Synthesis and dynamic structure of multinuclear Rh complexes of porphyrinoids†

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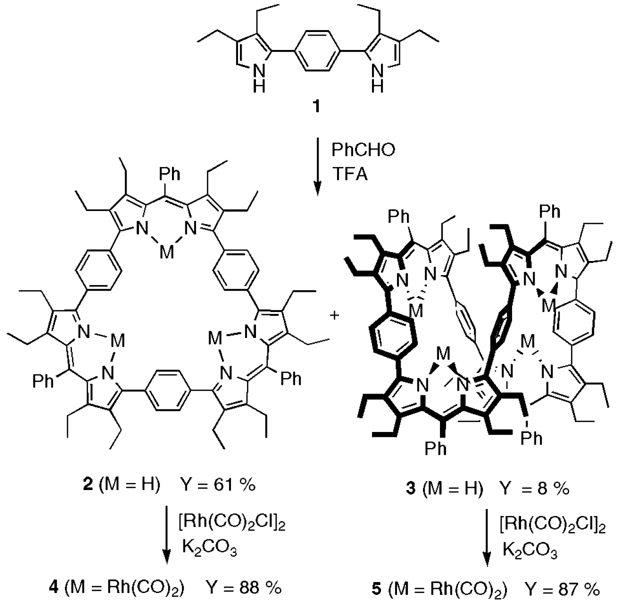
Large porphyrinoids with three $Rh(CO)_2$ groups at their dipyrrin units shows two-step metal transposition through the macrocycle in solution and the equilibrium between the C_{3v}-isomer and the C_s-isomer depends on the solvent polarity.

Increasing the ring size is a challenge in the chemistry of expanded porphyrins from the viewpoint of accommodating polyatomic entities within the ring.[1] We have previously synthesized porphyrinoids with 16, 20, and 24 pyrrole units using a 2,2′-bipyrrole building block.[2] However, it is generally more difficult to synthesize larger porphyrinoids by increasing the number of pyrrole units within a ring. Thus, we are also interested in synthesizing large porphyrinoids by introducing a spacer in the 2,2′-bipyrrole building block.[3] Metal complexes of large porphyrinoids are of great interest because a definite spatial arrangement of multiple metals can be constructed.[4] We describe here such multinuclear complexes of the expanded rosarin and octaphyrin having the 1,4-phenylene spacers where the $Rh(CO)_2$ group passes through the macrocycle and this oscillating movement of the $Rh(CO)_2$ group depends on the ring size, the number of metals, and the solvent polarity.

The dipyrrole **1**[5] was reacted with benzaldehyde in the presence of trifluoroacetic acid (TFA) at room temperature for 24 h and then oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The expanded rosarin **2** with three dipyrrole units was obtained in 61% yield along with the expanded octaphyrin **3** in 8% yield (Scheme 1). It is remarkable that the yield of **2** by this Rothemund-type synthesis is as high as that of the parent rosarin(1.0.1.0.1.0) reported originally by Sessler.[6] The UV-vis bands of **2** and **3** at 504 and 550 nm, respectively, are similar to those at 473 and 569 nm of the corresponding rosarin(1.0.1.0.1.0) and octaphyrin(1.0.1.0.1.0.1.0), respectively.[2] Reaction of **2** and **3** with $[Rh(CO)_2Cl]_2$ (5-fold molar equiv.) and K_2CO_3 (excess) in CH_2Cl_2 for 24 h at room temperature gave the tris(dicarbonylrhodium) complex **4** and tetrakis(dicarbonylrhodium) complex **5**, respectively, in good yields after chromatographic purification on silica gel. The X-ray crystallography of **4** showed that three $Rh(CO)_2$ groups are ligated by three dipyrrin units of the macrocycle.‡ The $Rh(CO)_2$ groups are pushed out of the dipyrrin mean planes by the steric constraint of the 1,4-phenylene linkers and sitting on the same face of the macrocycle (Fig. 1). The three dipyrrin units are almost coplanar and the 1,4-phenylene linkers are tilted by 42.6°–52.3° with respect to the adjacent dipyrrin mean planes to make a bowl-shaped macrocycle structure.

The ^1H NMR spectrum of **4** in CD_2Cl_2 at 20 °C showed a pair of multiplets at 2.50 and 2.25 ppm due to the diastereotopic methylene protons of the ethyl groups next to the 1,4-phenylene linkers and a pair of singlets at 8.14 and 7.36 ppm due to the 1,4-phenylene protons, which are consistent with the C_{3v} symmetric structure in accord with the X-ray crystallography. Since the 1,4-phenylene protons appear as a single singlet at 7.80 ppm for **2** but as two singlets for **4**, rotation of the 1,4-phenylene linker is inhibited at room temperature on the NMR time scale by the steric constraint with three $Rh(CO)_2$ groups. The observed chemical shifts for the inner and outer phenylene protons of **4** are not evidently indicative of antiaromaticity expected for 36π macroring system. This is in contrast with the chloroCd(II) *p*-benziporphyrin where the 1,4-phenylene ring incorporated in the 18π macroring system



Scheme 1 Synthesis of expanded rosarin and octaphyrin Rh complexes.

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† Electronic supplementary information (ESI) available: Synthesis and spectroscopic data for **1**, **2**, **3**, **4**, **5**, and **6**, including ROESY NMR for **4** and VT ^1H NMR spectra for **6**. See DOI: 10.1039/b717022j

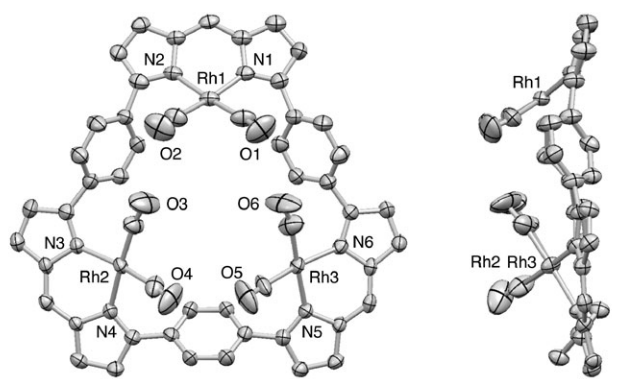


Fig. 1 X-Ray crystal structure of **4** with thermal ellipsoids at the 50% level (a top view (left) and a side view (right)). The peripheral ethyl and phenyl groups and solvent molecules are omitted for clarity. Rh1–Rh2 7.227(1); Rh2–Rh3 6.751; Rh3–Rh1 7.206; O2–O3 3.079; O4–O5 2.909; O6–O1 3.015 Å.

is tilted by 45° but shows a large chemical shift difference (6.6 ppm at 298 K) between the inner and outer phenylene protons.[7] A pair of multiplets at 2.56 and 2.33 ppm due to the C_{3v} symmetric isomer in toluene-d_8 at 20 °C are overlapped with a multiplet at 2.56 ppm due to the second component with a molar ratio of 1 : 1 (Fig. 2). Two singlets at 8.22 and 7.53 ppm due to the 1,4-phenylene protons of the C_{3v} symmetric isomer are also overlapped with a broad signal at 8.25 ppm in toluene-d_8 at 20 °C. These solvent-dependent spectral changes were observed in the UV-vis spectra of **4** as well as in the NMR spectra. A single absorption band in the visible region was observed at 556 nm in CH_2Cl_2, whereas a major band at 578 nm with a shoulder band at 556 nm were observed in toluene (Fig. 3). Equilibrium between two species is indicated by the presence of an isobestic point at 567 nm when the volume ratio of CH_2Cl_2 and toluene was changed continuously without changing concentration.

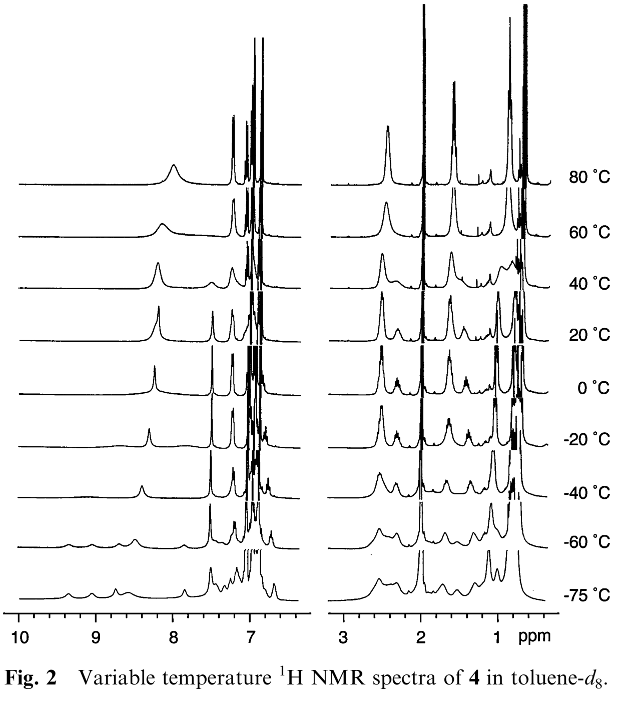


Fig. 2 Variable temperature ^1H NMR spectra of **4** in toluene-d_8.

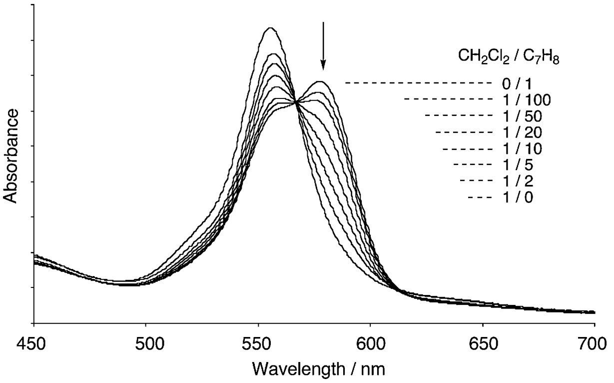
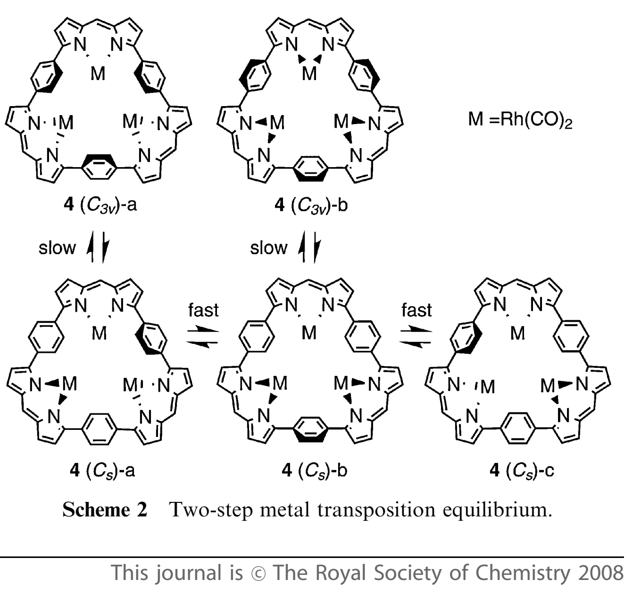


Fig. 3 UV-Vis spectra of **4** in various compositions of CH_2Cl_2/toluene.

The NMR signals due to the methylene protons coalesced to a single resonance at 2.47 ppm at 80 °C in toluene-d_8, and at the same time the signals due to the 1,4-phenylene protons coalesced to a single resonance at 8.05 ppm at 80 °C (Fig. 2). These changes indicate that the $Rh(CO)_2$ group passes through the macrocycle rapidly on the NMR time scale at 80 °C to make both faces of the macrocycle magnetically equivalent (Scheme 2, equilibrium between **4**(C_{3v}) and **4**(C_s)). On the other hand, a shoulder signal at 8.25 ppm due to the second component at 20 °C was split into six resonances at 9.4, 9.1, 8.8, 7.8, 7.4, and 7.3 ppm at −75 °C. This splitting pattern is consistent with the C_s-symmetric structure where three $Rh(CO)_2$ groups are distributed to both faces of the macrocycle and the rotation of the 1,4-phenylene linker is restricted. The coalescence of these six signals can be rationalized in terms of the transposition of one of the two $Rh(CO)_2$ groups on the same face into the other face of the macrocycle, which not only equalizes the magnetic circumstances of both faces of the macrocycle but also causes three 1,4-phenylene groups to be magnetically equivalent (Scheme 2, equilibrium between **4**(C_s)-a, **4**(C_s)-b, and **4**(C_s)-c). Therefore, the D_{3h}-symmetric spectral pattern is seen at 20 °C for the C_s-symmetric isomer. Since three $Rh(CO)_2$ units are on the same face of the macrocycle in the C_{3v}-isomer, the dipole moment of the C_{3v}-isomer is larger than that of the C_s-isomer. Therefore, the C_{3v}-



Scheme 2 Two-step metal transposition equilibrium.

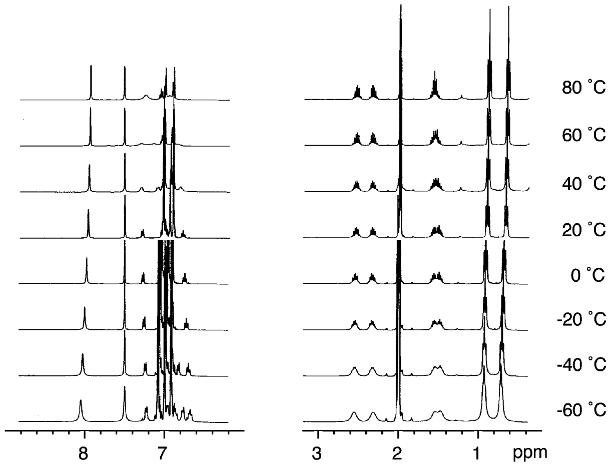


Fig. 4 Variable temperature ^{1}H NMR spectra of **5** in toluene-d_8.

isomer is favored in CH_2Cl_2 that is a more polar solvent than toluene. It is reasonable that the crystal of **4** obtained from polar solvents ($CHCl_3$ and acetone) shows the C_{3v}-structure in the X-ray analysis.

The monorhodium complex **6** was obtained in 31% yield when an equimolar mixture of **2** and $[Rh(CO)_2Cl]_2$ was stirred for 3 h in CH_2Cl_2 at room temperature. The $Rh(CO)_2$ group of **6** is rapidly oscillating between two faces of the macrocycle even at −40 °C in toluene-d_8 as evidenced by the C_{2v} symmetric ^{1}H NMR spectral pattern where six quartets and six triplets due to the peripheral ethyl groups were observed. Since the protons due to the 1,4-phenylene linker appeared as a AB quartet at 8.02 and 7.84 ppm and a singlet at 7.66 ppm at 20 °C, the 1,4-phenylene groups are freely rotating at 20 °C (ESI†).

The conformational change of the expanded octaphyrin **3** is very fast in solution to give a simple ^{1}H NMR pattern similar to that of **2**; only one singlet for the 1,4-phenylene protons and a pair of quartets for methylene protons. Coordination of four $Rh(CO)_2$ groups to **3** fixes the macrocycle conformation probably in the S_4 symmetric saddle shape. This is evidenced by the ^{1}H NMR spectrum of **5**; two singlets at 7.63 and 8.08 ppm for the 1,4-phenylene protons, two pairs of multiplets due to the diastereotopic methylene protons. Since this spectral pattern in toluene-d_8 was not changed between 80 °C and −60 °C, metal is not moving through the macrocycle of **5** (Fig. 4).

In summary, the expanded rosarin and octaphyrin showed unique coordination chemistry. The Rh_3 complex of the expanded rosarin exists as the C_{3v}-isomer in CH_2Cl_2 as well as in the crystal state, but relatively slow metal transposition passing through macrocycle was observed in the toluene solution to cause interchange between the C_{3v}-isomer and the C_s-isomer. On the other hand, four metals are fixed in the Rh_4 complex of the expanded octaphyrin. This work shows that the highly flexible molecular structure characteristic of big macrocycle can be configurated by metallation, which is the basis for binding large guest molecules and then bringing to cooperative reactions by multiple metals using large porphyrinoids.

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Notes and references

‡ Crystal data for **4** $C_{93}H_{87}N_6O_6Rh_3{\cdot}CHCl_3{\cdot}C_3H_6O$, M = 1870.86, T = 300(2) K, monoclinic, space group $P2_1$, a = 10.3920(6), b = 31.0783(17), c = 14.7868(8) Å, β = 109.9440(10)°, V = 4489.2(4) Å^3, Z = 2, ρ_{calc} = 1.384 g cm^{-3}, μ(Mo-Kα) = 0.692 mm^{-1}, reflections collected: 16261, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0444, wR_2 = 0.1077, R indices (all data) R_1 = 0.0497, wR_2 = 0.1144. CCDC 666201. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717022j

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