Organometallic boxes built from 5,10,15,20-tetra(4-pyridyl)porphyrin panels and hydroxyquinonato-bridged diruthenium clips

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A B S T R A C T

Self-assembly of 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H₂) tetradentate panels with dinuclear arene ruthenium clips [Ru₆(η⁶-arene)₂(dhbq)³Cl₂] (arene = C₈H₈Me, P-PrC₆H₄Me, C₆Me₆) and 2,5-dihydroxy-1,4-benzoquinonato affords the cationic organometallic boxes [Ru₆(η⁶-C₈H₈Me)₂(tpp-H₂)₂(dhbq)⁴Cl]⁺ (1)⁰⁺, [Ru₆(η⁶-p-PrC₆H₄Me)₂(tpp-H₂)₂(dhbq)⁴Cl]⁺ (2)⁰⁺ and [Ru₆(η⁶-C₆Me₆)₂(tpp-H₂)₂(dhbq)⁴Cl]⁺ (3)⁰⁺. These octanuclear cations have been isolated as their triflate salts and characterised by mass spectrometry, NMR and IR spectroscopy. The molecular structure of these systems was deduced by one-dimensional and two-dimensional NMR experiments (ROESY, COSY, HMQC).

Keywords: Bridging ligands, Arene ligands, Ruthenium, Supramolecular chemistry, Cage compounds

Organometallic half-sandwich complexes of Ru(II), Rh(III) and Ir(III) are becoming more and more popular as versatile building blocks in supramolecular chemistry. The lability of the ligands opposite to the inert η⁶-ligand can generate a pre-organised arrangement that allows the controlled formation of supramolecular assemblies. These three facial coordination sites have been extensively exploited to build up rectangles, macrorings and cages [1–9].

Recently we have used arene ruthenium complexes as building blocks for the assembly of a series of caticonic triangular metalloprisms containing bridging chloro [10], oxalato [11] and 2,5-dihydroxy-1,4-benzoquinonato [12] ligands connected by 2,4,6-triaryl-1,3,5-triazine subunits. Herein we report the synthesis and characterisation of three rectangular metallo-prismatic cages incorporating arene ruthenium building blocks (arene = C₈H₈Me, P-PrC₆H₄Me, C₆Me₆), bridged by 2,5-dihydroxy-1,4-benzoquinonato (dbhq) ligands, and connected by 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H₂) tetradentate ligands.

The dinuclear arene ruthenium complexes [Ru₆(η⁶-arene)Cl₂] (arene = C₈H₈Me, P-PrC₆H₄Me, C₆Me₆) react in methanol with 2,5-dihydroxy-1,4-benzoquinone (dbhq-H₂) to form in good yield the dinuclear complexes [Ru₆(η⁶-C₈H₈Me)₂(dhbq)Cl₂] [13], [Ru₂(η⁶-p-PrC₆H₄Me)₂(dhbq)Cl₂] [12a] and [Ru₂(η⁶-C₆Me₆)₂(dhbq)Cl₂] [12c], respectively. Addition of silver powder to these dinuclear clips in the presence of 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H₂) leads to the connection of two tetratentate panels, affording the octanuclear metallo-prismatic cations [Ru₆(η⁶-C₈H₈Me)₂(tpp-H₂)₂(dhbq)⁴Cl]⁺ (1)⁰⁺, [Ru₆(η⁶-p-PrC₆H₄Me)₂(tpp-H₂)₂(dhbq)⁴Cl]⁺ (2)⁰⁺ and [Ru₆(η⁶-C₆Me₆)₂(tpp-H₂)₂(dhbq)⁴Cl]⁺ (3)⁰⁺ in good yield (≈80%), see Scheme 1. These rectangular prismatic cations are isolated as their trifluoromethanesulfonate salt [14].

The ¹H NMR spectra of 1, 2 and 3 display a similar signal pattern for the tpp-H₂ protons. Interestingly, diastereotopic protons are observed upon formation of the cationic cages, suggesting a tilt of the bi-metallic clips, thus introducing helical-type chirality [15]. A similar chiral conformation was observed in the oxalato-bridged analogous cage [Ru₆(η⁶-p-PrC₆H₄Me)₂(tpp-H₂)₂(dhbq)⁴Cl]⁺, for which a racemic mixture of two helical isomers was found in the crystal [16]. Surprisingly, in this oxalato-bridged analogue, the NH signal of the tpp-H₂ panels is found unchanged, as compared to free tpp-H₂ at δ = −3.1 ppm, while in the cage molecules 1–3 this signal is strongly shifted upfield to δ = −7.0 ppm. Moreover, in the oxalato-bridged analogue, the CH and CH₂ signals of the p-cymene ligands are superimposed at δ = 3.35 ppm, while in 2 the two signals are well separated at δ = 3.13 (CH) and 2.43 (CH₂), respectively.

Multiple one-dimensional and two-dimensional NMR experiments (ROESY, COSY, HMQC) allow the complete assignment of the proton signals of the cages 1–3. Fig. 1 shows the two-dimensional ¹H COSY spectrum of the pyridyl and pyrrolyl region of the tpp-H₂ panels in 2. Strong cross-peaks attributed to ¹H–H–H coupling together with weak cross-peaks for ¹H–coupling constant allow the assignment of two distinct series of pyridyl and pyrrolyl protons, identified as H and H respectively. The assignment is further confirmed by one-dimensional ¹H ROESY experiments in which strong cross-peaks are observed between H₆(dhbq) protons.
unsymmetrical spectra peak the ppm arene arene the [tpp-rectangular temperature, different metallo-pris straightfo solvents helical [solvents NMR. of molecules. and Ru demo- changes absorptions in electrospray set show is new with doublets pyridyl in H an analogou boxes agreement 1031(s), (CD 638(s) spectra hydroxyquinonat and shows coordinating and NH the conditions known singlet At well remarkable to a as acetone- additional of N at singlet exchange of single-crystal in to the Ru+ to the O correspond dimethylsulfoxi peaks solution, (CF 3CF 2OH) corresponding the deformed and the 2 diastereotopic H of the unsymmetrical pyridyl groups (H and H) [17].

The infrared spectra of 1–3 are dominated by absorptions of the 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H 2) and 2,5-dihydroxy-1,4-benzoquinonato (dhbq) ligands [19]. In addition to the tpp-H 2 and dhbq bands, strong absorptions attributed to the triflate anions are observed in the infrared spectra of [1]([CF 3SO 3] 3, [2]([CF 3SO 3] 3 and [3]([CF 3SO 3] 3 [1260(s), 1031(s), 638(s) cm 1]

[20]. Under conditions of electrospray mass spectrometry, the cages 1–3 show a remarkable stability. The ESI-MS spectra of 1–3 show peaks corresponding to [1 + (CF 3SO 3)] 3+, [2 + (CF 3SO 3)] 4+ and [3 + (CF 3SO 3)] 4+ at m/z 983.0, 1067.3 and 1123.3, respectively [21]. These peaks can be assigned unambiguously on the basis of their characteristic Ru isotope pattern. Furthermore, in the ESI-MS spectra of 1 and 2, the second major peak corresponding to [1 + (CF 3SO 3)] 3+ and [2 + (CF 3SO 3)] 4+ is observed at m/z 1359.3 and 1472.5, respectively. Fig. 2 shows the ESI-MS spectrum of [1]([CF 3SO 3] 3 in acetonitrile.

It is well known that in coordinating solvents ligand exchange can occur with arene ruthenium complexes [10]. In order to examine the stability of the rectangular metallo-prism 2 in solution, we recorded the 1H NMR spectra in various deuterated solvents (CD 2 Cl 2, CD 3 CO, CD 3 CN, (CD 3 ) 2 SO) with different coordinating ability. At room temperature and even elevated temperature, 1H NMR experiments for 2 in dichloromethane- d 2, acetone- d 4 and acetonitrile- d 3 showed no signal changes which could indicate the cleavage of the hydroxyquinonato bridges or the presence of free tpp-H 2 molecules. However, in dimethylsulfoxide- d 6 at 40 °C, compound [2]([CF 3SO 3] 3 shows an additional new set of signals clearly attributed to the different components of the cage after decomplexation: doublets at 9.0 ppm and 8.2 ppm corresponding to H 3 and H 4 of the uncoordinated tpp-H 2 pyridyl protons as well as a singlet at 8.9 ppm for the pyrrolyl protons; the NH signal at 7.0 ppm being replaced by a new singlet at −3.0 ppm. The decomplexation is complete and irreversible at 60 °C, as shown by 1H NMR.

In conclusion, we have shown a simple and straightforward synthesis of hydroxyquinonato-bridged arene ruthenium rectangular metallo-prisms using tetradentate porphyrin panels. The organometallic boxes 1–3 possess helical chirality, as demonstrated by NMR spectroscopy. These data are in agreement with the analogous compound [Ru dodecaphenyl cyclohexane (tpp-H 2) 2(C 6 O 2) 2][CF 3SO 3] 3, for which a chiral deformed cubic structure was confirmed by single-crystal X-ray structure analysis [16].
Fig. 2. ESI-MS of [1][CF3SO3]2.

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References

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[13] [Ru2(p-arene)(arene)2(dhbq)Cl2] (arene = C6H5Me, 191 mg, 0.32 mmol; p-C6H4Me, 218 mg, 0.32 mmol; C6H6, 235 mg, 0.32 mmol) in CH2Cl2 (80 mL) is stirred at room temperature for 3 h, then filtered. To the red filtrate, tpp-H2 (99 mg, 0.16 mmol) is added. The solution is stirred for 15 h, and then the solvent removed under vacuum. The residue is dissolved in CH3Cl (3 mL), and diethyl ether is added, and the mixture stand overnight, to precipitate the purple solid. [1][CF3SO3]2: Yield: 300 mg (83 %), IR (cm⁻¹): 3470 (m, CHaryl), 3075 (w, CHdiao), 1520 (s, C=O), 1473 (s, CHaryl), 1411 (m, C=O), 1104 (s, C=O), 1057 (s, C=O), 1028 (s, C=O), 922 (s, CHaryl), 837 (s, CHaryl), 725 (s, CHaryl), 693 (s, CHaryl), 609 (s, CHaryl), 570 (m, 3H, Hq), 2.13 (s, 6H, CH0).
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The one-dimensional $^1$H ROESY experiments have been recorded using the MP-ROESY mixing sequence, which has shown its effectiveness with regard to TOCSY transfer suppression and cross-relaxation peak intensity enhancement [18].