Diverse reactivity of rhodium β-(tetraphenyl)tetraphenyl porphyrin chlorides with benzonitrile: formation of Rh porphyrin arene and imine complexes

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Abstract

The reaction of rhodium trichloride with β-(tetraphenyl)tetraphenyl porphyrin, $H_2(tpp)(Ph)_4$, and β-(tetraphenyl)tetrakismesityl porphyrin, $H_2(tmp)(Ph)_4$, in refluxing benzonitrile gave novel rhodium porphyrin chlorides, *m*-cyanophenyl and imine complexes. The *m*-cyanophenyl and imine complexes were formed from chloride complexes by arene C–H activation via electrophilic aromatic substitution and reductive nucleophilic addition with the solvent benzonitrile. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Rhodium porphyrins have been studied widely for their unique structural and chemical reactivities [1–12]. Indeed the chemistry of rhodium[II] and [III] porphyrins are rich and versatile. Rhodium[II] porphyrins form novel non-bridged metal dimers [1,8a], Dimeric and monomeric rhodium[II] porphyrin complexes react with olefins and carbon monoxide to yield insertion products, and with alkylaromatics to yield C–H activation products, all via radical pathways [3,4]. Monomeric rhodium porphyrina undergo novel activation of methane through termolecular transition states [3g]. Rhodium[III] porphyrins serve as molecular recognition templates for amino acids, nucleobases, and self-assembly units [2]. Rhodium[III] porphyrin cations undergo arene C–H activation through electrophilic aromatic substitution [1d,8b]. Rhodium[III] porphyrin hydrides insert into carbon monoxide to give novel stable formyl complexes [3a–c,4]. Rhodium porphyrin halides catalyze cyclopropanation and insertion reactions [5,6]. Structurally and electronically modified complexes would be important for the fine tuning of the reactivity. Consequently, facile preparation of the starting rhodium porphyrin chloride complexes would be most advantageous.

$Rh^I(CO)_2Cl$ reacts with porphyrins in dichloromethane or benzene with subsequent oxidation, to yield rhodium[III] porphyrin chlorides [1,3,11]. Novel rhodium[II] [11] and rhodium[IV] [12] porphyrins have also been isolated depending the solvent of choice in the reaction, and therefore exhibited the rich and diverse chemistry both in the preparation and oxidation states of rhodium porphyrins. Alternatively, when the more accessible rhodium trichloride is employed as the rhodium source in amide solvents such as dimethylformamide or its derviaties [13], a formal C–N activation of the amide bond is observed to yield small amounts of rhodium porphyrin alkyls [13d]. Therefore, the solvent of choice is crucial. We have reported recently that benzonitrile may be used as a solvent for the introduction of rhodium trichloride into porphyrins to yield rhodium porphyrin chlorides. Rhodium porphyrin aryls were also resulted from intermolecular arene C–H activation of the solvent [8b]. We now report further progress in the activation of benzonitrile solvent in the course of the reaction of rhodium trichloride with β-substituted porphyrins [14] to yield both arene activation products and a novel addition product involving the nitrile.

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2. Result and discussion

2.1. Reaction of rhodium porphyrin with PhCN

When β-(tetraphenyl)tetraphenyl porphyrin (**1**), H_2(tpp)(Ph)$_4$ [14b], was reacted with two equivalents of RhCl$_3$ in refluxing benzonitrile for 48 h in air, the expected product ClRh(tpp)(Ph)$_4$ (**2**), the arene C–H activation product (mcph)Rh(tpp)(Ph)$_4$ (**3**), the unexpected nitrile addition product (CNHPh)Rh(tpp)(Ph)$_4$ (**4**), and 2,4,6-triphenyl-1,3,5-triazine (**5**) were obtained in 42, 21, 8 and 47% yields, respectively (Scheme 1). Likewise RhCl$_3$ reacted with sterically hindered β-(tetraphenyl)tetrakismesitylporphyrin (**6**), H_2(tmp)(Ph)$_4$ [14c] to give ClRh(tmp)(Ph)$_4$(**7**), and (mcph)Rh(tmp)-(Ph)$_4$ (**8**), in 42 and 20% yields, respectively (Scheme 2). All rhodium porphyrin complexes were isolated and separated by silica gel chromatography in air.
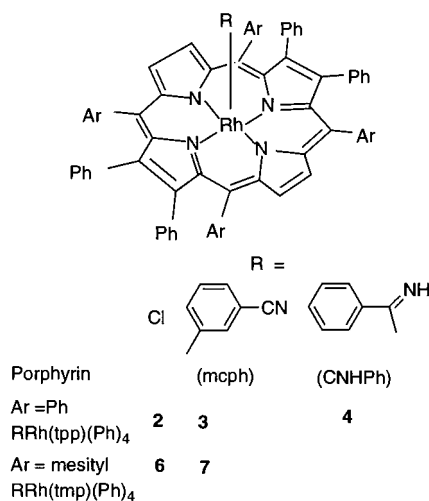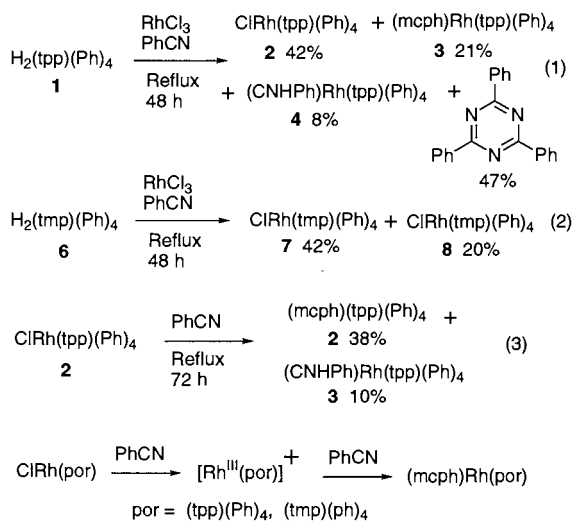
2.2. Spectroscopic characterization of rhodium porphyrins

The rhodium porphryins were well-characterized by spectroscopic methods. The infrared absorption of **3** and **8** at 2222 and 2223 cm^{-1}, respectively confirmed the presence of a CN group while that of **4** at 1727, 3390 cm^{-1} supported C=N and N–H stretching frequencies, respectively and therefore an imine group. Porphyrin complexes **3** and **8** showed high-field aromatic proton resonances of the *meta*-cyanophenyl group ($\delta = 1.07$, 1.09, 5.05, and 5.64 ppm and 1.18 (overlapped signals), ~4.90, and 5.63 ppm, respectively) due to porphyrin ring current effect in their ^{1}H-NMR spectra.

The ^{1}H-NMR of **3** showed that an ethanol molecule coordinated weakly to the rhodium atom. Two signals at 1.03 and 3.38 ppm were assigned to the methyl and methylene protons of coordinated EtOH, respectively. When a CDCl$_3$ solution of **3** was left at RT for a month, a new spectrum in CDCl$_3$ of the same solid was taken. These two singals disappeared.

The structures of **3** and **4** were further established by single crystal X-ray crystallography. Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre (Section 5). Raw data intensities were collected on a Rigaku RAXIS-II camera with rotating source (50 kV 90 mA) at room temperature (293 K). The structures were solved by direct method, and all non-hydrogen atoms were located on an E-map. All computations were performed using SHELXTL PC program package on a PC 486 computer [15,16]. Reddish–brown plate crystals of (mcph)Rh(tpp)(Ph)$_4$ (**3**) and red blocks crystals of (CNHPh)Rh(tpp)(Ph)$_4$ (**4**) were prepared by slow diffusion of ethanol into CHCl$_3$ solution. The collection and refinement data for **3** and **4** are listed in Table 1. The selected bond lengths and angles are listed in Tables 2 and 3, respectively.

The molecular structure and atomic labellings for (mcph)Rh(tpp)(Ph)$_4$ are shown in Fig. 1. The Rh atom is displaced 0.03 Å from the mean plane of porphyrin ring and displaced 0.05 Å from the four nitrogen atoms plane. The average distance of Rh–N is 2.005 Å for non-substituted pyrrole and 2.060 Å for substituted pyrrole. The N–C$_\alpha$ bond length is also affected by rhodium insertion (average bond length 1.383 Å for rhodium complex, 1.371 Å for porphyrin ligand). The distance between C$_{45}$ and C$_{51}$ is 2.992 Å, and that of C$_{51}$ and C$_{57}$ is 2.988 Å with paralleling arrangement. The largest deviation relative to the mean plane of four pyrrole rings is at C$_5$ (0.13 Å), whereas N$_3$ lies approximately above the mean plane by about 0.008 Å.

The dihedral angles between *meso*-phenyl plane and the mean porphyrin plane are 91.7, 83.5, 91.8 and

Scheme 1.

Scheme 2.

Table 1
Crystal data for compound **3** and **4**

Formula	$(C_{68}H_{44}N_4)$ (C_6H_4CN) $(C_2H_5OH)Rh$	$(C_{68}H_{44}N_4)$ $(C_6H_5CNH)Rh$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	P1 (no. 2)
Formula weight	1168.2	1124.1
a (Å)	22.25690(8)	13.736(1)
b (Å)	11.9499(6)	13.846(1)
c (Å)	24.8388(9)	15.855(2)
α (°)		101.64(1)
β (°)	115.392(3)	100.81(1)
γ (°)		101.58(1)
Z	4	1
$F(000)$	2516	7008
V (Å^3)	5868.7(4)	2814.1(14)
$D_{calc.}$ (g cm^{-3})	1.300	1.327
Crystal size (mm)	$0.05 \times 0.12 \times 0.12$	$0.05 \times 0.12 \times 0.12$
Diffrractometer	Rigaku RAXIS-II	Rigaku RAXIS-II
Radiation	Mo–K$_\alpha$ $(\lambda = 0.71073$ Å$)$	Mo–K$_\alpha$ $(\lambda = 0.71073$ Å$)$
Monochromator	Graphite	Graphite
No. of unique reflections	10774	10088
No. of reflections	5228 $(I > 3\sigma)$	7312 $(I > 6\sigma)$
No. of variables	748	726
R, R_w (observed data)	0.057, 0.050 [a]	0.052, 0.052 [b]
Goodness-of-fit	2.13	1.56
largest and mean shift (σ)	0.004, −0.001	0.12, 0.01
Res extrema in final difference map (e Å^{-3})	+0.70 to −0.53	+0.52 to −0.63

[a] $w = [\sigma^2|F_o| + 0.001|F_o|^2]^{-1}$.
[b] $w = [\sigma^2|F_o| + 0.0001|F_o|^2]^{-1}$. $\quad R = \Sigma|F_o| - |F_o|/\Sigma|F_o|$, $\quad wR = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and bond angles (°) of (mcph)Rh(tpp)(Ph)$_4$ (**3**)

Bond lengths

Rh(1)–N(1)	2.073(6)	Rh(1)–N(2)	2.010(5)
Rh(1)–N(3)	2.046(6)	Rh(1)–N(4)	1.998(5)
Rh(1)–O(1)	2.349(7)	Rh(1)–C(69)	1.985(9)
N(1)–C(3)	1.376(11)	N(1)–C(6)	1.378(7)
N(2)–C(8)	1.386(7)	N(2)–C(11)	1.374(11)
N(3)–C(13)	1.394(10)	N(3)–C(16)	1.403(7)
N(4)–C(1)	1.379(11)	N(3)–C(18)	1.373(8)
C(1)–C(2)	1.397(10)	C(1)–C(20)	1.443(9)
C(2)–C(3)	1.390(8)	C(2)–C(21)	1.496(13)
C(3)–C(4)	1.463(10)	C(4)–C(5)	1.366(10)

Bond angles

N(1)–Rh(1)–N(2)	90.1(2)	N(1)–Rh(1)–N(3)	176.4(3)
N(2)–Rh(1)–N(3)	89.6(2)	N(1)–Rh(1)–N(4)	90.1(2)
N(1)–Rh(1)–C(69)	90.3(3)	N(2)–Rh(1)–C(69)	93.2(3)
N(3)–Rh(1)–C(69)	88.2(2)	N(4)–Rh(1)–C(69)	88.5(3)

91.8, 83.5, 81.7, 71.9°, respectively. The eight phenyl groups are in a parallel arrangement. The dihedral angles between NC$_4$ pyrroles and mean plane are 3.6, 0.2, 2.8 and 6.7°, respectively. The dihedral angle between benzonitrile and mean plane is 96°. The selected bond lengths and bond angles are given in Table 2.

The molecular structure and atomic labellings for (CNHPh)Rh(tpp)(Ph)$_4$ (**4**) are shown in Fig. 2. The Rh atom is displaced by 0.07 Å from the mean plane of porphyrin ring which is longer than that of (mcph)Rh(tpp)(Ph)$_4$ (0.03 Å). The average distance of Rh–N is 2.015 Å for non-substituted pyrrole and 2.056

Table 3
Selected bond lengths (Å) bond angles (°) of (CNHPh)Rh(tpp)(Ph)$_4$ (**4**)

Bond lengths

Rh(1)–N(1)	2.057(3)	Rh(1)–N(2)	2.017(4)
Rh(1)–N(3)	2.055(3)	Rh(1)–N(4)	2.012(4)
Rh(1)–C(75)	1.963(5)		

Bond angles

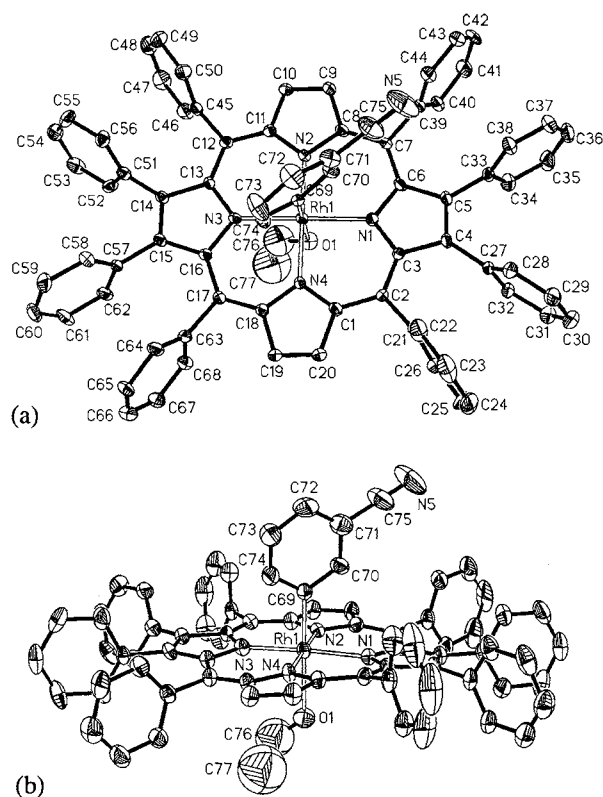|			
N(1)–Rh(1)–N(2)	89.7(1)	N(1)–Rh(1)–N(3)	177.9(2)
N(2)–Rh(1)–N(3)	90.0(1)	N(1)–Rh(1)–N(4)	89.9(1)
N(2)–Rh(1)–N(4)	171.0(2)	N(3)–Rh(1)–N(4)	90.0(1)
N(1)–Rh(1)–C(75)	93.3(2)	N(2)–Rh(1)–C(75)	99.9(2)
N(3)–Rh(1)–C(75)	88.9(2)	N(4)–Rh(1)–C(75)	89.1(2)

(a)

(b)

Fig. 1. (a). Molecular structure and atomic labelings of (mcph)-Rh(tpp)(Ph)$_4$. (b) Edge-on view plot of the skeleton of (mcph)-Rh(tpp)(Ph)$_4$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

83.5°, respectively (Fig. 1). The dihedral angles between β-substituted phenyls and the porphyrin mean plane are
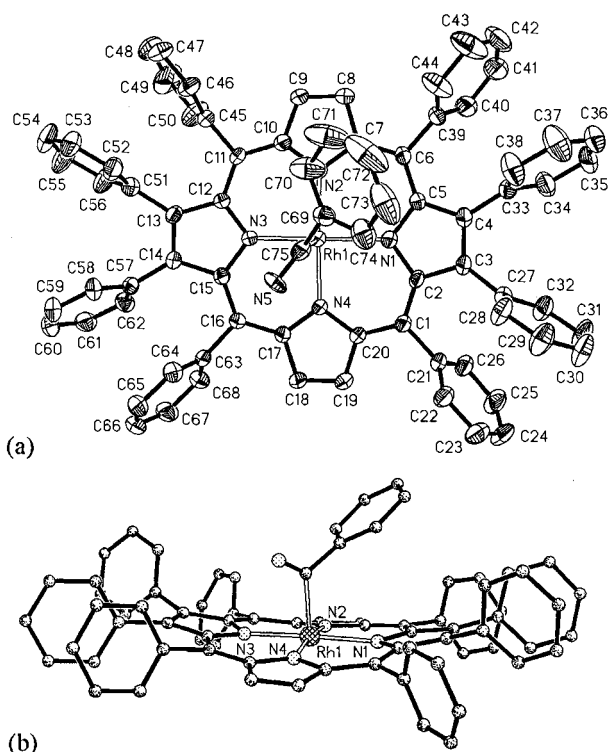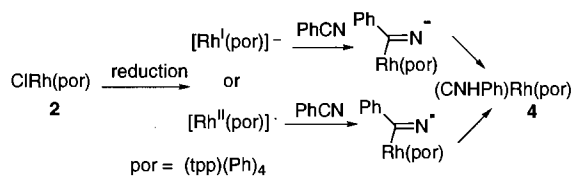
Fig. 2. (a). Molecular structure and atomic labellings of (CNHPh)-Rh(tpp)(Ph)₄. (b). Edge-on view plot of the skeleton of (CNHPh)-Rh(tpp)(Ph)₄ Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

Scheme 3.

Å for substituted pyrrole. Insertion of rhodium into the β-substituted porphyrins decreases the porphyrin core size more compared with that of β-substituted porphyrin. The N–C_α bond length was also shortened by rhodium inserting (average bond length of 1.383 Å in rhodium complex, 1.371 Å in porphyrin ligand). The largest deviations relative to the mean plane of four pyrrole rings is at C_{13} (0.42 Å), whereas N_3 lies approximately above the mean plane by about 0.03 Å. The atom deviations from the mean plane in PhCN are larger than those of (mcph)Rh(tpp)(Ph)₄, which showed larger deviation than that of (mcph)Rh(tpp)(Ph)₄. The selected bond lengths and bond angles are given in Table 3.

The dihedral angles between *meso*-phenyl and the porphyrin mean plane are 71.2, 79.4, 109.6, and 74.7°, respectively. The dihedral angles between β-substituted phenyls and mean plane are 108.0, 79.9, 104.2, and 108.9°, respectively. The dihedral angles between NC₄ pyrroles and mean plane are 9.6, 5.5, 9.5 and 10.1°, respectively. The dihedral angle between benzonitrile and mean plane is 96°.

The bond length between Rh(1) and C(69) is 1.985 Å in **3** and Rh(1) and C(75) is 1.963 Å in **4**. These are typical of a Rh–C bond distance and are somewhat shorter than a Rh–C(sp³) bond length [11,17].

From the arrangements of the porphyrins in the unit cells of **3** and **4**, the porphyrins pack in parallel layers. The closest center to center approach of the porphyrin rings is 10.55 Å for **3** and 4.20 Å for **4**. The least-square distances between two layers are 5.00 Å for **3** and 5.62 Å for **4**. The intermolecular contacts of **3** and **4** are greater than 4 Å [18]. Therefore, no evidence for π–π interaction between neighboring molecules was found in these structures. This indicates that the observed planarity and non-planarity [18] does not arise from crystal packing forces but from a minimization of steric repulsions between the peripheral phenyl rings. The conformation of the macrocycle and the tilting of the phenyl rings into the porphyrin plane effectively minimize unfavorable contacts between the peripheral substituents.

2.3. Mechanistic reaction

meta-Cyanophenyl rhodium complexes **3** and **8** were likely formed via a S_EAr pathway from the selective carbon hydrogen activation of the PhCN at a *meta*-position with **2** and **7** [8b]. When **2** was refluxed in PhCN either in air or under nitrogen for 48 h, **3** and **4** were formed in 38 and 10% yield, respectively supporting that **2** is an intermediate for the formation of **3** and **4** (Fig. 2). Assisted by the highly polar and donating PhCN, **2** likely ionized into Rh[III] porphyrin cation before its electrophilic reaction with PhCN [1d] (Scheme 2). Furthermore, the *meta*-substituted pattern is typical of an electrophilic substitution product of an electron deficient arene [1d].

Possible C–H activation of other arenes was invesitgated. ClRh(tpp)(Ph)₄ (**2**) was refluxed with toluene, pyridine or anisole, but no reactions occurred with **2** recovered only. As the proposed reaction intermediate carries a positive charge, a polar solvent favors its formation. PhCN serves both as a good solvent and reagent since it is a high boiling and highly polar solvent that can stabilize intermediates well.

Co(tpp)Cl was dissolved and refluxed in benzonitrile for 72 h both in air and under nitrogen, no desired C–H activation product was obtained. Co(tpp)Cl was recovered in 96% yield. Presumably, the ionization of cobalt porphyrin chloride to cobalt porphyrin cation is less favorable than that of rhodium porphyrins.

The origin of the formation of **4** is less clear. The formation of **4** from **2** in refluxing PhCN both in air or under nitrogen (Scheme 3) suggests that **2** was possibly

reduced to give either rhodium(I) or rhodium(II) porphyrins. A preliminary experiment of the reduction of **3** by Na/Hg in toluene with subsequent reaction with PhCN yielded small amount of **4**. The highly nucleophilic rhodium(I) porphyrins [1b,c] added to the electrophilic nitrile carbon and subsequent protonation yielded **4**. Alternatively, the rhodium(II) porphyrin radical [1b,d,e] generated added to the nitrile carbon to give nitrogen centered radical; subsequent hydrogen atom abstraction yielded **4**.

The formation 2,4,6-triphenyl-1,3,5-triazine, might be due to the catalytic trimerization of PhCN either by HCl generated in the ligand substitution reaction [19] or a rhodium complex.

Beta substituents of porphyrins do not seem to affect the yields of the formation of rhodium porphyrin chlorides and aryl rhodium porphyrins (Scheme 2). The formation of imine **4** seems to be unique to **2**. Other beta-substituted planar or non-planr porphyrins produced no imine product [8b].

The formation of novel rhodium porphyrins in various solvent have been reported and exihibit diverse chemcial reactivities. Rhodium[II] [11] and rhodium[IV] [12] porphyrins have been formed in acetic acid and benzene when [Rh^I(CO)$_2$Cl]$_2$ was reacted with tetraphenyl porphyrin. Oxidation of rhodium[I] porphyrin insertion intermediate [1a–b] to rhodium[II] [12] likely accounts its formation. Electrophilic aromatic substitution of resultant rhodium[III] porphyrin with benzene might account the formation of rhodium[IV] complex [11]. Novel reaction of a rhodium[III] porphyrin chloride with boiling diethylacetamide yielded ethyl rhodium porphyrin via the interemediacy of aminoethyl rhodium porphyrin [13d]. While the mechanism of these novel chemistry remains unclear, the rich chemistry of rhodium porphyrins with solvents to yield rhodium(II), (III), and (IV) species exists.

3. Conclusion

We have discovered that RhCl$_3$ reacted with porphyrins in refluxing benzonitrile to yield rhodium aryl and imine complexes **3** and **4**. Rhodium porphyrin aryls were formed from arene C–H activation from the reaction of rhodium porphyrin chlorides with benzonitrile solvent. The imine complex **4** was formed likely from a reduced rhodium porphyrin for only the chloride complex **2**.

4. 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 tetramethylsilane $\delta = 0.00$ ppm. Mass spectra were obtained in FAB mode using *m*-nitrobeznyl alcohol (NBA) as the matrix with a Bruker APEX 47e Mass Spectrometer. Elemental analysis were performed by the 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).

4.1. Synthesis of rhodium porphyrin complexes: (2,3,5,10,12,13,15,20-octaphenylporphyrinato)-(3-cyanophenyl)rhodium(III) chloride (2), (2,3,5,10,12, 13,15,20-octaphenylporphyrinato)-(3-cyanophenyl)-rhodium(III) (3) and (2,3,5,10,12,13,15,20-octaphenyl-porphyrinato)(α-phenylimine) rhodium(III) (4)

H$_2$(tpp)(Ph)$_4$ (100 mg, 0.109 mmol) and RhCl$_3$·3H$_2$O (57.5 mg, 0.218 mmol) were refluxed in PhCN (15 ml) in air for 48 h. After removal of the solvent, the reaction mixture was purified by chromatography using a solvent mixture of CH$_2$Cl$_2$–hexane (2:1) as the eluent and the different fractions were collected for **2**, **3**, and **4**. ClRh(tpp)(Ph)$_4$ (**2**) (48 mg, 42% yield). $R_f = 0.12$ (hexane: CH$_2$Cl$_2$ = 2:1). ^{1}H-NMR(250 MHz, CDCl$_3$) δ 5.46 (t, 2 H, $J = 6.7, 7.2$ Hz), 6.48 (d, 2 H, $J = 7.5$ Hz), 6.84–7.24 (m, 32 H), 7.57 (bs, 4 H), 7.80 (bs, 4 H), 8.39 (s, 4 H). Anal. Calc. for RhC$_{68}$H$_{44}$N$_4$Cl·3H$_2$O: C, 73.61; H, 4.54; N, 5.05. Found: C, 73.80; H, 4.60; N, 5.21. UV–vis λ_{max} (CH$_2$Cl$_2$, nm, log ε): 436.0 (5.08), 545.0 (4.13), 582.0 (3.49). FABMS (matrix: NBA) m/e: 1020 (M$^+$–Cl). (mcph)Rh(tpp)(Ph)$_4$ (**3**) (26 mg, 21% yield). $R_f = 0.48$ (hexane: CH$_2$Cl$_2$ = 2:1). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 1.03 (t, 3 H, $J = 6.9$ Hz, cordinated Me group of EtOH), 1.07 (s, 1 H), 1.09 (d, 1 H, $J = 9.3$ Hz), 3.38 (q, 2 H, $J = 6.7$ Hz, cordinated methylene group of EtOH), 5.05 (t, 1 H, $J = 7.8$ Hz), 5.64 (d, 1 H, $J = 7.5$ Hz), 6.70–6.82 (m, 17 H), 7.02–7.21 (m, 15 H), 7.58 (d, 4 H, $J = 7.4$ Hz), 7.74 (d, 4 H, $J = 7.2$ Hz), 8.31 (s, 4 H). Anal. Calc. for RhC$_{75}$H$_{48}$N$_5$·C$_2$H$_5$OH: C, 79.17; H, 4.66; N, 5.99. Found: C, 78.86; H, 4.60; N, 5.94. FABMS (matrix: NBA) m/e: 1122.1 (M$^+$ + 1). UV–vis λ_{max} (CH$_2$Cl$_2$, nm, log ε): 426.0 (5.13), 531.0 (4.20). IR(film) v_{CN} (cm^{-1}): 2222. (CNHPh)Rh(tpp)(Ph)$_4$, **4**. (6 mg, 48% yield). $R_f = 0.86$ (hexane: CH$_2$Cl$_2$ = 1: 2). ^{1}H NMR (250 MHz, CDCl$_3$) δ 2.94 (d, 2 H, $J = 7.9$ Hz), 3.50 (bs, 1 H) 6.21 (t, 2 H, $J = 7.8$ Hz), 6.59 (t, 1 H, $J = 7.4$ Hz), 6.81–6.93 (m, 21 H), 7.07–7.23 (m, 11 H), 7.62 (d, 4 H, $J = 7.4$ Hz), 7.70 (d, 4 H, $J = 7.0$ Hz), 8.28 (s, 4 H). Anal. Calcd for RhC$_{75}$H$_{50}$N$_5$H$_2$O: C, 78.87; H, 4..62; N, 5.91. Found: C, 78.87; H, 4.59; N, 6.13. FABMS (matrix: NBA) m/e: 1124 (M$^+$). UV–vis λ_{max} (CH$_2$Cl$_2$, nm, log ε): 425.0 (4.92), 531.0(4.01), 644.0 (3.03). IR(film) v_{CNH} (cm^{-1}): 1462, 1727, 3390.

4.2. (2,3,12,13-Tetrakis-phenyl-5,10,15,20-tetra-mesitylporphyrin)(3-cyanophenyl)rhodium(III) chloride (7) and (2,3,12,13-tetrakis-phenyl-5,10,15,20-tetra-mesitylporphyrin)(3-cyanophenyl) rhodium(III) (8)

$H_2(tmp)(Ph)_4$ (90 mg, 0.083 mmol) and $RhCl_3 \cdot 3H_2O$ (60 mg, 0.207 mmol) were refluxed in PhCN (15 ml) in air for 48 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 and the different fractions were collected for **7** and **8**. $ClRh(tmp)(Ph)_4$ (**7**) (43 mg, 42% yield). $R_f = 0.10$ (hexane:$CH_2Cl_2 = 1:2$). ^1H-NMR (250 MHz, $CDCl_3$) δ 1.81 (s, 12 H), 2.21 (s, 24 H), 6.48–6.62 (m, 8 H), 6.90 (s, 20 H), 8.42 (s, 4 H). UV–vis λ_{max} (CH_2Cl_2, nm, log ε): 435.0 (5.27), 544.0 (4.91). HRMS: Anal. Calc. for $RhC_{80}H_{70}N_4Cl$ and $RhC_{80}H_{70}N_4Cl$–Cl, 1224.4344 and 1189.4655. Found 1224.3782 and 1189.4358. (mcph)-$Rh(tmp)(Ph)_4$ (**8**) (45 mg, 42% yield). $R_f = 0.36$ (hexane:$CH_2Cl_2 = 1:2$). $Rh[tmp(Ph)_4](m\text{-PhCN})$: ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.18 (s, 12 H), 1.92 (br s, 2 H), 1.93 (s, 12 H), 2.20 (s, 12 H), 4.87–4.93 (unresolved dd, 1 H), 5.63 (d, 1 H, $J = 7.5$ Hz), 6.56 (br s, 8 H), 6.75–6.94 (m, 21 H), 8.24 (s, 4 H). UV–vis λ_{max} (CH_2Cl_2, nm, log ε): 427.0 (5.22), 533.0 (4.49). HRMS: Anal. Calc. for $C_{87}H_{72}N_5H^+$ 1290.4921. Found 1290.4833. FABMS (NBA) m/e: 1290.5 (M^+). IR(film) ν_{CN} (cm^{-1}): 2223.

4.3. Reaction of 3 in benzonitrile ClRh(tpp)(Ph)₄

Complex **2** (50 mg, 0.0473 mmol) was refluxed in benzonitrile (15 ml) for 48 h. During the reaction, **4** appeared firstly, as detected by TLC. After removal of the solvent, the reaction mixture was purified by chromatography using a solvent mixture of CH_2Cl_2–hexane (2:1) as the eluent and the fractions for **3**, $R_f = 0.36$ (CH_2Cl_2:hexane = 2:1), (20 mg, 38% yield) and **4** $R_f = 0.68$ (CH_2Cl_2:hexane = 2:1), (5.5 mg, 10.3% yield).were collected.

5. Supplementary material

X-ray diffraction data (crystal and data collection parameters, positional parameters, and intramolecular distances and angles) for **3** [CCDC 133535] and **4** [CCDC 133534] have been deposited in Cambridge Crystallographic Data Centre.

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