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Note

# Synthesis of rhodium porphyrin aryls via intermolecular arene carbon-hydrogen bond activation

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### Abstract

(*meta*-Cyanophenyl) rhodium porphyrins have been synthesized from the selective activation of a *meta* carbon-hydrogen bond of PhCN via the reaction of RhCl<sub>3</sub> with porphyrins in refluxing PhCN. © 1998 Elsevier Science S.A.

Keywords: Crystal structures; Rhodium complexes; Aryl complexes; Porphyrin complexes

The chemistry of rhodium and iridium porphyrins has aroused continuous interest. The unique chemical reactivities of non-bridged metal-metal dimers [1,2] and sterically hindered monomers [3] have been demonstrated in C-H activation [3], insertion into olefins [2,4] and in the fourelectron catalytic electrochemical reduction of dioxygen [5]. We would like to investigate the chemistry of rhodium and iridium porphyrins using  $\beta$ -substituted porphyrins [6]. In the course of the preparation of rhodium porphyrin chlorides with porphyrins, we have discovered an intermolecular arene C-H activation process in benzonitrile. Our initial attempt to prepare rhodium porphyrin chlorides as versatile intermediates to other rhodium porphyrins by refluxing the mixture of RhCl<sub>3</sub> and porphyrins in DMF has encountered problems of incomplete reaction, difficult separation of products and low yields of desired products [7]. Our earlier success of using benzonitrile (PhCN) as a high boiling solvent in preparing Pt porphyrins [8,9] has prompted us to employ it in preparing rhodium porphyrins<sup>1</sup>.

## 1. Results and discussion

## 1.1. Intermolecular arene C-H activation

In PhCN, the metalation went smoothly to give good yields of rhodium porphyrin chlorides together with the unexpected C-H activation products, *meta*-cyanophenyl rhodium porphyrins. They were separated by column chromatography in air. For example, when [H2(ttp)] (1) was refluxed with RhCl<sub>3</sub>·3H<sub>2</sub>O in PhCN in air for 72 h (Eq. (1)), the desired Rh(ttp)Cl (2) was obtained in 60% yield, together with the *meta*-cyanophenyl rhodium complex Rh(ttp)(mcph) (3) isolated in 28% yield. Octaethylporphyrin  $[H_2(oep)]$  (4) and dodecaphenyl porphyrin [H2(dpp)] (7) [10] likewise yielded the corresponding chlorides 5 and 6 and aryls 8 and 9 (Eq. (1), Scheme 1 and Table 1).

$$H_2 P \rightarrow Rh(P)Cl + Rh(P) (mcph)$$
(1)  
reflux

$$\frac{\text{PhCN}}{2} \xrightarrow{\text{PhCN}} \text{Rh}(\text{ttp})(\text{mcph})$$
(2)

Rhodium porphyrin chlorides were formed from the uneventful ligand substitution of free base porphyrins with RhCl<sub>3</sub>. The intermolecular C-H activated arene products probably came from the electrophilic aromatic substitution of PhCN with Rh porphyrin chlorides. Firstly, the *meta*-sub-

 Table 1

 The yields and reaction times of rhodium porphyrins

Porphyrin	Reaction time (h)	Yield (%)	
		(p)RhCl	(p)Rh(mcph)
$H_2(ttp)$ 1	72	2 (60)	3 (28)
$H_2(oep)$ 4	72	5 (58)	6 (31)
H <sub>2</sub> (dpp) 7	36	8 (46)	9 (20)

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<sup>&</sup>lt;sup>1</sup> [5,10,15,20-Tetratkis (4-methylphenyl)porphyrin] =  $H_2(ttp)$ ; (2,3,7, 8,12,13,17,18-octaethylporphyrin) =  $H_2(oep)$ ; (2,3,5,7,8,10,12,13,15,17, 18,20-dodecaphenylporphyrin) =  $H_2(dpp)$ ;  $H_2(p)$  = porphyrin; (mcph) = meta-cyanophenyl anion.

Table 2



stitution pattern is typical of the S<sub>E</sub>Ar product of an electrondeficient arene. Secondly, after refluxing the solution of **2** in PhCN for 72 h, **3** was obtained in 32% yield (Eq. (2)). The intermediacy of **2** is thus established. Rh(ttp)Cl possibly ionized into [Rh(ttp)]<sup>+</sup> with the assistance of the highly polar PhCN solvent. Furthermore, a precedence of this type of electrophilic aromatic substitution of aromatics with a preformed rhodium porphyrin cation has been reported by Ogoshi [11].

Red blocks of crystals of Rh(oep)(mcph) **6** were prepared by slow diffusion of ethanol into CHCl<sub>3</sub> solution. **6** is a fivecoordinate Rh-porphyrin without any nitrile group coordination from another molecule. The Rh-C distance is 2.0005(12) Å [12] (Fig. 1, Tables 2 and 3). The individual NC4 pyrrole rings are nearly planar. The dihedral angles between pyrrole rings and the mean plane of the porphryin ring are 4.2, 7.1, 4.1 and 3.9°. The dihedral angle between cyanophenyl ring and the mean plane of the porphryin ring



Fig. 1. ORTEP drawing of 6. Thermal ellipsoids are drawn at the 35% probability level. Hydrogen has been omitted for clarity.

Formula	C₄3H₄ <sub>8</sub> N₅Rh	
Formula weight	737.8	
Crystal system	monoclinic	
Space group	РĪ	
a (Å)	12.992(3)	
b (Å)	13.134(3)	
c (Å)	13.497(3)	
α (°)	86.21(3)	
γ(°)	65.84(3)	
V (Å <sup>3</sup> )	1842.5(9)	
Z	2	
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	0.501	
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.330	
Size (mm)	0.2×0.26×0.30	
Temperature (K)	293	
Diffractometer	Siemens R3m/V	
Monochromator	graphite	
Scan type	ω	
Wavelength λ (Å)	0.71073	
Radiation	Μο Κα	
$2\theta$ scan limits (°)	3.0-48.0	
Scan speed (° min <sup>-1</sup> )	4.98-29.3	
No. reflections collected	6102	
No. independent reflections	$5812 (R_{int} = 3.24\%)$	
No. observed reflections	$3476(F > 4.0\sigma(F))$	
No. parameters	442	
Method	Full-matrix least-squares	
R <sub>f</sub> (%)	5.60	
R(wF) (%)	5.79, $w^{-1} = \sigma^2(F) + 0.00002F^2$	

Table 3

Selected bond lengths (Å) and bond angles (°) of RhOEP  $\cdot$  mPhCN (6)

Bond lengths			
Rh(1)N(1)	2.028(8)	Rh(1) - N(2)	2.046(6)
Rh(1)-N(3)	2.040(8)	Rh(1) - N(4)	2.026(5)
Rh(1)-C(42)	2.005(12)	N(1)-C(1)	1.390(11)
N(1) - C(4)	1.378(10)	N(2)-C(6)	1.360(11)
N(2)-C(9)	1.401(12)	N(3)-C(11)	1.385(11)
N(3)-C(14)	1.357(11)	N(4) - C(16)	1.384(11)
N(4)-C(19)	1.362(11)	C(1) - C(2)	1.444(14)
Bond angles			
N(1)-Rh(1)-N(2)	89.8(3)	N(1)-Rh(1)-N(3)	176.6(4)
N(2)-Rh(1)-N(3)	90.5(3)	N(1)-Rh(1)-N(4)	89.8(3)
N(2)-Rh(1)-N(4)	174.3(4)	N(3)-Rh(1)-N(4)	89.5(3)
N(1)-Rh(1)-N(4)	91.9(4)	N(2)-Rh(1)-C(42)	93.0(3)
N(3)-Rh(1)-C(42)	91.5(4)	N(4)-Rh(1)-C(42)	92.7(3)
Rh(1)-N(1)-C(1)	128.1(5)	Rh(1)-N(1)-C(4)	126.4(5)
C(1)-N(1)-C(4)	105.4(7)	Rh(1)-N(2)-C(6)	126.2(6)
Rh(1)-N(2)-C(9)	126.6(6)	C(6)-N(2)-C(9)	106.8(6)
Rh(1)-N(3)-C(11)	124.6(6)	Rh(1)-N(3)-C(14)	127.3(6)
C(11)-N(3)-C(14)	108.1(8)	Rh(1)-N(4)-C(16)	126.5(5)
Rh(1)-N(4)-C(19)	127.1(5)	C(16)-N(4)-C(19)	106.1(6)

is 88.7°. The largest deviation relative to the mean plane of four pyrrole rings is at C-17 (0.18 Å). The distances between ethyl carbons are 3.235 Å (C-33 and C-35) and 4.192 Å (C-34 and C-36). The ethyl groups are arranged with up, up, down, down order. The largest distance between the carbon and the mean plane is 1.7 Å. The distance of the Rh(III) ion from the mean plane of the porphyrin is 0.053 Å.

In summary, we have shown that rhodium trichloride reacted with porphyrins and benzonitrile to give intermolecular C-H arene activation product. Further studies of the arene activations with porphyrins and the coordination properties of the cyano group are being carried out.

## 2. Experimental

## 2.1. General

IR spectra were recorded on a Fourier transform IR spectrophotometer using neat films on KBr plates. <sup>1</sup>H NMR spectra were recorded on a Bruker WM250 (250 MHz) spectrometer and chemical shifts were referenced with tetramethylsilane ( $\delta = 0.00$  ppm). Mass spectra were obtained either in EI mode at 70 eV or in FAB mode using *m*-nitrobenzyl alcohol (NBA) as the matrix with a JEOL JMS-HX 110 mass spectrometer at the National Tsing Hua University in Taiwan. Elemental analyses were performed by Medac Ltd., Department of Chemistry, Brunel University, UK. Flash chromatography was performed with silica gel (70-230 or 230-400 mesh).

# 2.2. [5,10,15,20-Tetratkis (4-methylphenyl)porphyrinato]-(3-cyanophenyl)rhodium(III) chloride (2) and [4-methylphenyl)porphyrinato](3-cyanophenyl)rhodium(III)(3)

 $H_2(ttp)$  (1) (100 mg, 0.149 mmol) and RhCl<sub>3</sub>·3H<sub>2</sub>O (79 mg, 0.298 mmol) were refluxed in PhCN (15 ml) in air for 72 h. 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 different red fractions were collected for 2 and 3 which were further recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH. Rh(ttp)Cl (2) [13] (72 mg, 60% yield).  $R_f = 0.12$  (hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2). <sup>1</sup>H NMR  $(CDCl_3) \delta 2.70 (s, 12 H), 8.07 (d, 8 H, J=7.5 Hz), 8.20$ (d, 8 H, J = 7.5 Hz), 8.94 (s, 8 H). UV–Vis  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>, nm,  $\log \epsilon$ ): 428.0 (5.25), 539.0 (4.39), 575.0 (4.16). Rh(ttp)(mcph) (3) (36 mg, 28% yield).  $R_f = 0.28$  (hexane: $CH_2Cl_2 = 1:2$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta 0.37$  (s, 1 H), 0.42 (d, 1 H, J = 8.0 Hz), 2.68 (s, 12 H), 4.79 (t, 1 H, J = 7.7 Hz),5.48 (d, 1 H, J = 6.6 Hz), 7.52 (d, 8 H, J = 7.6 Hz), 7.96– 8.04 (m, 8 H), 8.78 (s, 8 H). Anal. Calc. for RhC<sub>55</sub>H<sub>40</sub>N<sub>5</sub>·H<sub>2</sub>O: C, 74.07; H, 4.75; N, 7.85. Found: C, 73.67; H, 4.58; N, 7.78%. FAB-MS (NBA) m/e: 1426.4  $(M^+)$ . UV-Vis  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>, nm, log  $\epsilon$ ): 414.0 (5.16), 522.0 (4.31). IR (film)  $\nu_{\rm CN}$  (cm<sup>-1</sup>): 2222.

# 2.3. (2,3,7,8,12,13,17,18-Octaethylporphyrinato)(3-cyanophenyl) rhodium(III) chloride (5) and (2,3,7,8,12,13,17,18octaethylporphyrinato)(3-cyanophenyl)rhodium(III) (6)

 $H_2(\text{oep})$  (4) (60 mg, 0.112 mmol) and RhCl<sub>3</sub>·3H<sub>2</sub>O (59 mg, 0.225 mmol) were refluxed in PhCN (15 ml) in air for 72 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 red fractions were collected for 5 and 6 which were further recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH. Rh(oep)Cl (5) [1] (43 mg, 58% yield).  $R_f = 0.08$  (hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2). <sup>1</sup>H NMR  $(\text{CDCl}_3) \delta 1.92 (t, 24 \text{ H}, J = 7.5 \text{ Hz}), 4.07-4.16 (m, 16 \text{ H}),$ 10.1 (s, 4 H). UV-Vis  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>, nm, log  $\epsilon$ ): 403.0 (5.16), 519.0 (4.18), 550.0 (4.45). Rh(oep)(mcph) (6)(26 mg, 31% yield).  $R_f = 0.67 \text{ (hexane: CH<sub>2</sub>Cl<sub>2</sub> = 1:2)}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta - 0.20$  (s, 2 H), 1.89 (t, 24 H, J = 7.6 Hz),  $3.94-4.15 (m, 16 H), 4.53 (\approx t, 1 H J = 7.6 Hz), 5.27 (1 H,$ d, J = 7.3 Hz), 10.14 (4 H, s). Anal. Calc. for RhC<sub>43</sub>-H<sub>48</sub>N<sub>5</sub>·0.5C<sub>2</sub>H<sub>5</sub>OH: C, 69.46; H, 6.76; N, 9.20. Found: C, 69.88; H, 7.00; N, 8.37%. UV–Vis  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>, nm, log  $\epsilon$ ): 393.0(5.21), 508.0(4.43), 542.0(4.83). EIMS  $m/e: (M^+)$ 738.3. IR(film)  $\nu_{CN}$  (cm<sup>-1</sup>): 2221.

2.4. (2,3,5,7,8,10,12,13,15,17,18,20-Dodecaphenylporphyrinato)rhodium(III) chloride (8) and (2,3,5,7,8, 10,12,13,15,17,18,20-dodecaphenylporphyrinato)-(3-cyanophenyl)rhodium(III) (9)

 $H_2(dpp)$  (7) (72 mg, 0.059 mmol) and RhCl<sub>3</sub>·3H<sub>2</sub>O (31 mg, 0.118 mmol) were refluxed in PhCN (15 ml) in air for 36 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 red fractions were collected for 8 and 9 which were further recrystallized from  $CH_2Cl_2/EtOH$ .  $Rh(dpp)Cl \cdot C_5H_5CN$  (8) (36.7 mg, 46% yield).  $R_f = 0.08 \text{ (hexane: CH}_2\text{Cl}_2 = 1:1)$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.27 (t, 1 H, J = 6.8 Hz), 5.41 (d, 1 H, J = 8.1 Hz, 6.01 (d, 1 H, J = 7.4 Hz), 6.44–6.90 (m, 48 H), 7.17–7.91 (m, 12 H). UV–Vis  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>, nm, log  $\epsilon$ ): 450.0 (5.35), 552.0 (4.75). HRMS calc. for RhC<sub>92</sub>H<sub>62</sub>N<sub>4</sub>Cl  $(M^+ - PhCN)$  1360.3718, found 1360.3330. Rh(dpp)-(mcph) (9) (28 mg, 33% yield).  $R_f = 0.33$  (hexane:  $CH_2Cl_2 = 1:1$ ). <sup>1</sup>H NMR (2CDCl\_3)  $\delta$  2.10 (m, 1 H), 5.42 (t, 1 H, J=8.3 Hz), 6.02 (d, 1 H, J=7.7 Hz), 6.30-6.50(bs, 7 H), 6.50-6.70 (m, 45H), 7.18 (d, 4 H, J = 7.8 Hz),7.36 (d, 4 H, J = 6.9 Hz), Anal. Calc. for RhC<sub>99</sub>H<sub>64</sub>N<sub>5</sub> · 2.5C<sub>2</sub>H<sub>5</sub>OH: C, 81.02; H, 5.16; N, 4.54. Found: C, 80.76; H, 4.76; N, 4.65%. UV–Vis  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>, nm,  $\log \epsilon$ ): 447.0 (5.25), 553.0 (4.65), 587.0 (4.56). FABMS (matrix: NBA) m/e: 1426.4 ( $M^+$ ). IR (film)  $\nu_{CN}$  (cm<sup>-1</sup>): 2223.

### 3. Supplementary material

Tables of atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, hydrogen atom positions, and structure factors for 6 are available from the authors.

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