Rhodium(I), rhodium(III) and iridium(III) carbaporphyrins

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Experimental

Carbaporphyrin **2a** was prepared by a literature procedure.¹ All other reagents were purchased from Aldrich or Acros and were used without further purification. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded using a 500 MHz NMR spectrometer and were run at 300 K unless otherwise indicated. ¹H NMR values are reported as chemical shifts δ , relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak) and coupling constant (*J*). Chemical shifts are reported in parts per million (ppm) relative to CDCl₃ (¹H residual CHCl₃ δ 7.26, ¹³C CDCl₃ triplet δ 77.23) and coupling constants were taken directly from the spectra. NMR assignments were made with the aid of ¹H-¹H COSY, HSQC, DEPT-135 and nOe difference proton NMR spectroscopy. 2D experiments were performed using standard software. The UV-Vis spectra were collected on a Cary 100 Bio spectrophotometer. High-resolution mass spectra (HRMS) were carried out using a double focusing magnetic sector instrument.



[8,12,13,17-Tetraethyl-7,18-dimethylbenzo[b]-21-carbaporphyrinato](dicarbonyl)-

rhodium(I) (9). Anhydrous sodium acetate (113.3 mg, 1.381 mmol) and $[Rh(CO)_2Cl]_2$ (53.7 mg, 0.138 mmol) were added to a solution of benzocarbaporphyrin **2a** (69.0 mg, 0.138 mmol) in dichloromethane (150 mL), and the resulting mixture was refluxed with stirring under nitrogen overnight. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica column eluting with 20% dichloromethane-hexanes. A broad dirty green

band was collected, the solvent evaporated, and the residue was recrystallized from chloroformhexanes to give **9** (81.4 mg, 0.1238 mmol, 90%) as dark green crystals, mp 220-222 °C; IR (KBr) v_{CO} 2065, 1998 cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} (log ε) 368 (4.67), 480 (4.84), 559 (3.99), 626 nm (3.73); ¹H NMR (500 MHz, CDCl₃): δ -5.52 (1H, s, 21-H), -2.54 (1H, br s, NH), 1.67 (3H, t, J =7.7 Hz), 1.78-1.83 (9H, 3 overlapping triplets) (4 x CH₂CH₃), 3.50 (3H, s, 7-CH₃), 3.62 (3H, s, 18-CH₃), 3.77-4.02 (4H, m), 4.04-4.12 (4H, m) (4 x CH₂CH₃), 7.66-7.73 (2H, m, 2²,3²-H), 8.71 (1H, d, , J = 7.1 Hz, 3¹-H), 8.80 (1H, d, , J = 7.1 Hz, 2¹-H), 9.78 (1H, s), 9,82 (1H, s) (10,15-H), 10.03 (1H, s, 20-H), 10.29 (1H, s, 5-H); ¹³C NMR (125 MHz, CDCl₃): δ 11.5 (18-CH₃), 12.3 (7-CH₃), 17.4, 17.5, 18.2, 18.3, 19.87, 19.94, 19.99, 20.6, 93.4, 99.0 (20-CH), 103.1, 106.8 (5-CH), 118.1, 120.7 (2¹-CH), 120.8 (3¹-CH), 126.6, 126.8, 132.1, 132.4, 133.2, 135.2, 136.02, 136.09, 138.8, 139.0, 140.0, 140.1, 143.0, 143.6, 146.7, 147.8, 154.2, 154.7, 177.4 (d, ¹*J*_{Rh-C} = 69.0 Hz), 178.5 (d, ¹*J*_{Rh-C} = 67.3 Hz); HR-MS (ESI-MS) calcd for C₃₇H₃₆N₃O₂Rh + H 658.1941, found 658.1934.



[8,12,13,17-Tetraethyl-7,18-dimethylbenzo[b]-21-carbaporphyrinato](dipyridine)-

rhodium(III) (10a). Rhodium(I) complex **9** (20.0 mg, 0.0304 mmol) was dissolved in pyridine (20 mL) and refluxed with stirring under nitrogen for 1 h. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica column, eluting with toluene. A deep red band was collected, the solvent evaporated, and the residue was recrystallized from chloroform-hexanes to give the rhodium(III) complex (12.6 mg, 0.0167 mmol, 55%) as dark

red crystals, mp 295-298 °C, dec; UV-vis (CH₂Cl₂): λ_{max} (log ε) 333 (4.81), 409 (sh, 4.83), 447 (5.17), 467 (4.77), 520 (4.36), 556 (4.22), 572 (4.18), 620 nm (3.90); ¹H NMR (500 MHz, 323 K, CDCl₃): δ 1.17 (4H, d, *J* = 6.0 Hz, 4 x β-pyridine-H), 1.80 (6H, t, *J* = 7.6 Hz), 1.86 (6H, t, *J* = 7.6 Hz) (4 x CH₂CH₃), 3.53 (6H, s, 7,18-CH₃), 3.95-4.04 (8H, m, 4 x CH₂CH₃), 4.80 (4H, t, *J* = 6.9 Hz, 4 x β-pyridine-H), 5.75 (2H, t, *J* = 7.5 Hz), 7.38-7.40 (2H, m), 8.54-8.57 (2H, m), 9.33 (2H, v br), 9.74 (2H, v br); ¹³C NMR (125 MHz, CDCl₃-trace toluene): δ 11.8 (7,18-CH₃), 18.2, 18.6, 20.0, 20.2, 117.7 (2¹,3¹-CH), 120.9 (β-pyridine-CH), 124.6 (2²,3²-CH), 132.7 (br), 133.4 (γ-pyridine-CH), 138.4 (br), 138.9 (br), 137.5, 140.0, 140.2, 147.7, 148.4 (α-pyridine-CH); HR-MS (ESI-MS) calcd for C₄₅H₄₄N₅Rh 757.2652, found 757.2642.



[8,12,13,17-Tetraethyl-7,18-dimethylbenzo[b]-21-carbaporphyrinato](dipyridine)-

iridium(III) (10b). Benzocarbaporphyrin **2a** (14.0 mg, 0.0280 mmol) was dissolved in anhydrous *p*-xylene (30 mL). Anhydrous sodium acetate (22.9 mg, 0.2802 mmol), pyridine (100 μ L) and [Ir(COD)Cl]₂ (30.1 mg, 0.0448 mmol) were added to the solution and the mixture was refluxed with stirring under nitrogen overnight. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica column eluting with dichloromethane. A red band was collected, the solvent evaporated, and the residue recrystallized from chloroform-hexanes to give to give **10b** (5.2 mg, 0.0062 mmol, 22%) as dark red crystals, mp >300 °C; UV-

vis (CH₂Cl₂): λ_{max} (log ε) 326 (4.29), 353 (4.35), 393 (4.76), 437 (4.70), 452 (sh, 4.64), 521 (sh, 4.12), 553 (3.91), 618 nm (3.11); ¹H NMR (500 MHz, CDCl₃): δ 1.43-1.45 (4H, m, 4 x α -pyridine-H), 1.76 (6H, t, , J = 7.6 Hz), 1.81 (6H, t, J = 7.6 Hz) (4 x CH₂CH₃), 3.51 (6H, s, 7,18-CH₃), 3.89 (4H, q, J = 7.6 Hz), 3.95 (4H, q, J = 7.6 Hz) (4 x CH₂CH₃), 4.84 (4H, t, J = 7.2 Hz, 4 x β -pyridine-H), 5.81 (2H, tt, J = 1.5, 7.6 Hz, 2 x γ -pyridine-H), 7.31-7.35 (2H, m, 2²,3²-H), 8.42-8.46 (2H, m, 2¹,3¹-H), 9.40 (2H, s, 10,15-H), 9.83 (2H, s, 5,20-H); ¹³C NMR (125 MHz, CDCl₃): δ 11.6 (7,18-CH₃), 18.2, 18.5, 19.8, 20.0, 94.7 (10,15-CH), 104.4 (5,20-CH), 117.5 (2¹,3¹-CH), 121.5 (β -pyridine-CH), 124.5 (2²,3²-CH), 131.2, 132.4, 132.9 (γ -pyridine-CH), 137.1, 137.5, 138.1, 138.5, 139.6, 148.5, 149.4 (α -pyridine-CH); HR-MS (EI) calcd for C₄₅H₄₄IrN₅ 847.3226, found 847.3226.

Crystallographic Experimental Details of 9. X-ray quality crystals of **9** ($C_{37}H_{36}N_3O_2Rh\cdot CHCl_3$) were suspended in mineral oil at ambient temperature and a suitable crystal was selected. A mineral oil coated green block thereby obtained of approximate dimensions 0.57 mm x 0.10 mm x 0.085 mm was mounted on a 50 µm MicroMesh MiTeGen Micromount and transferred to a Bruker AXS SMART APEX CCD X-ray diffractometer. The X-ray diffraction data were collected at 100(2) K using Mo-K_a ($\lambda = 0.71073$ Å) radiation. A total of 3672 frames were collected. The total exposure time was 5.10 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.² The integration of the data yielded a total of 71454 reflections to a maximum θ angle of 32.284° (0.67 Å resolution), of which 11961 were independent (completeness = 94.4%, $R_{sig} = 2.48\%$) and 11047 (92.36%) were observed with $F_o^2 > 2\sigma(F_o^2)$. The final triclinic cell constants of a = 11.7176(8) Å, b = 12.3793(8) Å, c = 13.4720(9) Å, $a = 104.215(3)^\circ$, $\beta = 96.743(3)^\circ$, $\gamma = 106.479(3)^\circ$, volume = 1779.4(2) Å³, are based upon the refinement of the XYZ-centroids of 9646 reflections above 20 $\sigma(I)$ with 5.346° < 2 θ < 64.04°. Limiting indices were as

follows: $-17 \le h \le 17$, $-18 \le k \le 18$, $-19 \le l \le 20$. Data were corrected for absorption effects using the multi-scan method (SADABS).² The ratio of minimum to maximum apparent transmission was 0.89 with minimum and maximum SADABS generated transmission coefficients of 0.6677 and 0.7464. Solution and data analysis were performed using the WinGX software package.³ The structure was solved and refined in the space group P-1 (no. 2) with Z = 2.4 The solution was achieved by charge-flipping methods using the program SUPERFLIP⁵ and the refinement was completed using the program SHELXL-2014/7.6 PLATON SQUEEZE7 was used to correct for the presence of one disordered chloroform molecule per main residue. 109 electrons in the unit cell is consistent with one CHCl₃ (58 electrons each; 116 electrons in a unit cell) per main residue with perhaps some solvent loss having occurred. While it seems most likely that the disordered residue was chloroform, since it could not be confirmed, it was not included in the crystallographic formula used in the refinement. All non-H atoms were refined anisotropically. All non-solvent H atoms were identifiable in the difference Fourier; however, with the exception of the internal C-H and N-H H atoms, all non-solvent H atoms were included in the refinement in the riding-model approximation (C--H = 0.95, 0.98, and 0.99 Å for Ar--H, CH₃, and CH₂; U_{iso} (H) = 1.2 U_{eq} (C) except for methyl groups, where $U_{iso}(H) = 1.5U_{eq}(C)$). The internal C-H and N-H H atoms were freely refined except for the restraint DFIX 1.950 0.002 H24 H21. Full-matrix least-squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta/\sigma)_{\text{mean}} = 0.000$, with $R_1 = 0.0211$ and $wR_2 = 0.0552$ for 11047 data with $F_o^2 > 2\sigma(F_o^2)$ using 1 restraint and 398 parameters. A final difference Fourier synthesis showed features in the range of $\Delta \rho_{max} = 0.512 \text{ e}^{-1}/\text{Å}^3$ to $\Delta \rho_{min} = -0.457 \text{ e}^{-1}/\text{Å}^3$. All residual electron density was within accepted norms and was deemed of no chemical significance. Molecular diagrams were generated using WinGX.³ CCDC-1491760 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the

Cambridge Crystallographic Data Centre via <u>https://summary.ccdc.cam.ac.uk/structure-</u> summary?ccdc=1491760.

Crystallographic Experimental Details of 10a. X-ray quality crystals of 10a (C₄₅H₄₄N₅Rh·CHCl₃) were suspended in mineral oil at ambient temperature and a suitable crystal was selected. A mineral oil coated red plate thereby obtained of approximate dimensions 0.135 mm x 0.030 mm x 0.015 mm was mounted on a 50 µm MicroMesh MiTeGen Micromount and transferred to a Bruker AXS SMART APEX CCD X-ray diffractometer. The X-ray diffraction data were collected at 100(2) K using Mo-K_a ($\lambda = 0.71073$ Å) radiation. A total of 3672 frames were collected. The total exposure time was 61.2 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.² The integration of the data using a monoclinic unit cell yielded a total of 155324 reflections to a maximum θ angle of 30.79° (0.69 Å resolution), of which 12544 were independent (average redundancy 12.382, completeness = 99.5%, $R_{\text{int}} = 11.73\%$, $R_{\text{sig}} = 5.61\%$) and 9020 (71.91%) were observed with $F_o^2 > 2\sigma(F_o^2)$. The final cell constants of a = 26.5254(13) Å, b = 15.7840(8) Å, c = 23.0842(12) Å, $\beta = 123.490(3)^{\circ}$, volume = 8060.3(7) Å³, are based upon the refinement of the XYZ-centroids of 9905 reflections above 20 $\sigma(I)$ with 4.399° < 2 θ < 54.97°. Limiting indices were as follows: -38 $\leq h \leq$ 38, -22 $\leq k$ ≤ 22 , $-33 \leq l \leq 33$. Data were corrected for absorption effects using the multi-scan method (SADABS).² The ratio of minimum to maximum apparent transmission was 0.941 with minimum and maximum SADABS generated transmission coefficients of 0.7019 and 0.7461. Solution and data analysis were performed using the WinGX software package.³ The structure was solved and refined in the space group $C_{2/c}$ (no. 15) with Z = 8.4 The solution was achieved by charge-flipping methods using the program SUPERFLIP⁵ and the refinement was completed using the program SHELXL-2014/7.⁶ All non-H atoms were refined anisotropically. All H atoms were included in the refinement in the riding-model approximation (C--H = 0.95, 0.98, 0.99, and 1.00 Å for Ar--H, CH₃, CH₂ and CH; U_{iso} (H) = $1.2U_{eq}$ (C) except for methyl groups, where U_{iso} (H) = $1.5U_{eq}$ (C)). Full-matrix least-squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{max} = 0.001$, $(\Delta/\sigma)_{mean} = 0.000$, with $R_1 = 0.0411$ and $wR_2 = 0.0947$ for 9020 data with $F_o^2 > 2\sigma(F_o^2)$ using 0 restraints and 498 parameters. A final difference Fourier synthesis showed features in the range of $\Delta\rho_{max} = 0.689$ er /Å³ to $\Delta\rho_{min} = -1.046$ e⁻/Å³. All residual electron density was deemed of no chemical significance. Molecular diagrams were generated using WinGX.³ CCDC-1491761 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>https://summary.ccdc.cam.ac.uk/structure-</u> summary?ccdc=1491761.

Crystallographic Experimental Details of 10b. X-ray quality crystals of 10b $(C_{45}H_{44}N_5Ir \cdot CHCl_3)$ were suspended in mineral oil at ambient temperature and a suitable crystal was selected. A mineral oil coated dark red-brown plate thereby obtained of approximate dimensions 0.015 mm x 0.115 mm x 0.185 mm was mounted on a 50 µm MicroMesh MiTeGen Micromount and transferred to a Bruker AXS SMART APEX CCD X-ray diffractometer. The Xray diffraction data were collected at 100(2) K using Mo-K_a ($\lambda = 0.71073$ Å) radiation. A total of 3672 frames were collected. The total exposure time was 10.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.² The integration of the data yielded a total of 159684 reflections to a maximum θ angle of 32.35° (0.66 Å resolution), of which 13957 were independent (average redundancy 11.449, completeness = 96.7%, R_{int} = 8.56%, $R_{\text{sig}} = 5.04\%$) and 10528 (75.43%) were observed with $F_o^2 > 2\sigma(F_o^2)$. The final monoclinic cell constants of a = 26.5093(10) Å, b = 15.8108(6) Å, c = 23.0204(9) Å, $\beta = 123.126(2)^{\circ}$, volume = 8080.4(6) Å³, are based upon the refinement of the XYZ-centroids of 9815 reflections above 20

 $\sigma(I)$ with 5.152° < 2 θ < 54.98°. Limiting indices were as follows: -39 ≤ h ≤ 39, -23 ≤ k ≤ 23, -34 $\leq l \leq 34$. Data were corrected for absorption effects using the multi-scan method (SADABS).² The ratio of minimum to maximum apparent transmission was 0.84 with minimum and maximum SADABS generated transmission coefficients of 0.6281 and 0.7464. Solution and data analysis were performed using the WinGX software package.³ The structure was solved and refined in the space group $C_{2/c}$ (no. 15) with Z = 8.4 The solution was achieved by charge-flipping methods using the program SUPERFLIP⁵ and the refinement was completed using the program SHELXL-2014/7.6 PLATON SQUEEZE7 was used to correct for the presence of one disordered chloroform molecule per main residue. 430 electrons in the unit cell is consistent with one CHCl₃ (58 electrons each; 464 electrons in a unit cell) per main residue with perhaps some solvent loss having occurred. While it seems most likely that the disordered residue was chloroform, since it could not be confirmed, it was not included in the crystallographic formula used in the refinement. All non-H atoms were refined anisotropically. All non-solvent H atoms were identifiable in the difference Fourier; however, all non-solvent H atoms were included in the refinement in the riding-model approximation (C--H = 0.95, 0.98, and 0.99 Å for Ar--H, CH₃, and CH₂; U_{iso} (H) = 1.2 U_{eq} (C) except for methyl groups, where $U_{iso}(H) = 1.5U_{eq}(C)$). Full-matrix least-squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta/\sigma)_{\text{mean}} = 0.000$, with $R_1 = 0.0507$ and $wR_2 = 0.1478$ for 10958 data with $F_o^2 > 2\sigma(F_o^2)$ using 0 restraints and 462 parameters. A final difference Fourier synthesis showed features in the range of $\Delta \rho_{max} = 2.439 \text{ e}^{-1}\text{Å}^3$ to $\Delta \rho_{min} = -7.738 \text{ e}^{-1}\text{Å}^3$. All residual electron density away was deemed of no chemical significance with the largest peaks being in the region from which the solvent was SQUEEZEd. Molecular diagrams were generated using WinGX.³ CCDC-1491762 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://summary.ccdc.cam.ac.uk/structure-summary?ccdc=1491762.

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Figure 1. Color POV-Ray rendered space-filling drawings of rhodium(I) complex **9**.



Figure 2. "Edge-view": Color POV-Ray rendered ORTEP III drawing (50% probability level, hydrogen atoms rendered arbitrarily small for clarity) of rhodium(III) complex **10a**.



Figure 3. 45° from "Edge-view": Color POV-Ray rendered ORTEP III drawing (50% probability level, hydrogen atoms rendered arbitrarily small for clarity) of **10a**.



Figure 4. Color POV-Ray rendered space-filling drawing of rhodium(III) complex **10a**.



Figure 5. "Edge-view": Color POV-Ray rendered ORTEP III drawing (50% probability level, hydrogen atoms rendered arbitrarily small for clarity) of iridium(III) complex **10b**.



Figure 6. 45° from "Edge-view": Color POV-Ray rendered ORTEP III drawing (50% probability level, hydrogen atoms rendered arbitrarily small for clarity) of **10b**.



Figure 7. Color POV-Ray rendered space-filling drawing of iridium(III) complex **10b**.

	9.CHCl.	10a-CHCL	10b	
mol formula (actual)	CH. N.O.Rb.CHCl	Curtue NaRhe CHCla	C.H.N.Ir:CHCl	
mol formula (refined)	$C_{37}H_{36}N_{3}O_{2}KHCHCH_{3}$	C H N - R h · CHCl	C - H - N-Ir	
mol wt (refined)	657.6	877.13	847.05	
crystal system	triclinic	monoclinic	monoclinic	
space group	P_{-1}	C	C	
radiation ($\lambda = \hat{\Delta}$)	0 71073	0.71073	0.71073	
	11 7176(8)	26 5254(13)	26 5093(10)	
$h \hat{\Delta}$	12 3793(8)	15 7840(8)	15 8108(6)	
	13 4720(9)	23 0842(12)	23 0204(9)	
	104 215(3)	90	90	
<u> </u>	96 743(3)	123 490(3)	123 126(2)	
<u> </u>	106 479(3)	90	90	
V Å3	1779 4(2)	8060 3(7)	8080 4(6)	
7	2	8	8	
calcd density	2	0	0	
$\sigma \text{ cm}^{-3}$	1.227	1.446	1.393	
absorb coeff				
mm ⁻¹	0.513	0.663	3.341	
temperature, K	100(2)	100(2)	100(2)	
θ range (deg)	1.592-32.284	1.585 - 30.786	1.599 - 32.353	
index ranges		20. 20. 22. 22. 22. 22.	-39, 39; -23, 23; -34, 34	
(h, k, l)	-17, 17; -18, 18; -19, 20	-38, 38; -22, 22; -33, 33		
no. of total	71454	155224	150(04	
reflns	/1454	155324	159684	
no. of indep	110(1 (0.0248)	12544 (0 1172)	12047 (0.0856)	
reflns (R_{int})	11961 (0.0248)	12344 (0.1173)	13947 (0.0856)	
reflns with	11047	9020	10058	
$I > 2\sigma(I)$	11047	9020	10938	
R_1 index	0.0211	0.0/11	0.0507	
[data with $I > 2\sigma(I)$]	0.0211	0.0411	0.0307	
wR_2 index	0.0552	0 0947	0 1478	
[data with $I > 2\sigma(I)$]	0.0352	0.0747	0.1478	
R_1 (all data)	0.0243	0.0753	0.0688	
GOF	1.06	1.024	1.09	
no. of	398/1	498/0	462/0	
restraints/params	570/1	0/07	102/0	
$\Delta \rho(\max, \min), e^{A^{-3}}$	0.512, -0.457	0.689, -1.046	2.439, -7.738	
CCDC number	1491760	1491761	1491762	

Table S1. Crystal Data for New Compounds





10a M = Rh 10b M = Ir

	9 (M = Rh)	10a (M = Rh)	10b (M = Ir)
C25-O26	1.1358(14)		
C27-O28	1.1372(14)		
Rh-C25	1.8635(11)		
Rh-C27	1.8536(11)		
M-C21		1.988(2)	1.999(4)
M-N22	2.0846(9)	2.0392(19)	2.043(4)
M-N23	2.0920(9)	2.1076(19)	2.094(4)
M-N24		2.0499(19)	2.050(4)
M-N25		2.059(2)	2.063(4)
M-N31		2.061(2)	2.070(4)
C2-C2a	1.3900(14)	1.387(3)	1.386(6)
C2a-C2b	1.3986(16)	1.394(3)	1.388(7)
C2b-C3b	1.3910(16)	1.377(4)	1.388(8)
C3b-C3a	1.3998(14)	1.403(3)	1.408(7)
C3a-C3	1.3901(14)	1.384(3)	1.391(7)
C21-C1	1.4053(14)	1.422(3)	1.426(6)
C1-C2	1.4762(14)	1.471(3)	1.471(6)
C2-C3	1.4143(14)	1.411(3)	1.411(7)
C3-C4	1.4743(13)	1.483(3)	1.461(6)
C4-C21	1.4098(14)	1.416(3)	1.428(7)
C4-C5	1.3948(14)	1.389(3)	1.391(7)
C5-C6	1.4055(13)	1.392(3)	1.395(7)
C6-N22	1.3814(13)	1.379(3)	1.385(6)
C6-C7	1.4460(13)	1.441(3)	1.435(6)
C7-C8	1.3772(14)	1.367(3)	1.362(7)
C8-C9	1.4389(14)	1.446(3)	1.445(6)
C9-N22	1.3756(12)	1.381(3)	1.383(6)
C9-C10	1.3991(14)	1.396(3)	1.404(6)
C10-C11	1.3931(14)	1.389(3)	1.394(7)
C11-N23	1.3859(12)	1.370(3)	1.371(6)
C11-C12	1.4427(14)	1.453(3)	1.445(6)
C12-C13	1 3698(14)	1 367(3)	1 365(7)

C13-C14	1.4480(14)	1.457(3)	1.445(6)
C14-N23	1.3814(13)	1.371(3)	1.373(6)
C14-C15	1.4029(14)	1.384(3)	1.395(7)
C15-C16	1.3912(14)	1.396(3)	1.380(7)
C16-N24	1.3666(13)	1.378(3)	1.378(6)
C16-C17	1.4382(14)	1.445(3)	1.448(7)
C17-C18	1.3813(14)	1.367(3)	1.360(7)
C18-C19	1.4371(14)	1.444(3)	1.443(7)
C19-N24	1.3738(12)	1.381(3)	1.382(6)
C19-C20	1.3899(14)	1.395(3)	1.400(7)
C20-C1	1.4038(15)	1.388(3)	1.383(6)
C21-M-N22		90.58(8)	90.47(17)
N22-M-N23	85.90(3)	89.46(7)	89.72(15)
N23-M-N24		89.41(7)	89.53(15)
N24-M-C21		90.55(8)	90.29(17)
C21-M-N23		179.96(11)	179.81(17)
N22-M-N24		178.78(8)	179.21(15)
N25-M-N31		178.37(8)	178.91(15)
C21-M-N25		89.68(8)	90.00(17)
C21-M-N31		89.01(9)	89.36(17)
N22-Rh-C25	91.86(4)		
N22-Rh-C27	173.99(4)		
N23-Rh-C25	177.11(4)		
N23-Rh-C27	92.25(4)		
C25-Rh-C27	89.79(5)		
Rh-C25-O26	178.55(11)		
Rh-C27-O28	176.78(10)		

Orange – more aromatic (1.38-1.41), green – single bond limit (≥1.46), blue – more single bond like (1.42-1.45), purple more double bond like (≤1.37).



Figure 8. UV-vis spectrum of rhodium(I)dicarbonyl carbaporphyrin 9 in dichloromethane.



Figure 9. IR spectrum of rhodium(I)dicarbonyl carbaporphyrin 9.



Figure 10. UV-vis spectrum of rhodium(III) complex 10a in dichloromethane



Figure 11. UV-vis spectrum of iridium(III) complex **10b** in dichloromethane.



Figure 12. 500 MHz proton NMR spectrum of rhodium(I) carbaporphyrin 9 in CDCl₃.



Figure 13. COSY and HSQC NMR spectra for rhodium(I) carbaporphyrin 9 in CDCl₃.



Figure 14. Selected nOe difference proton NMR spectra for 9 in CDCl₃.



Figure 15. DEPT-135 NMR spectrum of rhodium(I) complex 9 in CDCl₃.



Figure 16. 125 MHz carbon-13 NMR spectrum of rhodium(I) carbaporphyrin 9 in CDCl₃.



Figure 17. 500 MHz proton NMR spectrum of **10a** in CDCl₃ containing trace amounts of toluene at 323 K. * toluene and water peaks



Figure 18. 500 MHz proton NMR spectrum of **10a** in CDCl₃ in the absence of toluene.

Figure 19. ¹H-¹H COSY NMR spectrum of **10a** in CDCl₃ containing trace toluene at 323 K.

Figure 20. HSQC NMR spectrum of **10a** in CDCl₃ containing trace toluene at 323 K.

Figure 21. DEPT-135 NMR spectrum of 10a in CDCl₃ containing trace toluene at 323 K.

Figure 22. 125 MHz carbon-13 NMR spectrum of **10a** in CDCl₃ containing trace toluene at 323 K. * toluene peaks

Figure 23. 500 MHz proton NMR spectrum of iridium(III) complex 10b in CDCl₃.

Figure 24. Selected nOe difference proton NMR spectra of **10b** in CDCl₃.

Figure 25. ¹H-¹H COSY NMR spectrum of iridium(III) complex **10b** in CDCl₃.

Figure 26. HSQC NMR spectrum of iridium(III) complex 10b in CDCl₃.

Figure 27. DEPT-135 NMR spectrum of iridium(III) complex 10b in CDCl₃.

Figure 28. 125 MHz carbon-13 NMR spectrum of iridium(III) complex 10b in CDCl₃.

KA11-HR Qtof_56569a 50 (3.408) AM (Top,4, Ar,14000.0,716.4	46,0.70,LS 3); Cm (50:54)	1: TOF MS ES+ 1.38e+003
100 657.2009 0 657.2009 0 657.2009 657.2009 658.00	1934 658.3745 658.6484 659.1867 659.3727 658.3745 658.6484 659.1867 659.3727	660.1808 661.0087 661.2147 m/z

Figure 29. ESI MS of rhodium(I)dicarbonyl carbaporphyrin 9.

Figure 30. ESI MS of rhodium(III) carbaporphyrin 10a.

Figure 31. ESI MS of iridium(III) carbaporphyrin 10b.