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Intermolecular C–H activation to a novel Rh nitrile bridged porphyrin coordination polymer

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Abstract

A novel porphryin coordination polymer, (3′-cyanophenyl)[2,3,7,8,12,13,17,18–5,10,15,20-tetramesitylporphyrinato] rhodium(III) **3**, has been synthesized from the intermolecular C–H activation of the reaction of $RhCl_3$ with porphyrin $H_2(tmp)(Ph)_8$, **1**, in refluxing PhCN and the X-ray structure shows a ziz–zag chain. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: C–H activation; Rhodium; Porphyrin; Coordination polymer

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1. Introduction

Coordination polymers and porphyrin-based polymers have drawn a great deal of attention in the past decade because of their fundamentally important bonding and physical properties [1]. The electronic interactions among chromophores and magnetic centers have been addressed theoretically [2] and potential applications including non-linear optical materials, electrical conductors and magnetic materials have been documented [1,3].

The synthesis of organized molecular assemblies with well defined lattices, orientation and intermolecular interaction remains primitive and a challenge [3a]. Previous synthesis of coordination polymers are exemplified by the metal–nitrido pyridine complexes through metathesis [4] and the acetylide metal complexes [1]. The oxo bridged porphyrin polymer [3a] and the β-fused porphyrin molecular wire serve [5] as classical porphyrin-based polymers. While for porphyrin-based and related coordination polymers, highlights include the bis-nitrogen bridged ruthenium(II) porphyrins [6] and phthalocyanines [7] and the 2-D coordination zinc porphyrin polymers [8]. In the course of studying rhodium and iridium porphyrin chemistry [9], we have discovered a novel intermolecular C–H activation via the reaction of $RhCl_3$ with the non-planar porphyrin $[H_2(tmp)(Ph)_8]$ **1** [10] in refluxing PhCN to give a novel *meta*-cyanophenyl rhodium porphyrin nitrile bridged coordination polymer bearing a ziz–zag chain.

2. Results and discussion

The non-planar porphyrin $H_2(tmp)(Ph)_8$ [10] **1** (tmp is the dianion of 5,10,15,20-tetrakismesityl porphyrin) was reacted with $RhCl_3 \cdot 3H_2O$ in refluxing benzonitrile for 2 days in air to form $ClRh(tmp)(Ph)_8$ **2** and $[(mcph)Rh(tmp)(Ph)_8]_n$ **3** in a 28 and 32% yield, respectively (Eq. (1)). In **3**, not only did we find C–H activation at a *meta* position in PhCN, but also surprisingly a rhodium porphyrin coordination polymer with the CN group coordinated to the axial sixth position of another octahedral Rh molecule. The spectroscopic data obtained are consistent with the formulation of **3**. Proton resonances of the substituted PhCN revealed characteristic high-field shifts ($\delta = 5.99$, 5.34, 2.23, 1.87 ppm). The *meta*-substituted pattern of PhCN was fur-

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ther determined from ^{1}H-^{1}H COSY studies. The IR spectra shows a coordinated CN group with multi-peaks of 2259, 2238, 2225 cm^{-1} which suggested no significant π-bonding with the rhodium metal [11] (ν_{CN} of PhCN = 2229 cm^{-1}) [12].

$$\underset{\mathbf{1}}{H_2(tmp)(Ph)_8} \xrightarrow[\text{48 h reflux}]{RhCl_3\ \ PhCN} \underset{\mathbf{2}\ 28\%}{ClRh(tmp)(Ph)_8} + \underset{\mathbf{3}\ 32\%}{[(mcph)Rh(tmp)(Ph)_8]_n} \qquad (1)$$

The unequivocal structural assignment came from a single-crystal X-ray diffraction analysis (Table 1 and Fig. 1). Red plate crystals of $[(mcph)Rh(tmp)(Ph)_8]_n$ were prepared by slow diffusion of ethanol into a $CHCl_3$ solution. The collection and refinement data are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

The crystal structure was determined by the direct method, which yielded the positions of all non-hydrogen atoms. Refinement of all parameters was not performed because of the limitation of maximum 800 parameters in SHELTXL 97 program [13]. Two block refinements were employed. The new refinement was against $\hat{F}2$ and used all 11 776 reflections, the total number of parameters was 1102, but each cycle only involved 715 parameters as the structure was refined in two blocks. The final R factors were high because the data was weak, as indicated by $R(\sigma) = 0.193$, and the disorder of solvent molecules.

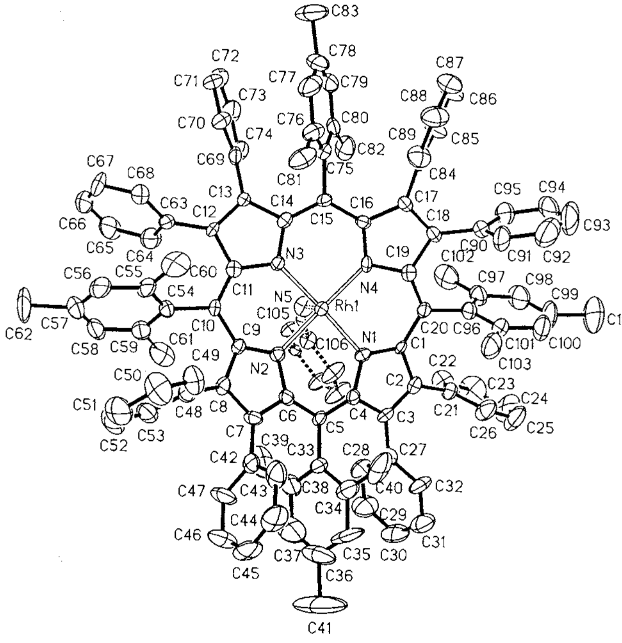

Fig. 1. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogens have been omitted for clarity.

All the non-hydrogen atoms, except the disordered EtOH (O1, C113 and C114), were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H) bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. Empirical absorption corrections were applied by PSI-scan data.

Table 1
Crystal data for compound **3**

Empirical formula	$C_{112.5}H_{91.5}Cl_{1.5}N_{5.0}ORh_{0.5}$
Crystal system	Orthorhombic
Space group	*Pbca* (no 61)
Formula weight	1677.49
Unit cell dimensions	
a (Å)	16.987(5)
b (Å)	31.846(6)
c (Å)	34.490(1)
Z	8
V (Å^3)	18658.0(14)
$D_{calc.}$ (g cm^{-3})	1.194
Crystal size (mm)	0.16 × 0.40 × 0.42
Radiation	M_o–K_α ($\lambda = 0.71073$ Å)
Monochromator	Highly oriented graphite crystal
θ range for data collection (°)	1.68–22.5.0
μ (mm^{-1})	0.278
Reflections collected	12810
No. of unique reflections	11776
No. of variables	1102
R, $R_{w\ (obs\ data)}$	0.0845, 0.1928
G-O-F	1.060
Res extrema in final diff map (e Å^{-3})	+1.216 to −0.377

Table 2
Selected bond lengths (Å) and angles (°) of **3**

Bond length			
Rh(1)–N(1)	2.040(5)	Rh(1)–N(2)	2.020(5)
Rh(1)–N(3)	2.008(5)	Rh(1)–N(4)	2.019(5)
Rh(1)–N(5)	2.2606(5)	Rh(1)–C(108) # 1	1.999(6)
N(5)–C(105)	1.148(8)	C(105)–C(106)	1.464(10)
C(106)–C(107)	1.386(7)	C(107)–C(108)	1.393(7)
C(108)–Rh(1) # 2	1.999(6)		
Bond angle			
C(108) # 1–Rh(1)–N(1)	94.6(2)	C(108) # 1–Rh(1)–N(2)	86.5(2)
C(108) # 1–Rh(1)–N(3)	92.9(2)	C(108) # 1–Rh(1)–N(4)	87.8(2)
N(1)–Rh(1)–N(5)	85.65(14)	N(2)–Rh(1)–N(5)	93.14(15)
N(3)–Rh(1)–N(5)	86.86(14)	N(4)–Rh(1)–N(5)	92.53(14)
N(3)–Rh(1)–N(2)	89.7(2)	N(4)–Rh(1)–N(2)	174.3(2)
N(3)–Rh(1)–N(4)	90.1(2)	N(3)–Rh(1)–N(1)	172.5(2)
C(1)–N(1)–Rh(1)	125.0(4)	C(4)–N(1)–Rh(1)	125.4(5)
C(9)–N(2)–Rh(1)	124.2(4)	C(6)–N(2)–Rh(1)	124.0(5)
C(108) # 1–Rh(1)–N(5)	179.6(2)	C(108) # 1–Rh(1)–N(1)	94.6(2)

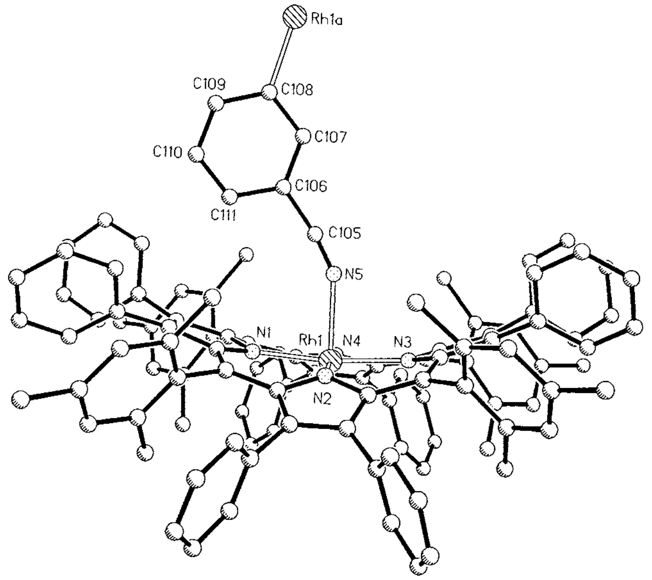

Fig. 2. Coordination perspective of **3**.

The coordination sphere of the rhodium atom shows an octahedral geometry with the four porphyrinato N atoms occupying the equatorial sites and the C and N atoms of two μ-3-cyano-phenyl ligands residing in the axial positions (Figs. 1 and 2). Rhodium resides co-planarly with the porphyrin plane and the four N atoms of the porphyrin deviate alternatively from the porphyrin plane. The bond length between Rh(1) and N(1) is 2.040(5) [11] and Rh(1) and C(108) is 1.999(6) Å, respectively (Table 1) which is typical of a Rh–C bond length in Rh porphyrin complexes [14].

The 3-cyanophenyl group bridges two rhodium centers, thereby generating a zig–zag chain (Fig. 2). The porphyrinato ring exhibits a saddle configuration [15]. The origin of the Rh–N coordination in the solid state remains unclear since other steric less hindered rhodium porphryins do not form nitrile bridged coordination polymer [16]. Inter porphyrin distance is more than 4 Å and therefore any attractive interaction is unlikely. Presumably, this highly non-planar prophryin may promote a more favorable coordination polymerization due to lesser inter porphyrin repulsion.

The formation of the intermolecular C–H activation product **3** most likely comes from the electrophilic aromatic C–H activation of benzonitrile by the rhodium porphyrin cation whose formation from rhodium porphyrin chloride is likely assisted by the highly polar and aprotic benzonitrile solvent [16]. The selective *meta*-substitution of **3** lends further support. Such kind of electrophilic aromatic subsitution with the preformed rhodium porphyrin cation has been reported by Ogoshi [17].

A binding study of **3** with pyridine in dichlorimethane was carried out using UV–Vis spectroscopy to estimate its coordination property in solution. Compound **3** formed a one to one adduct with pyridine in dichloromethane with the log K (K is the equilibrium constant of the adduct formation) estimated to be 7.7 [18]. In view of this rather large binding constant with pyridine, the nitrile coordination is likely to be a weak one which was further supported by the lack of Rh to nitrile back π-bonding in the IR stretching frequency of CN [11].

In conclusion, we have demonstrated that this simple and facile intermolecular C–H activation provides a unique entry to the coordination polymer **3**. Studies are continuing with other arenes.

3. Experimental

IR spectra were recorded on a FT-IR spectrophotometer as neat films on KBr plates. ^{1}H-NMR spectra were recorded on a Bruker WM 250 super-conducting (250 MHZ) spectrometers or a Bruker ARX 500 (500 MHz) spectrometer. Chemical shifts were referenced with TMS $\delta = 0.00$ ppm. Mass spectra were obtained in FAB mode using NBA (*m*-nitrobenzyl alcohol) as the matrix with a Bruker APEX 47e and or in time of flight mode with a Bruker bench TOF Mass Spectrometer. Elemental analysis were performed by Medac Ltd, Department of Chemistry, Brunel University, UK. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Flash chromatography was performed with silica gel (70–230 or 230–400 mesh).

*3.1. [2,3,7,8,12,13,17,18-Octaphenyl-5,10,15,20-tetramesityl-porphyrinato]rhodium(III) chloride (**2**) and (3′-cyanophenyl)[2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetramesitylporphyrinato]rhodium(III) (**3**)*

A sample of H_2(tmp)(Ph)$_8$ (100 mg, 0.072 mmol) and $RhCl_3 \cdot 3H_2O$ (37.9 mg, 0.144 mmol) were refluxed in PhCN (15 ml) in air for 16 h. After removal of the solvent, the reaction mixture was purified by chromatography using a solvent mixture of CH_2Cl_2/hexane (1:1) as the eluent to form **3**. After the faster moving band of **3** was eluted off, the elutent was changed to $CHCl_3$, the second red band of **2** was collected.

*3.1.1. Rh(tmp)(Ph)$_8$Cl (**2**)*

(25.3 mg, 23% yield). $R_f = 0.12$ ($CHCl_3$). ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.69 (s, 12 H), 1.82 (s, 12 H), 1.98 (s, 12 H), 6.00 (m, 8 H), 6.67 (m, 32 H). UV–vis λ_{max} (CH_2Cl_2, nm, log ε): 449.0 (5.16), 552.0 (4.51). HRMS calc. for $RhC_{104}H_{86}N_4Cl$ 1528.5596, found 1528.4519.

*3.1.2. [(mcph)Rh(tmp)(Ph)$_8$]$_n$ (**3**)*

(43 mg, 38% yield). $R_f = 0.32$ (CH_2Cl_2:hexane = 1:1).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.67 (s, 12 H), 1.85 (s, 12 H), 1.87 (s, 12 H), 2.23 (d, 1 H, $J = 8.5$ Hz), 2.27 (s, 1 H) 5.34 (t, 1 H, $J = 7.9$ Hz), 5.97–6.00 (m, 9 H), 6.34 (d, 8 H, $J = 7.5$ Hz), 6.34–6.72 (m, 32 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$) 21.3, 22.42, 121. 4, 125.5, 126.3, 128.2, 128.3, 129.6, 130.1, 135.1, 135.8, 136.7, 138.1, 139.1, 139.2, 143.5, 146.8. TOFMS (matrix: dithranol): 1591 ($M^+ + 2$). Red plates were crystallized from slow diffusion of ethanol into a $CHCl_3$ solution and the sample was vacuum-dried overnight at room temperature before submission for microanalysis. Anal. Calc. for $(C_{104}H_{84}N_4)(C_7H_4N)Rh$: C, 83.59; H, 5.56; N, 4.39. Found: C, 82.21; H, 5.55; N, 4.28. UV–Vis λ_{max} (CH_2Cl_2, nm, log ε): 445.0 (5.09), 548.0 (4.22). IR(film) ν_{CN} (cm^{-1}): 2259, 2238, 2225.

4. Supplementary material available

X-ray diffraction data of **3** has been deposited in the Cambridge Crystallographic Data Centre.

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