalysed one-pot deprotection–condensation sequence. The central all-carbon core is clearly reflected in the electronic and electrochemical properties of the novel complex, rendering it a good electron acceptor. Work is currently under way to further explore the synthetic potential of **2**, to chemically differentiate between the two coordination sites and to further elucidate the photophysical properties of **1**.

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## Notes and references

‡ All compounds have been fully characterised by $^1$H, $^{13}$C NMR, mass spectrometry and microanalysis.


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