1,2-Rearrangements of β-Nitrogen Substituted Porphyrinatorhodium(III) Ethyls

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Supporting Information

Contents:

(1) Experimental instrumentation:

All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Benzene was distilled from sodium. Dichloromethane and hexanes for reaction were distilled from calcium hydride. Hexanes for chromatography were distilled from anhydrous calcium chloride. *N,N*-Dimethylformamide (DMF) was distilled from magnesium sulfate under reduced pressure.[1]

Thin layer chromatography was performed on Merck pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) and neutral aluminium oxide (Merck, activity I, 170-230 mesh) were used for column chromatography.

^{1}H NMR spectra were recorded on a Brüker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), tetrakistrimethylsilysilane ($(TMS)_4Si$, δ

0.00 ppm) or with C_6D_6 (δ 7.15 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS or $(TMS)_4Si$. ^{13}C NMR spectra were recorded on a Brüker DPX 300 (75 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.00 ppm). Coupling constants (*J*) were reported in Hertz (Hz). High resolution mass spectra (HRMS) were performed on a Thermofinnign MAT 95 XL (FABMS).

(2) General procedures:

(a) Preparation of 2-bromoethylamine[2] [(2-Bromoethyl)-*N,N*-dibenzylamine as an example]

(2-Hydroxyethyl)-*N,N*-dibenzylamine[3] (178 mg, 2.00 mmol) was dissolved in cyclohexane (15 mL). *N,N*-dimethylformamide (0.10 mL, 1.2 mmol) and thionyl bromide (0.19 mL, 2.4 mmol) were added successively under a nitrogen atmosphere. The yellow reaction mixture, separated into two layers, was then stirred for 3 h at room temperature. The reaction suspension was diluted with dichloromethane until it became homogeneous, then the pale yellow solution was neutralized with saturated $NaHCO_3$ solution. The organic layer was washed with water (3 x 5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford the desired (2-bromoethyl)-N,N-dibenzylamine as a yellow liquid (0.24 g, 1.58 mmol, 78%). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.86 (t, 2 H, *J* = 7.6 Hz), 3.31 (t, 2 H, *J* = 7.6 Hz), 3.64 (s, 4 H), 7.21-7.39 (m, 10 H).

***N*-(2-Bromoethyl)-pyrrolidin-2-one.**[2] A yellow liquid (0.24 g, 1.26 mmol, 49%). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.03 (q, 2 H, *J* = 7.8 Hz), 2.43 (t, 2 H, *J* = 7.9 Hz), 3.48 – 3.57 (m, 4 H), 3.69 (t, 2 H, *J* = 6.3 Hz).

(b) Preparation of Porphyrinatorhodium(III) Alkyls [Rh(por)R]: General procedure.[4]

(5,10,15,20-Tetratoylporphyrinato)2-(N-phthalimido)ethyl rhodium(III) (**1a**) by reductive alkylation of Rh(ttp)Cl was described as a typical example for the preparation of porphyrinatorhodium(III) alkyl complex.

A suspension of Rh(ttp)Cl[5] (150 mg, 0.186 mmol) in EtOH (50 mL) and a solution of $NaBH_4$ (28.2 mg 0.743 mmol) in aq NaOH (0.1 M, 3 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannular. The solution mixture was heated at 50 ˚C under N_2 for 1 h to give a brown suspension. The solution was then cooled to 30 ˚C under N_2 and *N*-(2-Bromoethyl)phthalimide (360 mg , 1.2 mmol) was added. A reddish orange suspension was formed. After stirred at room temperature for another 15 min under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250 - 400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (4:1) as the eluent. The major orange fraction was collected and gave reddish orange solid (101 mg, 1.07 mmol, 71%) as the product after rotary evaporation. The product was further purified by recrystallization from CH_2Cl_2/CH_3OH. R_f = 0.59 (hexane/CH_2Cl_2 = 1:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ -5.05 (dt, 2 H, $^2J_{Rh\text{-}H}$ = 3.0 Hz, $^3J_{H\text{-}H}$ = 9.0 Hz), -2.39 (t, 2 H, *J* = 9.0 Hz), 2.69 (s, 12 H), 7.08(d, 2 H, *J* = 9.0 Hz), 7.19(dd, 2 H, *J* = 3.0, 6.0 Hz), 7.51 (t, 8 H, *J* = 6.0 Hz), 8.04 (dd, 8 H, *J* = 3.0, 9.0 Hz), 8.78 (s, 8 H); HRMS (FABMS):

Calcd for $(C_{58}H_{44}N_5O_2Rh)^+$: m/z 945.2545. Found: m/z 945.2495. Anal. Calcd for $C_{59}H_{45}Cl_3N_5O_2Rh\cdot H_2O$: C, 72.27; H, 4.60; N, 7.27. Found C, 72.12; H, 4.52; N, 7.05.

(5,10,15,20-Tetratoylporphyrinato)-2-(*N*-pyrrolidin-2-onyl)ethyl Rhodium(III) (2a). Reddish orange solids (50%). ^{1}H NMR (C_6D_6, 300 MHz) δ -5.10 (dt, 2 H, $^2J_{Rh\text{-}H}$ = 3.2 Hz, $^3J_{H\text{-}H}$ = 9.2 Hz), -2.70 (t, 2 H, *J* = 8.7 Hz), -0.27 (q, 2 H, *J* = 7.7 Hz), 0.57 (t, 2 H, *J* = 8.1 Hz), 1.07 (p, 2 H, *J* = 4.0 Hz), 2.15 (s, 12 H), 7.03 (d, 4 H, *J* = 7.4 Hz), 7.09 (d, 4 H, *J* = 7.5 Hz), 7.95 (t, 8 H, *J* = 9.2 Hz), 8.76 (s, 8 H); HRMS (FABMS): Calcd for $(C_{54}H_{46}N_5ORh)^+$: m/z 883.2752. Found: m/z 883.2692. Anal. Calcd for $C_{54}H_{46}N_5ORh\cdot CH_3OH$: C, 70.73; H, 5.61; N, 7.50. Found C, 70.97; H, 5.29; N, 7.45.

(5,10,15,20-Tetratoylporphyrinato)-2-(*N,N*-dibenzylamino)ethyl Rhodium(III) (3a). Red solid (39%) ^{1}H NMR (C_6D_6, 300 MHz) δ -4.74 (dt, 2 H, $^2J_{Rh\text{-}H}$ = 3.0 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz), - 3.43 (t, 2 H, *J* = 7.8 Hz), -1.31 (s, 4 H), 2.17 (s, 12 H), 5.71 (d, 4 H, *J* = 6.8 Hz), 6.53 – 6.62 (m, 6 H), 7.03 (d, 8 H, *J* = 7.8 Hz), 7.66 (d, 4 H, *J* = 7.6 Hz), 7.90 (d, 4 H, *J* = 7.7 Hz), 8.66 (s, 8 H); HRMS (FABMS): Calcd for $(C_{64}H_{54}N_5Rh)^+$: m/z 996.3507. Found: m/z 996.3417. Anal. Calcd for $C_{64}H_{54}N_5Rh\cdot CH_3OH$: C, 75.94; H, 5.69; N, 6.81. Found C, 76.11; H, 5.46; N, 6.74.

(5,10,15,20-Tetratoylporphyrinato)-1-(*N*-phthalimido)ethyl Rhodium(III) (1b). Complex **1b** was purified by column chromatography over silica gel (250 - 400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (4:1) as the eluent after **1a** (10 mg, 0.015 mmol) was heated in anhydrous benzene for 1 month. The major orange fraction was collected and gave reddish orange solid (4 mg, 0.004 mmol 42%) as product after rotary evaporation. The product was further purified by recrystallization from

CH_2Cl_2/CH_3OH. R_f = 0.58 (hexane/CH_2Cl_2 = 1:1); ^{1}H NMR (C_6D_6, 300 MHz) δ -3.56 (d, 3 H, J = 6.9 Hz), -1.51 (dt, 1 H, $^2J_{Rh-H}$ = 2.7 Hz, $^3J_{H-H}$ = 6.6 Hz), 2.43 (s, 12 H), 6.66-6.95 (m, 2 H), 6.85-6.95 (m, 2 H), 7.29 (d, 8 H, J = 7.9 Hz), 8.01 (d, 4 H, J = 7.6 Hz), 8.18 (d, 4 H, J = 7.5 Hz), 8.98 (s, 8 H); HRMS (FABMS): Calcd for $(C_{58}H_{44}N_5O_2Rh)^+$: m/z 945.2545. Found: m/z 945.2571.

(5,10,15,20-meso-Tetrakis(3,5-di-*t*-butylphenyl)porphyrinato)-2-(*N*-phthalimido)ethyl Rhodium(III) (5a). Red solid (65%) ^{1}H NMR (C_6D_6, 300 MHz) δ -4.91 (dt, 2 H, $^2J_{Rh-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.5 Hz), - 2.26 (t, 2 H, J = 9.0 Hz), 1.51 (s, 36 H), 1.56(s, 36 H), 7.04-7.07 (m, 4 H), 7.19-7.22 (m, 4 H), 7.75 (t, 4 H, J = 3.0 Hz), 8.05-8.07 (m, 8 H), 8.81 (t, 8 H); HRMS (FABMS): Calcd for $(C_{86}H_{100}N_5O_2Rh)^+$: m/z 1337.6927. Found: m/z 1337.6915. Anal. Calcd for $C_{86}H_{100}N_5O_2Rh{\cdot}CH_3OH$: C, 76.23; H, 7.65; N, 5.11. Found C, 76.53; H, 7.46; N, 5.09.

(5,10,15,20-meso-Tetrakis(3,5-di-*t*-butylphenyl)porphyrinato)2-(*N,N*-dimethylamino)ethyl Rhodium(III) (7a). Reddish orange solid (68%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ -4.87 (dt, 2 H, $^2J_{Rh-H}$ = 3.0 Hz, $^3J_{H-H}$ = 9.0 Hz), - 3.73 (t, 2 H, J = 9.0 Hz), 0.32 (s, 6H), 1.51 (s, 72 H), 7.76 (t, 4 H, J = 3.0 Hz), 7.95 (t, 4 H, J = 3.0 Hz), 8.07 (t, 4 H, J = 3.0 Hz), 8.76 (s, 8 H); Anal. Calcd for $C_{80}H_{102}N_5Rh{\cdot}CH_3OH$: C, 76.68; H, 8.42; N, 5.52. Found C, 76.69; H, 8.31; N, 5.42.

(5,10,15,20-Tetratoylporphyrinato)-2-aminoethyl Rhodium(III) (4). Complex **4** was described as a typical example for the preparation of porphyrinatorhodium(III) alkyl complex.

Red suspension of Rh(ttp)Cl(PhCN) (103 mg, 0.113 mmol) in THF (50 mL) was heated at 50 ^{o}C for 1 h under N_2. After cooled to room temperature, $NaBH_4$ (32 mg, 0.84 mmol) in 0.1 M NaOH (2 mL) and the suspension were purged with N_2 separately for about 15 min. The $NaBH_4$ solution was then added dropwisely to the suspension for about 30 min. The suspension turned to brown in color. The brown suspension was heated to 50-60 ^{o}C for 1 h. Aziridine (0.5 ml) was then added through a syringe after the reaction mixture was cooled to 0 ^{o}C. The reaction mixture turned to red in color immediately. The crude product was extracted from CH_2Cl_2 (100 mL). The organic extract was dried over Na_2SO_4, filtered and rotary evaporated to driness. An reddish-orange solid (64 mg, 67%) was obtained after rotary evaporation. ^{1}H NMR (C_6D_6, 300 MHz) δ -5.76-5.87 (m, 2 H), - 3.98-4.10 (m, 2 H), 1.51 (s, 36 H), 2.17(s, 12 H), 6.88-6.91(m, 4 H), 7.04-7.06 (m, 4 H), 7.03-7.75(m, 8 H), 8.32(t, 8 H); Anal. Calcd for $C_{50}H_{42}N_5Rh\cdot(1/2)CH_3OH$: C, 72.92; H, 5.33; N, 8.42. Found C, 73.09; H, 5.18; N, 8.13.

(5,10,15,20-meso-Tetrakis(3,5-di-*t*-butylphenyl)porphyrinato)-2-aminoethyl Rhodium(III) (6a). Reddish orange solid (65%). ^{1}H NMR (C_6D_6, 300 MHz) δ -5.08 (dt, 2 H, $^2J_{Rh\text{-}H}$ = 3.0 Hz, $^3J_{H\text{-}H}$ = 8.0 Hz), - 3.16 (t, 2 H, J = 9.0 Hz), 1.19 (s, 36 H), 1.23(s, 36 H), 7.70 (t, 4 H, J = 1.5 Hz), 8.11 (t, 4 H, J = 3.0 Hz), 8.15 (t, 4 H, J = 1.5 Hz), 8.84 (s, 8 H); HRMS (FABMS): Calcd for $(C_{78}H_{98}N_5Rh)^+$: m/z 1207.6872. Found: m/z 1207.6875. Anal. Calcd for $C_{78}H_{98}N_5Rh\cdot CH_3OH$: C, 76.23; H, 7.65; N, 5.11. Found C, 76.53; H, 7.46; N, 5.09.

Bis-(5,10,15,20-Tetratoylporphyrinatorhodium(III)) Ethane Rh(ttp)CH_2CH_2(ttp)Rh (8).[6] A suspension of Rh(ttp)Cl[5] (97 mg, 0.106 mmol) in

EtOH (50 mL) and a solution of $NaBH_4$ (34 mg 1.06 mmol) in aq NaOH (0.1 M, 3 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannular. The solution mixture was heated at 50 ˚C under N_2 for 1 h to give a brown suspension. The solution was then cooled to 30 ˚C under N_2 and 1,2-dichloroethane in 10 mL EtOH was added dropwisely. A reddish orange suspension was formed. After stirred at room temperature for 1 day under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250 - 400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (2:1) as the eluent. The major orange fraction was collected and gave reddish orange solid (51mg, 0.032 mmol, 31%) as the product after rotary evaporation. The product was further purified by recrystallization from CH_2Cl_2/CH_3OH. ^{1}H NMR ($CDCl_3$, 300 MHz) δ -10.61 (s, 2 H), 2.72 (s, 12 H), 7.22 (d, 4 H, J = 6.0 Hz), 7.39 (t, 8 H, J = 6.0 Hz), 7.69 (d, 2 H, J = 6.0 Hz), 8.19 (s, 8 H); HRMS (FABMS): Calcd for $(C_{96}H_{76}N_8Rh_2)^+$: m/z 1571.4376. Found: m/z 1571.4399.

(c) 1,2-Rearrangement Reaction of Porphyrinatorhodium(III) β-Aminoalkyl Complexes.

[Rh(por)R] (recrystallized from CH_3OH/CH_2Cl_2, 0.01 mmol) was dissolved in anhydrous benzene-d_6 (0.40 mL) in an NMR tube. Tetrakis(trimethylsilyl)silane (1

mg) was added as the internal standard for NMR integration. The solution was degassed for three freeze-thaw pump cycles and the NMR tube was flame sealed under high vacuum. The solution was protected from light and heated in an oil bath. The progress of the reaction was monitored by ^{1}H NMR and the composition of the reaction mixture was determined by NMR integration with reference to tetrakis(trimethylsilyl)silane.

(d) Reactions of Porphyrinatorhodium(III) Alkyls with Styrene at 80^{o}C. General procedure. A solution of Rh(por)R (0.005mmol) in freshly distilled C_6D_6 (0.4 mL) was mixed with vacuum-distilled styrene (7.8 mg, 0.075 mmol) in an NMR tube. The mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was flame sealed under high vacuum. The reaction was protected from light and heated to 80^{o}C. The progress of the reaction was monitored by ^{1}H NMR.

(3) Thermal reaction

(a) Thermal reaction of (5,10,15,20-Tetratoylporphyrinato)-2-(*N*-phthalimido)ethyl Rhodium(III) (1a)

The isomeric ratios converged at about 31 days with secondary complex **1b** being the favored isomer. The secondary / primary ratio was found to be 7.8.

(b) Thermal reaction of (5,10,15,20-Tetratoylporphyrinato)-1-(N-phthalimido)ethyl Rhodium(III) (1b)

The reversibility of the rearrangement of complex **1a** was established by the backward reaction of the secondary complexes **1b**.

The isomeric ratios converged at about 27 days with secondary 1-*N*-phthalimide ethyl complex **1b** being the favored isomer. The secondary / primary ratio is 6.9 which similar obtained as those from the primary complexes.

(c) (5,10,15,20-Tetratoylporphyrinato)-2-(*N*-pyrrolidin-2-onyl)ethyl Rhodium(III) (2a).

The isomeric ratios converged at about 8 hours with secondary 1-*N*-pyrrolidinonyl ethyl complex **2b** being the favored isomer at 90^{o}C. The secondary / primary ratio was found to be 19.2.

(d) (5,10,15,20-Tetratoylporphyrinato)-2-(*N,N*-dibenzylamino)ethyl rhodium(III) (3a).

The isomeric ratios converged at about 11 hours with secondary complex **3b** being the favored isomer at 80^{o}C. The secondary / primary ratio was found to be 992.

(e) (5,10,15,20-Tetratoylporphyrinato)-2-aminoethyl Rhodium(III) (4).

The ^{1}H NMR showed the integration of the methylene proton was decreased slowly at 80^{o}C without the formation of secondary isomer. All the starting material was consumed after heating for 3h. A peak at _ -10.58 (s) was formed and MS was found to be 1570 which the same as complex **8.** Complex **8** was found in 11 % NMR yield.

(f) (5,10,15,20-meso-Tetrakis(3,5-di-*t*-butylphenyl)porphyrinato)-2-(N-phthalimido)ethyl Rhodium(III) (5a).

The isomeric ratios converged at about 1275 hours with secondary complex **5b** being the favored isomer at 120^{o}C. The secondary / primary ratio was found to be 6.

(g) (5,10,15,20-meso-Tetrakis(3,5-di-*t*-butylphenyl)porphyrinato)-2-aminoethyl Rhodium(III) (6a).

The isomeric ratios converged at about 45 hours with secondary complex **6b** being the favored isomer at 80^{o}C. The secondary / primary ratio was found to be 4.

(h) (5,10,15,20-meso-Tetrakis(3,5-di-*t*-butylphenyl)porphyrinato)-2-(*N,N*-dimethylamino)ethyl Rhodium(III) (7a).

Complex 7b was observed as the only isomer after heating at 60^{o}C for 5 minutes.

(4) X-ray data and structure

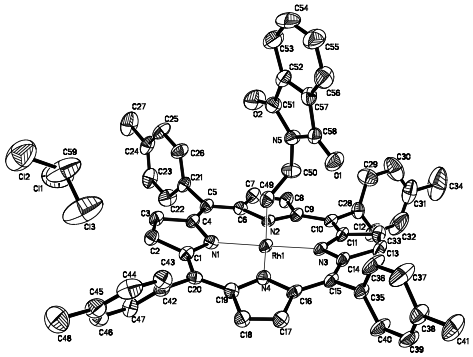


Figure 1. The structure of **1a**, showing the atomic labelling scheme and 30% probability displacement ellipsoids. Selected bond lengths (Å) Rh1–C49 2.032(10).

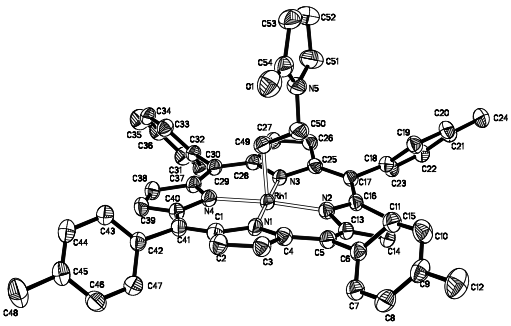


Figure 2. The structure of **2a**, showing the atomic labelling scheme and 30% probability displacement ellipsoids. Selected bond lengths (Å) Rh1–C49 2.043(5).

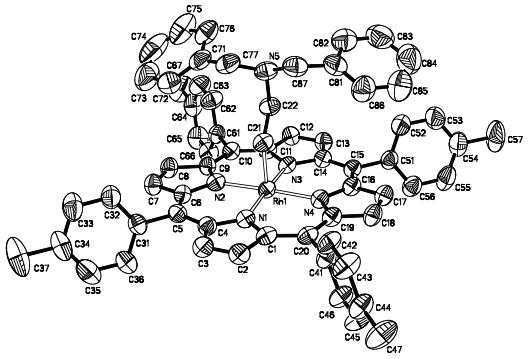
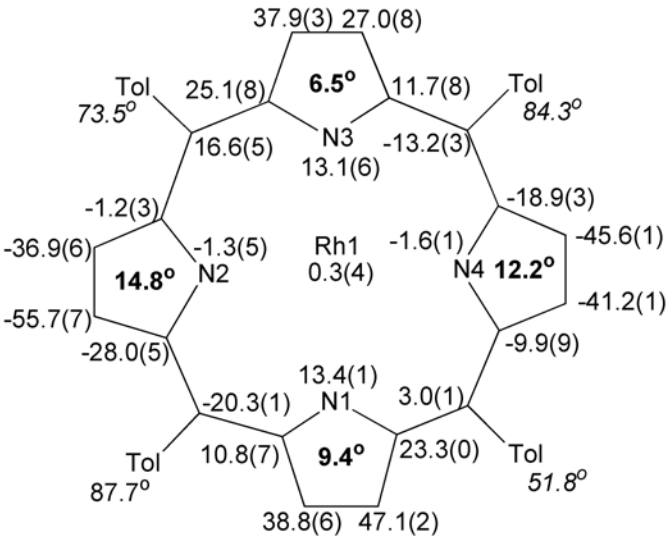


Figure 3. The structure of 3**a**, showing the atomic labelling scheme and 30% probability displacement ellipsoids. Selected bond lengths (Å) Rh1–C21 2.064(7).

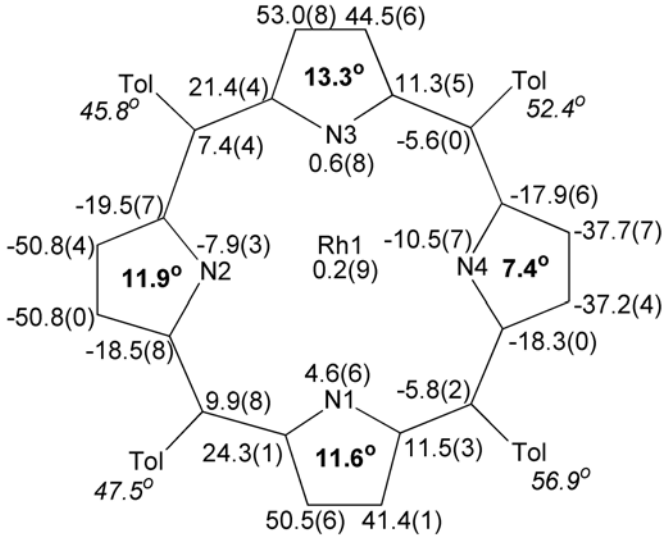
	1a	**2a**	**3a**
color, shape	Red prism	Red prism	Red prism
empirical formula	$C_{59}H_{45}N_5O_2Rh$	$C_{54}H_{46}N_5ORh$	$C_{64}H_{54}N_5Rh$
formula wt	1065.26	883.87	996.03
Temp (K)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	P2(1)/c
unit cell dimens			
a (Å)	12.9274(15)	13.263(3)	13.838(3)
b (Å)	13.2281(16)	13.699(3)	27.970(6)
c (Å)	15.4074(17)	143462(3)	15.520(3)
α (deg)	97.937(3)	94.28(3)	90
β (deg)	91.704(3)	100.58(3)	96.20(3)

γ (deg)	92.349(2)	113.76(3)	90
Volume (Å^3)	2605.6(5)	2331.5(8)	5972(2)
Z	2	2	4
Calcd density (g cm^{-3})	1.358	1.259	1.108
abs coeff (mm^{-1})	0.529	0.409	0.325
F(000)	1092	916	2072
cryst size (mm)	0.566 x 0.291 x 0.215	1.40 x 0.60 x 0.40	0.50 x 0.30 x 0.20
θ range for data collection (deg)	1.56 to 28.06	1.65 to 25.68	1.51 to 25.25
limiting indices	$-17 \le h \le 16$	$-16 \le h \le 14$	$0 \le h \le 15$
	$-17 \le k \le 16$	$0 \le k \le 15$	$-32 \le k \le 33$
	$-10 \le l \le 20$	$-17 \le l \le 17$	$-18 \le l \le 17$
no. of rflns collected/ unique	17896/12413 [*R*(int) = 0.0627]	7725,7725 [*R*(int) = 0.0000]	14242,8474 [*R*(int) = 0.0553]
completeness to θ = 28.24	98.2%	87.3%	78.2%
absorp corr	SADABS	ABSCOR	ABSCOR
max. and min. transmn	1.000 and 0.5403	1.038 and 0.938	0.9378 and 0.8542
refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
no. of data/ restraints/ params	12413/0/631	7725/0/550	8474/ 0/ 631
GOF	0.963	1.110	1.176
final *R* indices [*I*>2_(*I*)]	R1 = 0.0979	R1 = 0.0661	R1 = 0.0827
	wR2 = 0.2547	wR2 = 0.2192	wR2 = 0.2190
R indices (all data)	R1 = 0.2207	R1 = 0.0671	R1 = 0.1063
	wR2 = 0.3306	wR2 = 0.2214	wR2 = 0.2377
largest diff peak and hole (e Å^{-3})	1.372 and -0.853	2.060 and -0.852	0.615 and -0.730

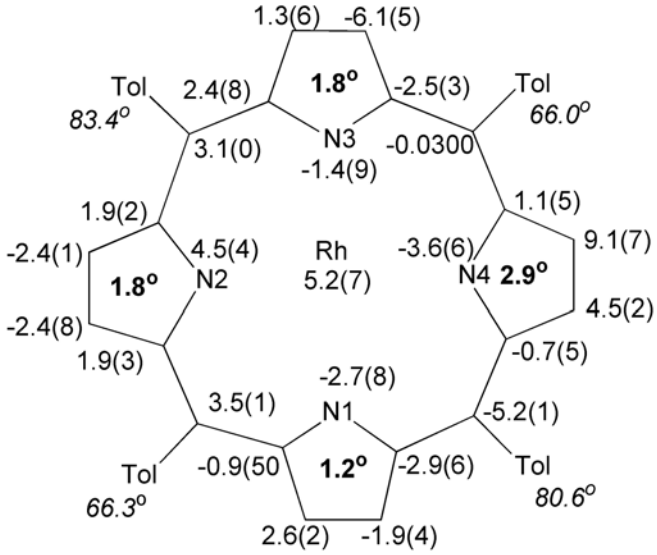
Table 1. Crystal data and structure refinement parameters for **1a, 2a, 3a**



complex **1a**



Complex **2a**



complex **3a**

Figure 4. The conformation of the porphyrin in **1a, 2a** and **3a**, showing the displacements of the core atoms and of Rh from the 24-atom least-squares plane of the prophyrin core (in pm; positive values correspond to displacement towards the β-aminoethyl ligands). Absolute values of the angles between the pyrrole rings and the least-squares plane of the 24-atom porphyrin core are shown in bold, and absolute values of the angles between the least-squares plane of the phenyl substituents and the 24-atom least-squares plane are shown in italics.

(5) References:

1. Perrin, D. D.; Armarego, L. F. *Purification of Laboratory Chemicals*, 3rd Ed. Pergamon Press: U.K., 1988.
2. Schwerdtfeger, J.; Kolczewski, S.; Weber, B.; Frohlich, R.; Hoppe, D. *Synthesis* **1999**, *9*, 1573-1592.
3. Nagle, A. S.; Salvatore, R. N.; Chong, B. D.; Jung, K. W. *Tetrahedron Lett.* **2000**, *41*, 3011-3014.
4. Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461-6466.
5. Buchler, J. W.; Dreher, C.; Künzel, F. M. *In Metal Complexes with Tetrapyrrole Ligands III: Structure and Bonding, vol. 84*; Bucher, J. W., Ed.; Springer-Verlag: Berln Heidelberg, 1995.
6. Collman, J. P.; MacLaury, R. *J. Am. Chem. Soc.* **1974**, *96,* 3019-3020.