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Stereospecific templated synthesis of a triruthenium butadiyne-linked cyclic porphyrin trimer

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A bis(ethynyl)-substituted porphyrin monomer of Ru(CO) has been prepared and oligomerised by Glaser–Hay coupling to give a cyclic butadiyne-linked trimer. Use of tri(4-pyridyl)triazine as template during the coupling ensured that only a single stereoisomer of the trimer was formed: all three CO groups are forced to be outside the cavity, leaving three potential ruthenium-binding sites facing into the cavity.

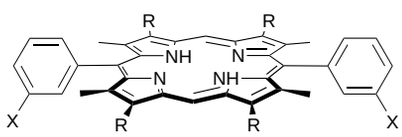
One of the key aims of supramolecular chemistry is to create enzyme mimics capable of recognition and catalysis. The first major milestone of our research in this area[1] was the controlled synthesis[2] of a butadiyne-linked cyclic Zn_3 trimer and related dimers and tetramers using templated Glaser–Hay coupling of preformed porphyrin (por) monomers [equation (1)]. This

$$\text{por}{-}C{\equiv}C{-}H + H{-}C{\equiv}C{-}\text{por} \longrightarrow \text{por}{-}C{\equiv}C{-}C{\equiv}C{-}\text{por} \quad (1)$$

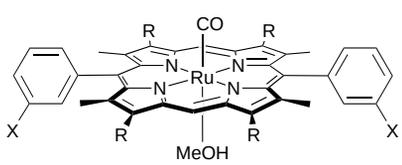
trimer has proved to be a versatile object for molecular recognition, binding a range of amine ligands,[3] stereoselectively accelerating an *exo*-Diels–Alder reaction,[4] and also catalysing acyl transfers.[5] However, it was an important part of our strategy that we should create a series of receptors using the same diarylporphyrin monomer **I** as a building block while exploring different metal recognition properties and a range of cavity shapes and sizes.[6,7]

In this paper we expand our repertoire of recognition building blocks to include the diamagnetic d[6] ruthenium carbonyl porphyrin **1**, and describe the stereospecific templated synthesis *via* **2** and **3** of the triruthenium complex **4**. Ruthenium porphyrins have several potentially attractive properties for molecular recognition: (*a*) the lifetimes of amine–Ru(CO)–porphyrin complexes are much longer than their zinc analogues, so that metal complexation and decomplexation are in slow exchange on the NMR chemical shift time-scale;[8] this makes the spectra much easier to interpret than in the zinc case and allows direct measurement of the co-operativity of binding of ruthenium porphyrins to bidentate ligands;[9] (*b*) the ruthenium centre also binds soft sulfur and phosphorus ligands, greatly expanding the range of substrates that can be recognised;[10] (*c*) the exterior face of the cavity can in principle be selectively blocked with carbonyl groups (this would have the effect that ligands could only bind inside the cavity, thus simplifying binding and kinetic analyses); the CO group is also spectroscopically useful, being sensitive to the *trans* ligand; (*d*) in a mixed-metal porphyrin oligomer, a Ru=O porphyrin could be used to oxidise selectively a substrate bound to another porphyrin moiety in the molecule.[11]

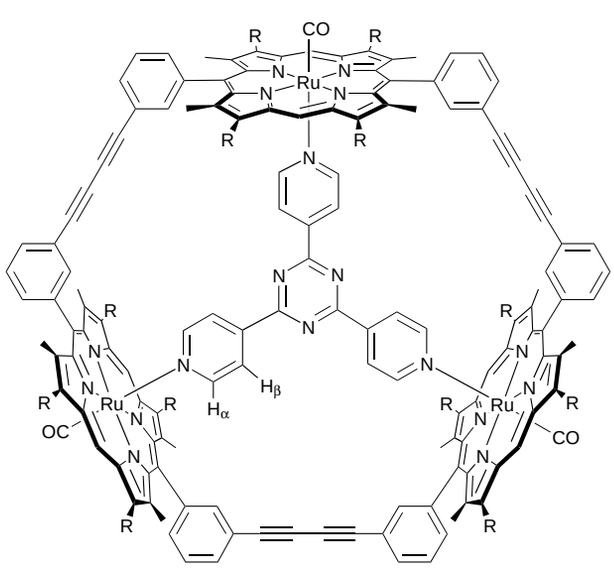
Unfortunately the tri(4-pyridyl)triazine template is so strongly held in complex **4** that it cannot be cleanly removed; however, the monomer building block **1** and this template approach have more recently been combined with our stepwise oligoporphyrin synthesis[1,6] to give a mixed-metal Zn_2Ru trimer where the template can be removed to leave a catalytically competent cavity.[12]



I R = $CH_2CH_2CO_2Me$, X = Br or I



1 X = I
2 X = C≡C–$SiMe_3$
3 X = C≡CH



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Results and Discussion

Our standard route[2] to metallated cyclic oligomers involves construction of the cavity *via* Glaser coupling of preformed

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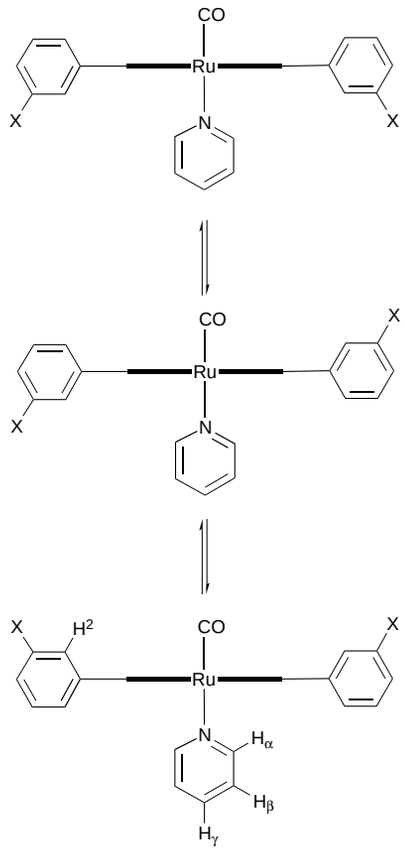
zinc porphyrin building blocks in the presence of a suitable template; for a trimer, tri(4-pyridyl)triazine is our usual template. The template and zinc are then removed with dilute acid to afford the free-base trimer which may be remetallated to generate binding sites. All attempts to insert ruthenium into this free-base trimer failed to give satisfactory products in this final step, apparently due to partial hydrogenation of the acetylenic links. Similar results were obtained when ruthenium insertion into an acetylenic monomer was attempted. We therefore protected the triple bonds of the free-base trimer by complexation with six $Co_2(CO)_6$ groups[13] and subsequently succeeded in the ruthenium metallation, but all attempts at deprotection using ammonium cerium nitrate,[13] iron(III) nitrate[13] or tetrabutylammonium fluoride[14] were unsuccessful, the porphyrins themselves being destroyed.

A new synthetic strategy was therefore required, the principle of which was to introduce the ruthenium into the porphyrin monomer before the acetylenic linkers; the last step would then be the formation of the cyclic trimer. Initially the bromoporphyrin **I** (X = Br) was synthesized by standard procedures[2,15] but this proved insufficiently reactive for the Pd-catalysed coupling that was required for attachment of the acetylene linkers, so the iodo derivative **I** (X = I) was used for all subsequent work on ruthenium porphyrins. Insertion of ruthenium into **I** was accomplished using a modification of the published[16] procedure to give complex **1**. Palladium-catalysed coupling of **1** with $Me_3Si{-}C{\equiv}CH$ then yielded the protected acetylenic monomer **2**; the Me_3Si protecting groups were removed using tetrabutylammonium fluoride in refluxing chloroform to give **3**.

Oxidative coupling of compound **3** in the absence of template gave, as expected, a multiplicity of products: these could be identified by mass and NMR spectroscopy (with and without added complementary ligands) as dimers, trimers and tetramers with CO randomly placed inside or outside the cavity, but it was not possible to separate cleanly any individual products. However, using 0.35 equivalent template (per monomer unit) gave in 32% isolated yield the ruthenium carbonyl trimer complex **4** with the three carbon monoxide groups outside the cavity and template inside;‡ this was fully characterised as described below. As expected, increasing the proportion of template decreased the yield of desired trimer, and led to production of some material with internal CO groups. It is not clear whether the templating involves trapping of linear intermediates as observed in zinc porphyrin analogues[18] or preassembly of three monomer units onto a single template before coupling takes place, which is the mechanism employed in more strongly binding situations.[19] Removal of the template from the final complex **4** proved very difficult, the porphyrin being sensitive to strong acid and oxidation, and the ruthenium–carbonyl bond sensitive to photochemical excitation. This difficulty in removing the template by protonation, by comparison with the ease of its removal from porphyrin trimers containing only a single Ru–N bond, is compelling evidence for the presence of multiple strong binding sites and therefore for binding within the cavity.

Spectroscopic characterisation

For the products **1**–**3**, addition of small amounts of pyridine to $CDCl_3$ solutions helped solubility and improved NMR spectral resolution; it appears that the ruthenium porphyrin always requires a sixth ligand, and in the absence of added ligand either porphyrin–porphyrin aggregation or weak intermolecular ligation of the sidechain ester occurs. The monomers **1**–**3** exist as a mixture of slowly exchanging *cis*- and *trans*-atropisomers; these are not readily distinguished spectroscopically in the free base or zinc forms, but in the ruthenium series with bound pyridine the three different environments (Scheme 1) give rise to multiple signals for most of the porphyrin resonances; the shift differences between atropisomers do not exceed 0.09 ppm (H^2), and for most signals are comparable with the width of the multiplet. Signals due to bound pyridine also always appear as complex ill resolved multiplets due to this overlap of signals from different atropisomers. The upfield shifts experienced by the protons of bound pyridine are substantially larger than in the zinc cases: for H_α $\Delta\delta$ is 7.7 rather than 6.0 ppm, and for H_β it is around 2.3 rather than 1.9 ppm. There is no evidence from other resonances that this is due to a larger ring current in the ruthenium case, so it is almost certainly due to the fact that the Ru is in the plane of the porphyrin (or even slightly displaced towards the CO group[20]) pulling the ligand into the porphyrin ring current.



Scheme 1 Three exchanging atropisomers of a ruthenium porphyrin; *cis–trans* isomerisation is faster than complexation–decomplexation

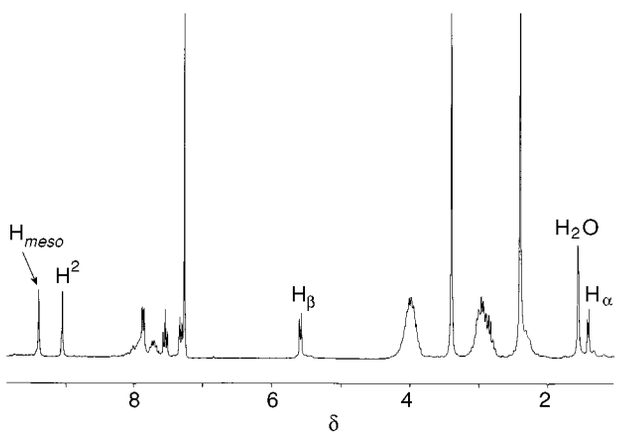


Fig. 1 The 250 MHz ^{1}H NMR spectrum of compound **4** in $CDCl_3$ solution

‡ Similarly, Glaser coupling in the presence of 0.5 equivalent of 4,4′-bipyridyl gave the corresponding ruthenium carbonyl dimer stereospecifically. This compound and its stereoisomers are described elsewhere.[17]

For cyclic oligomers the influence of the porphyrin ring current allowed us to identify the site of the ligand, either inside or outside the cavity. As an example, the ^{1}H NMR spectrum of compound **4** is shown in Fig. 1. The ring-current induced shifts of the pyridine α- and β-protons of the template in the complex (at δ 1.41 and 5.57, respectively) show that the three pyridyl groups bind inside the cavity. The internal aromatic protons of the host (H^2) experience an even larger downfield shift, to δ 9.03, than in the zinc analogue,[3] presumably due to the closer proximity of the guest ring current. The carbonyl IR stretch is sensitive to the *trans* ligand, shifting from 1931 cm^{-1} for methanol adducts to 1944 cm^{-1} for pyridine adducts.

Molecular modelling

Model building and simple molecular mechanics calculations[2,3] on the Zn_3 trimer had shown that the cavity is too large to bind the template without some distortion of the host or guest, but serious modelling of these complex systems has not been previously pursued. In the absence of suitable crystals for X-ray analysis, and with the advent of force fields that are appropriate for metal ions in porphyrins,[21,22] we undertook molecular modelling of complex **4**.

Fig. 2 summarises the modelling results: the template is indeed too small to fit perfectly within the undistorted cavity, but the trimer framework is flexible enough to respond to the geometrical demands of the ligand. The porphyrin units flex inwards [Fig. 2(*a*)] to optimise contact with the ligand: the predicted Ru–N (pyridyl) distance of 2.14 Å is very similar to the 2.193 Å found experimentally in [Ru(tpp)(CO)(py)][20] (H_2tpp = 5,10,15,20-*meso*-tetraphenylporphyrin, py = pyridine), while the inward flexing of the porphyrin is essentially the same as that found in the crystal structure of a related Zn_4 tetramer–tetrapyridylporphyrin complex.[23] Furthermore, rotation about the porphyrin–aryl linkage brings the whole porphyrin unit closer to the ligand and imparts a helical twist to the trimer framework [Fig. 2(*b*)]; distortion of such a linkage away from perpendicular has been observed experimentally in the crystal structure of a Zn_3 trimer–pyridine complex.[24]

Conclusion

The templating approach used in this study provides a route to ruthenium porphyrin oligomers with binding sites exclusively facing into the cavity; such molecules have potential for catalysis and for molecular electronics and electrochemistry. The combined strength of three ruthenium–pyridine binding sites has prevented satisfactory removal of the template in this particular case, even though the ligand is too small for strain-free complexation. The way forward is clearly to reduce the number of ruthenium centres as it is known that templates are readily removed from zinc oligomers.

Experimental

All solvents were distilled before use. All other reagents were obtained commercially as reagent-grade chemicals and used without further purification. For large-scale experiments (>10 mg) porphyrins were recrystallised by layered addition of methanol to a concentrated solution in chloroform or dichloromethane. Column chromatography was performed with 60 mesh silica gel or alumina activated II-III. Thin-layer preparative chromatography was performed with silica gel, type 60 on 20 × 20 cm glass plates (2.5 mm layer thickness).

The UV/VIS spectra were recorded with a Perkin-Elmer or a Uvikon 810 spectrophotometer, IR spectra of chloroform solutions with a Perkin-Elmer 1710 spectrometer in Fourier-transform mode, ^{1}H and ^{13}C NMR spectra on Bruker WM-250 or AM-400 MHz spectrometers and fast atom bombardment (FAB) mass spectra on a Kratos MS-50 instrument using a *m*-nitrobenzyl alcohol matrix.

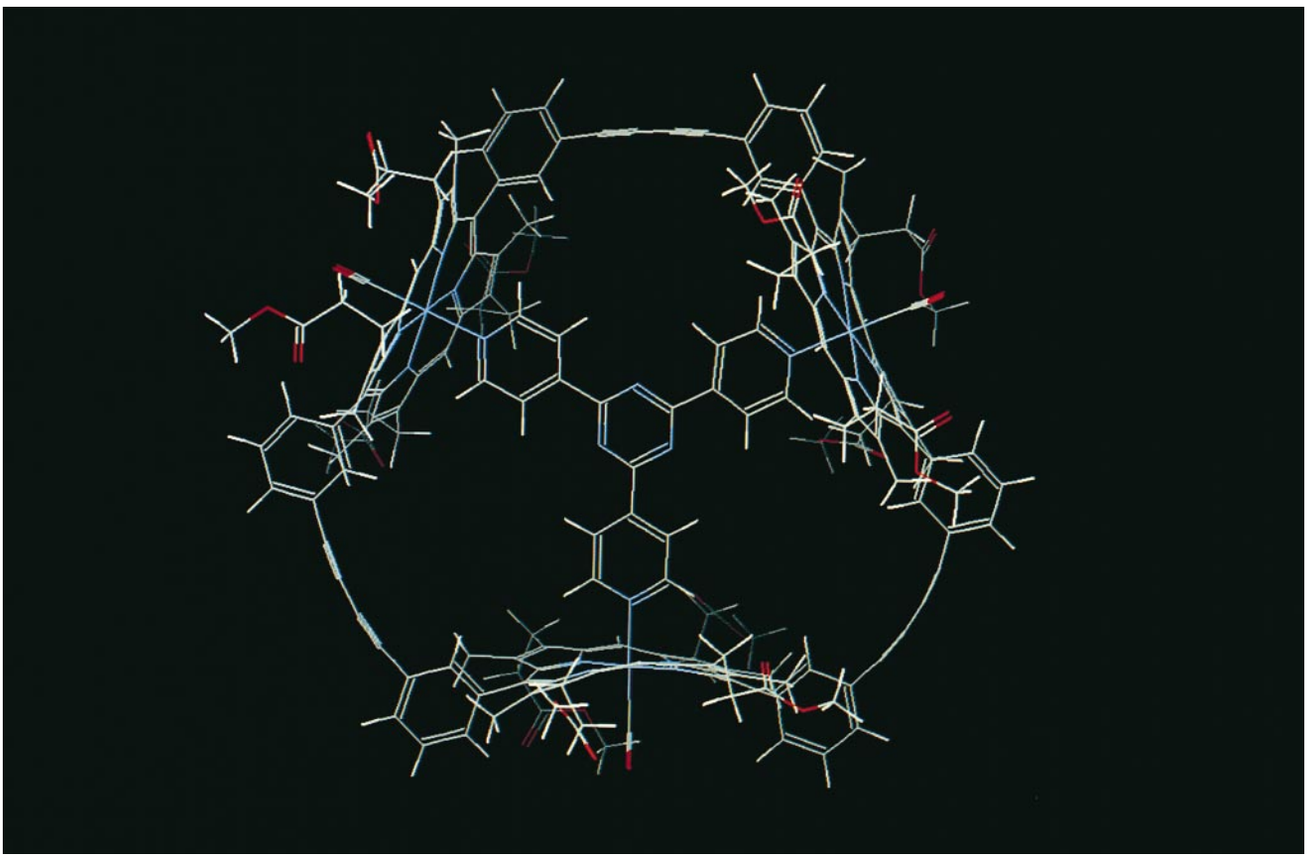
Molecular modelling was carried out on a Silicon Graphics Indigo workstation using CERIUS[2] Version 2.0 (BIOSYM/Molecular Simulations) with the UNIVERSAL 1.01 force field;[21] atom and bond parameters were taken directly from the program database. Electrostatic charge calculations were performed before minimisation using the charge-equilibration method.[22] Structures were minimised using the conjugate-gradient algorithm with a root mean square force convergence value of 0.01 kcal mol^{-1} $Å^{-1}$ (cal = 4.184 J). Dynamics calculations were performed at 400 K with 500 steps at 0.001 ps intervals.

Syntheses

5,15-Bis(3-iodophenyl)-2,8,12,18-tetra(2-methoxycarbonylethyl)-3,7,13,17-tetramethyl porphyrin I. Palladium on carbon (10%, 350 mg) was added to a solution of 5,5′-dibenzyloxycarbonyl-3,3′-di(2-methoxycarbonylethyl)-4,4′-dimethyl-2,2′-dipyrrolylmethane (6.15 g, 10 mmol)[2] in tetrahydrofuran (200 cm^3) containing 1% triethylamine and the mixture was stirred under a hydrogen atmosphere for 3 h. The catalyst was removed (Celite) and the filtrate evaporated. Trifluoroacetic acid (50 cm^3, argon saturated) was added under argon at 0 °C and the solution was stirred for 20 min followed by 20 min at room temperature (periodically the reaction vessel was evacuated and then saturated with argon to remove CO_2). At this stage, the solution was orange-brown. It was cooled to −30 °C (liquid N_2 in Pr^iOH) and 3-iodobenzaldehyde (2.32 g, 0.01 mol)[25] in methanol (50 cm^3, argon saturated) was added by a cannula and stirred for 2 h. During this period the temperature was allowed to rise from −30 to −20 °C. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2.35 g, 10 mmol) was then added and the mixture stirred for 30 min before careful addition of triethylamine (50 cm^3). The resulting mixture was poured into chloroform (250 cm^3) and the organic layer washed with water (2 × 500 cm^3). The solvent was evaporated, and the solid passed through a silica column [$CHCl_3$–NEt_3 (99:1) as eluent]. The red porphyrin fractions were gathered, the solvents removed and the product purified by at least two recrystallisations from dichloromethane–methanol. The resulting red solid was filtered off and dried *in vacuo* to yield compound **I** (2.55 g, 46% yield). λ_{max}/nm (CH_2Cl_2) (ε/dm^3 mol^{-1} cm^{-1}) = 410 (27400), 507.5 (2000), 541 (550), 575.5 (760) and 627.5 (110). NMR (250 MHz, $CDCl_3$): ^{1}H, δ −2.51 (s, 2 H, NH), 2.54 (s, 12 H, CH_3 of pyrrole), 3.16 (t, J = 7.8, 8 H, $CH_2CH_2CO_2Me$), 3.66 (s, 12 H, CO_2CH_3), 4.36 (t, J = 7.6 Hz, 8 H, $CH_2CH_2CO_2Me$), 7.46–8.45 (m, 8 H, CH of phenyl) and 10.29 (s, 2 H, H, *meso*); ^{13}C, δ 15.01 (CH_3 of pyrrole), 21.94 ($CH_2CH_2CO_2Me$), 36.93 ($CH_2CH_2CO_2Me$), 51.77 (CO_2CH_3), 93.74 (CI), 97.11 (*meso*-CH), 116.78 (*meso*-C of aryl), 129.39, 131.12, 137.70, 141.61 (CH of phenyl), 137.18, 141.26, 141.60, 144.06, 144.90 (pyrrole ring + C^1 of phenyl) and 173.42 (C=O). Positive-ion FAB mass spectrum: *m/z* 1115.9 (M^+) ($C_{52}H_{52}I_2N_4O_8$ requires 1114.2).

Carbonyl[5,15-bis(3-iodophenyl)-2,8,12,18-tetra(2-methoxycarbonylethyl)-3,7,13,17-tetramethylporphyrinato](methanol)-ruthenium 1. A mixture of compound **I** (540 mg, 4.84×10^{-4} mol), [$Ru_3(CO)_{12}$] (650 mg, 1.01×10^{-3} mol) and decalin (20 cm^3) was degassed, saturated with argon and heated overnight at 130 °C under argon. The progress of the reaction was monitored by UV/VIS spectroscopy. Upon completion of the reaction half of the decalin was removed under vacuum, and the red-orange product was filtered off, washed with cold methanol, dissolved in the minimum of chloroform–methanol (20:1) and then chromatographed on silica with chloroform elution. The initial fractions contained an excess of [$Ru_3(CO)_{12}$] which was collected and recycled, after which the ruthenium carbonyl complex **1** was collected as a red solution. The solvent was evaporated and the product recrystallised in a mixture of chloroform–methanol. Yield 466 mg (75%). λ_{max}/nm

(*a*)



(*b*)

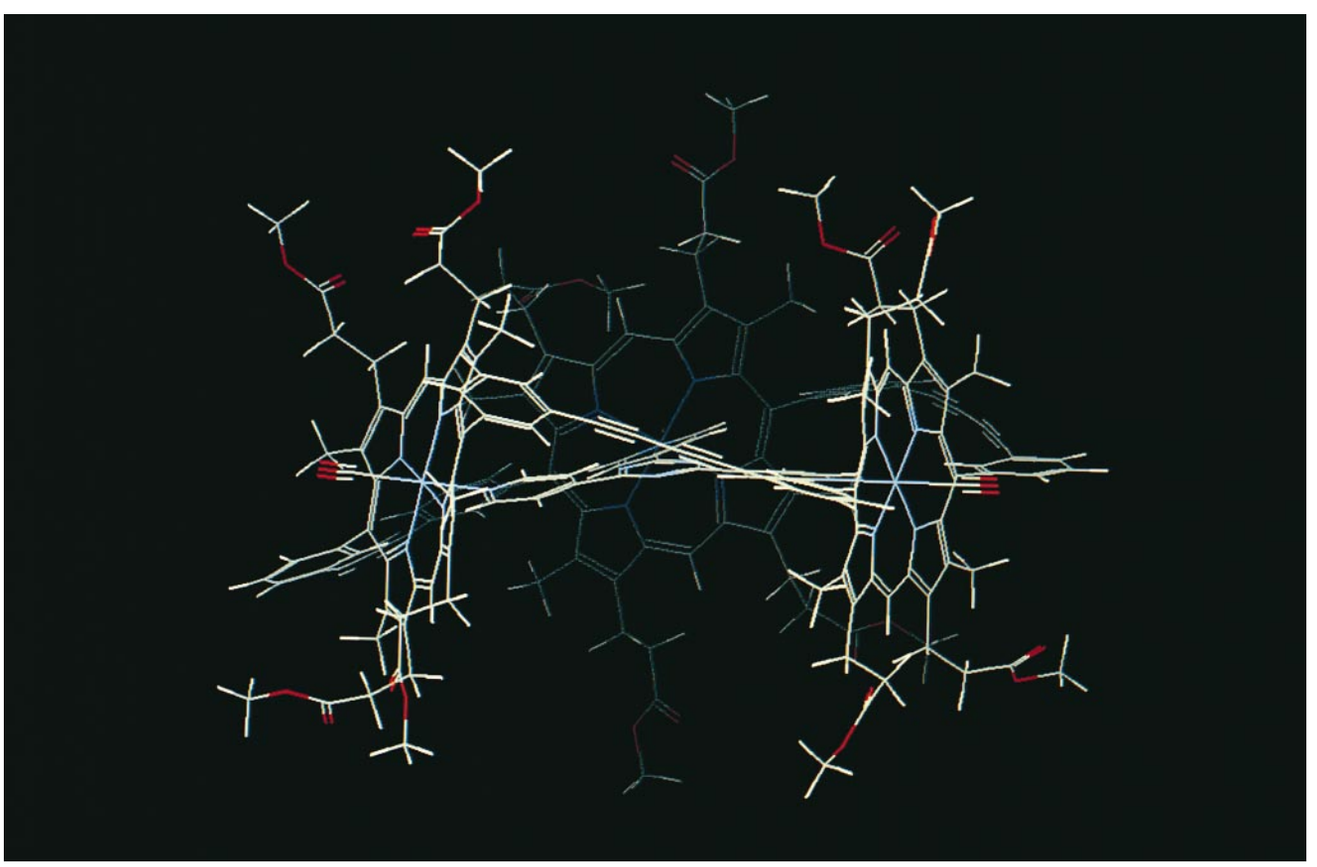


Fig. 2 Two views of complex **4** generated by molecular modelling using CERIUS[2] with the UNIVERSAL 1.01 force field: (*a*) from above, showing how the porphyrin units are bent inwards to allow formation of Ru–N bonds; (*b*) from the side showing how partial rotation of the porphyrin–aryl bond imparts a helical twist to the host and again brings the metal centres closer to the ligand

($CHCl_3$ + MeOH) = 305, 401.4, 523 and 554.2. $\tilde{\nu}_{max}/cm^{-1}$ ($CHCl_3$) = 1931 [CO, Ru(CO)]. ^{1}H NMR (250 MHz, $CDCl_3$ + C_5H_5N) (mixture of conformers): δ 1.18–1.24 (m, 2 H, H_α of py bound to Ru), 2.40 (3 s, 12 H, CH_3 of pyrrole), 3.14 (m, 8 H, $CH_2CH_2CO_2Me$), 3.60 (3 s, 12 H, CO_2CH_3), 4.19 (br s, 8 H, $CH_2CH_2CO_2Me$), 5.07–5.17 (m, 2 H, H_β of py), 6.01 (m, 1 H, H_γ of py), 7.45 (t, 2 H, aryl, J = 8), 7.96 (d, 2 H, aryl, J = 8), 8.02 (d, 2 H, aryl, J = 8 Hz), 8.36 + 8.45 (2 s, 2 H, aryl), 9.80 (s, 2 H, *meso*). Positive-ion FAB mass spectrum: *m/z* 1243 (M^+) and 1215 (M − CO) ($C_{53}H_{50}I_2N_4O_9Ru$ requires 1242.1).

Carbonyl(methanol){2,8,12,18-tetra(2-methoxycarbonylethyl)-3,7,13,17-tetramethyl-5,15-bis[3-(trimethylsilylethynyl)-phenyl]porphyrinato}ruthenium 2. Complex **1** (450 mg, 3.5×10^{-4} mol) was dissolved in freshly distilled tetrahydrofuran (25 cm^3); triethylamine (25 cm^3, freshly distilled), hexakis(acetato)tripalladium(II) (12 mg, Johnson Matthey) and triphenylphosphine (25 mg) were added and the mixture was carefully degassed and saturated with argon. Trimethylsilylacetylene (3 cm^3) was added *via* a syringe and the reaction mixture was heated overnight at 80 °C under an argon atmosphere. After evaporation of the solvent, the product was dissolved in the minimum of chloroform–methanol (20:1) and chromatographed on silica gel with chloroform elution. The product was recrystallised from chloroform–methanol to yield the red-orange complex **2** (335 mg, 78%). λ_{max}/nm ($CHCl_3$) = 310 (br), 401.3, 522.8 and 553.9. $\tilde{\nu}_{max}/cm^{-1}$ ($CHCl_3$) = 1931 [CO, Ru(CO)], 2153 (C≡CSi) and 846 (Si–Me). ^{1}H NMR (250 MHz, $CDCl_3$ + C_5H_5N): δ 0.25, 0.27 (2 s, 18 H, $SiMe_3$), 1.22 (m, 2 H, H_α of py bound to Ru), 2.36–2.40 (3 s, 12 H, CH_3 of pyrrole), 3.11 (m, 8 H, CH_2CO_2Me), 3.59 (2 s, 12 H, CO_2CH_3), 4.18 (br s, 8 H, $CH_2CH_2CO_2Me$), 5.13 (m, 2 H, H_β of py), 6.0 (m, 1 H, H_γ of py), 7.69 (m, 2 H, aryl), 7.88 (m, 2 H, aryl), 8.0–8.2 (m, 4 H, aryl) and 9.80 (br s, 2 H, *meso*). Positive-ion FAB mass spectrum: *m/z* 1182.5 (M^+) and 1154 (M − CO) ($C_{63}H_{68}N_4O_9RuSi_2$ requires 1182.4).

Carbonyl[5,15-bis(3-ethynylphenyl)-2,8,12,18-tetra(2-methoxycarbonylethyl)-3,7,13,17-tetramethylporphyrinato](methanol)ruthenium 3. The protected monomer **2** (256 mg, 2.1×10^{-4} mol) was dissolved in chloroform (50 cm^3) containing tetrahydrofuran (0.5 cm^3, freshly distilled) and the mixture heated to reflux under dry air. Tetrabutylammonium fluoride (1 cm^3, of a 1.1 mol dm^{-3} solution in tetrahydrofuran) was added and the reaction mixture was stirred for 10 min. Two spatulas full of $CaCl_2$ were added to the cooled mixture to remove the excess of fluoride and the product was washed with water (3 × 300 cm^3). The solvent was evaporated, the product dissolved in the minimum of chloroform–methanol (20:1) and chromatographed on silica gel with chloroform elution. It was recrystallised from a $CHCl_3$–MeOH mixture to yield a red-orange product (175 mg, 78%). λ_{max}/nm ($CHCl_3$) = 311 (br), 401.6, 523.7 and 554.4. $\tilde{\nu}_{max}/cm^{-1}$ ($CHCl_3$) = 1935.7 [CO, Ru(CO)]. ^{1}H NMR (250 MHz, $CDCl_3$ + C_5H_5N): δ 1.23 (m, 2 H, H_α of py bound to Ru), 2.39 (2 s, 12 H, CH_3 of pyrrole), 3.13 (m, 8 H, $CH_2CH_2CO_2Me$), 3.59 (s, 12 H, CO_2CH_3), 4.19 (br s, 8 H, $CH_2CH_2CO_2Me$), 5.13 (m, 2 H, H_β of py), 6.0 (m, 1 H, H_γ of py), 7.70 (m, 2 H, aryl), 7.94 (m, 2 H, aryl), 8.09 (m, 2 H, aryl), 8.13 (s, 2 H, aryl), 8.23 (s, 2 H, aryl) and 9.81 (s, 2 H, *meso*). Positive-ion FAB mass spectrum: *m/z* 1039.4 (M^+) and 1011.3 (M − CO) ($C_{57}H_{52}N_4O_9Ru$ requires 1038.3).

Trimer 4. Deprotected porphyrin monomer **3** (30 mg, 2.8×10^{-5} mol) and tri(4-pyridyl)triazine (3 mg, 9.9×10^{-6} mol, 0.35 equivalent) were dissolved in dichloromethane (200 cm^3, freshly distilled over CaH_2). After 5 min, when a bright clear solution was obtained, CuCl (0.207 g) was added followed by *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (0.3 cm^3). The mixture was stirred under dry air for 2 h at room temperature, and the progress of the reaction was monitored by TLC (chloroform). The product was washed with water (3 × 300 cm^3),§ the solvent was evaporated and the product purified by preparative TLC on silica with chloroform as eluent. The major fraction corresponded to the expected ruthenium trimer isomer (10.6 mg, 32%). λ_{max}/nm ($CHCl_3$) = 334.7, 401.7, 525.3 and 554.6. $\tilde{\nu}_{max}/cm^{-1}$ ($CHCl_3$) = 1944 [CO, Ru(CO)]. ^{1}H NMR (250 MHz, $CDCl_3$) (one isomer): δ 1.41 (d, 6 H, J = 6, H_α of template), 2.39 (s, 36 H, CH_3 of pyrrole), 2.99 (m, 24 H, $CH_2CH_2CO_2Me$), 3.39 (s, 36 H, CO_2CH_3), 4.02 (m, 24 H, $CH_2CH_2CO_2Me$), 5.57 (d, 6 H, J = 6, H_β of template), 7.30 (d, 6 H, J = 8, aryl), 7.53 (t, 6 H, J = 8, aryl), 7.85 (d, 6 H, J = 8 Hz, aryl), 9.03 (s, 6 H, CH of phenyl) and 9.38 (s, 6 H, *meso*). Positive-ion FAB mass spectrum: *m/z* 3421 (M^+) and 3336.8 (M − 3 CO) ($C_{189}H_{162}N_{18}O_{27}Ru_3$ requires 3420.9).

Acknowledgements

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§ The trimer solution should not be dried with potassium or sodium carbonate as it appears to form an uncharacterised adduct from which it could not be reisolated.

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