Electronic Supplementary Information

Conformational Isomers of Extraordinary Stability: Carboxamidate-Bridged Dimetalloorganic Compounds

Jian-Hua Xie,[a] Lei Zhou,[a] Peter Zavalij,[a] Michael P. Doyle,[a*] Yinxin Sun,[b] Yang Liu,[b] and Huai Sun[b*]

CONTENTS

Synthesis of O: To a dry flask 110.5 mg (150 μmol) $Rh_2(cap)_4(CH_3CN)_2$ and 34.0 mg (300 μmol) ε-caparolactam was added, followed by 15 mL (0.36 mg/mL, 90 μmol) of acetic acid in toluene and 10 mL of toluene. The mixture was heated to reflux in an oil bath. The color of the reaction solution changed from purple to blue after refluxing for 10 minutes. Refluxing was continued for 4 hrs after which the solvents were removed under reduced pressure to provide a blue residue. Then 92 mg (0.75 mmol) of phenylboronic acid and 126 mg (1.50 mmol) of sodium bicarbonate were added, followed by 20 mL of dichloromethane (DCM), and the mixture was stirred at room temperature for a few minutes, after which 5.0 mL of a $CuSO_4.5H_2O$ solution (3 μmol/mL, 15 μmol) in MeOH was added. After stirring at room temperature for 18 h the solvents were removed under reduced pressure and the residue was chromatographed on silica gel to yield **O** 34.5 mg (28.5 %) and **G** 23.6 mg (19.5%). (A small amount of the minor green isomer was also obtained, 2 mg, 1% yield). HPLC analysis of the two conformers that shows **O** eluting faster than **G** (Figure S-1) is consistent with their expected behavior based on size exclusion.

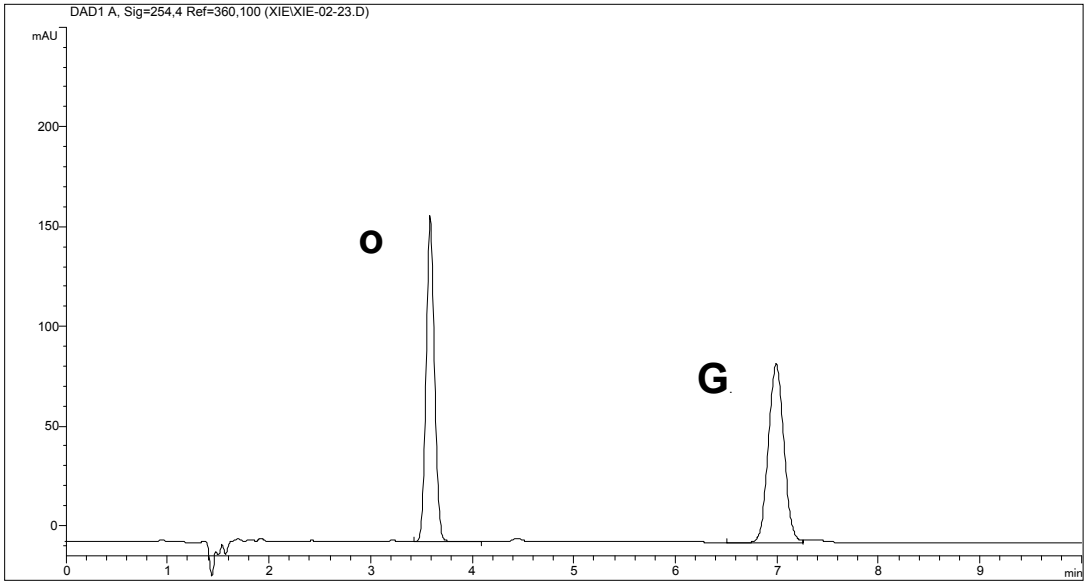
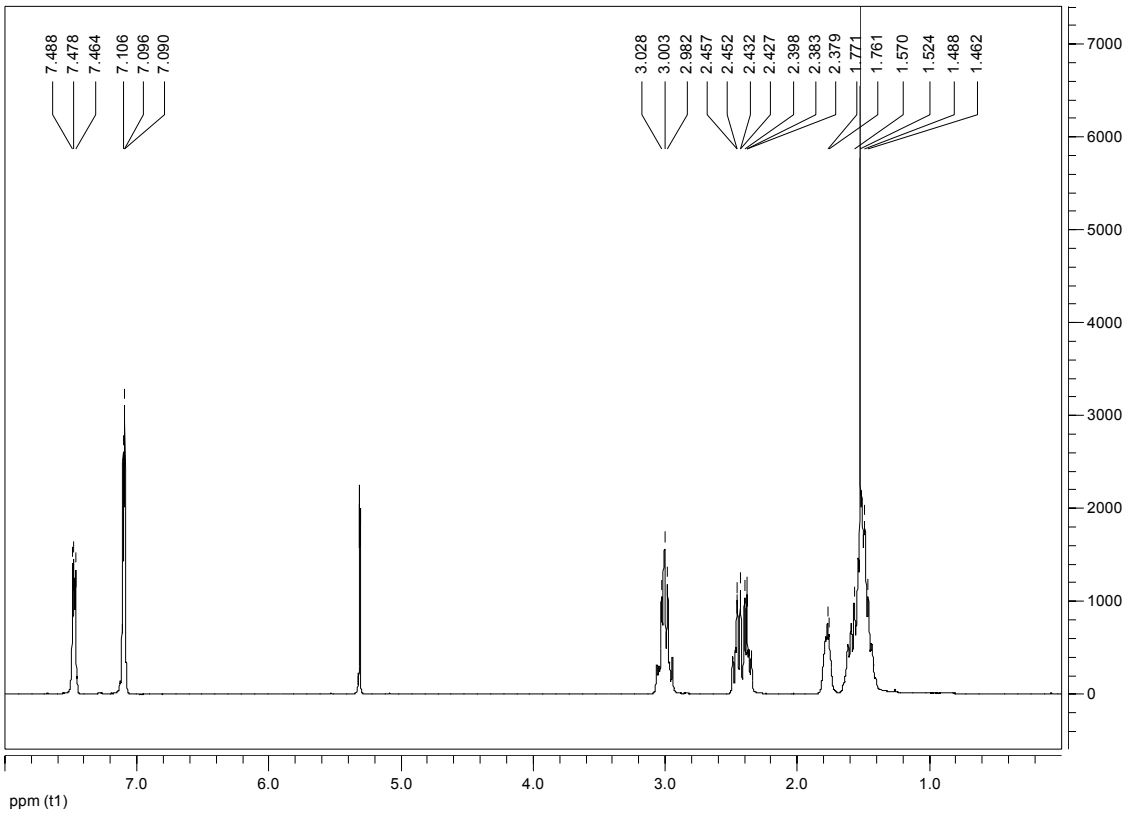
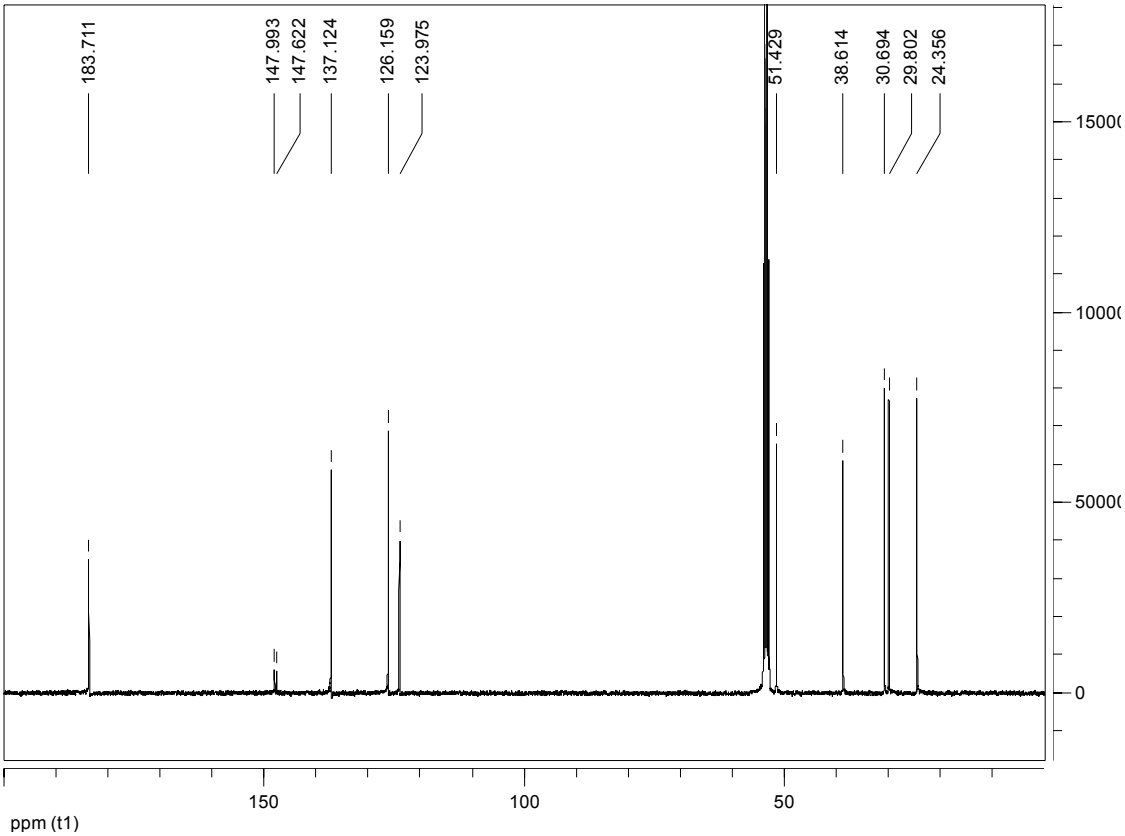


Figure S-1. HPLC of a solution of **O** and **G** (*i*PrOH:MeCN = 13:87 on a 15 cm. C-18 column).

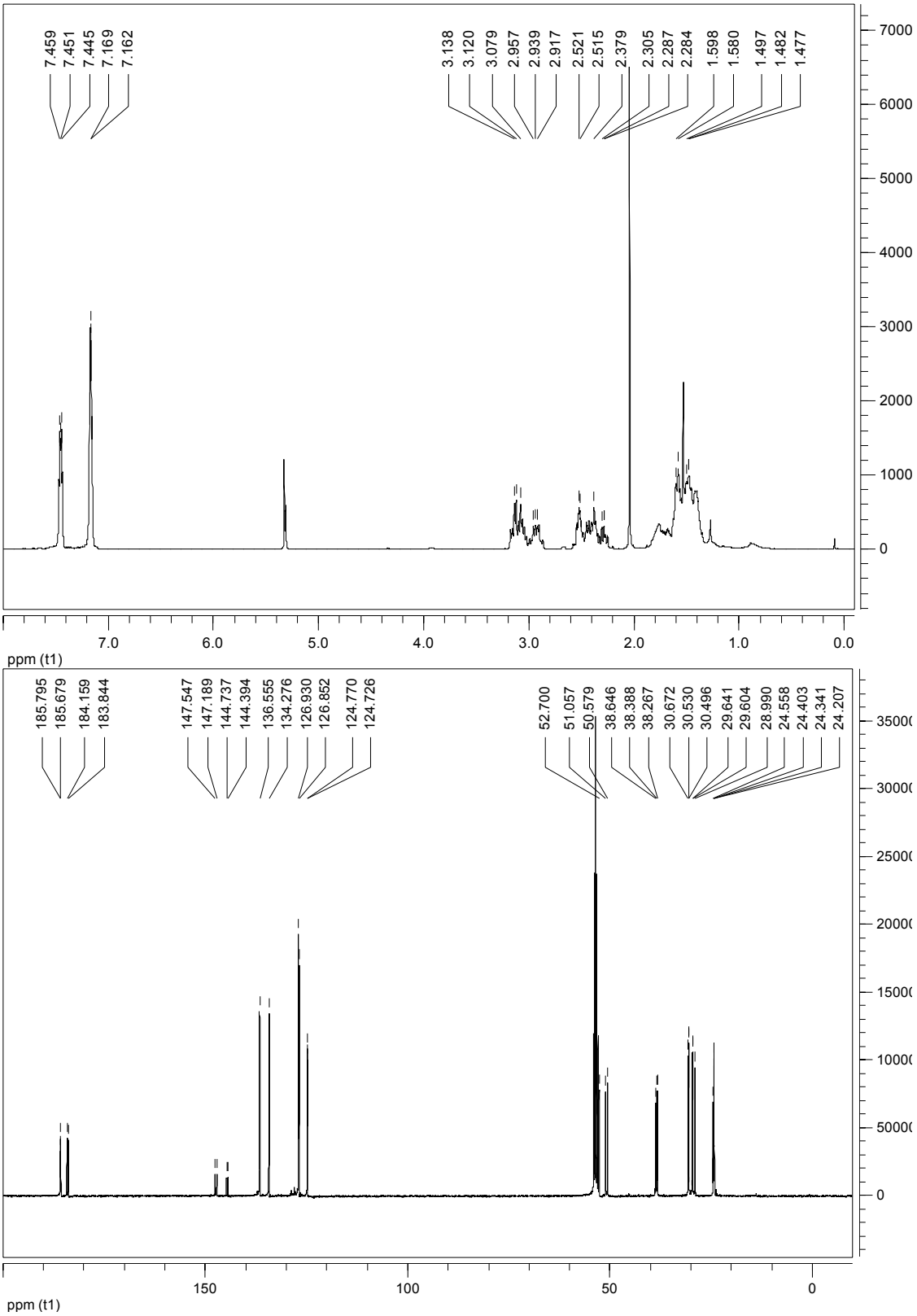
Data for G and O

G: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.49–7.46 (comp, 4H), 7.11–7.08 (comp, 6H), 3.07–2.94 (comp, 8H), 2.50-2.34 (comp, 8H), 1.81–1.72 (comp, 4H), 1.66–1.38 (comp, 20H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 183.71, 147.81 (d, $^{1}J_{C\text{-}Rh}$ = 37.1 Hz), 137.12, 126.16, 123.98, 51.43, 38.61, 30.69, 29.80, 24.36 ppm; UV/Visible (CH_2Cl_2): 430 nm (ε = 6590 $M^{-1}cm^{-1}$). IR (neat): 1550(s), 1583(s) cm^{-1}; HRMS (ESI) Calcd for for $C_{36}H_{51}N_4O_4Rh_2$([M+H]$^+$) 809.2020; found 809.2018 (M+H).)



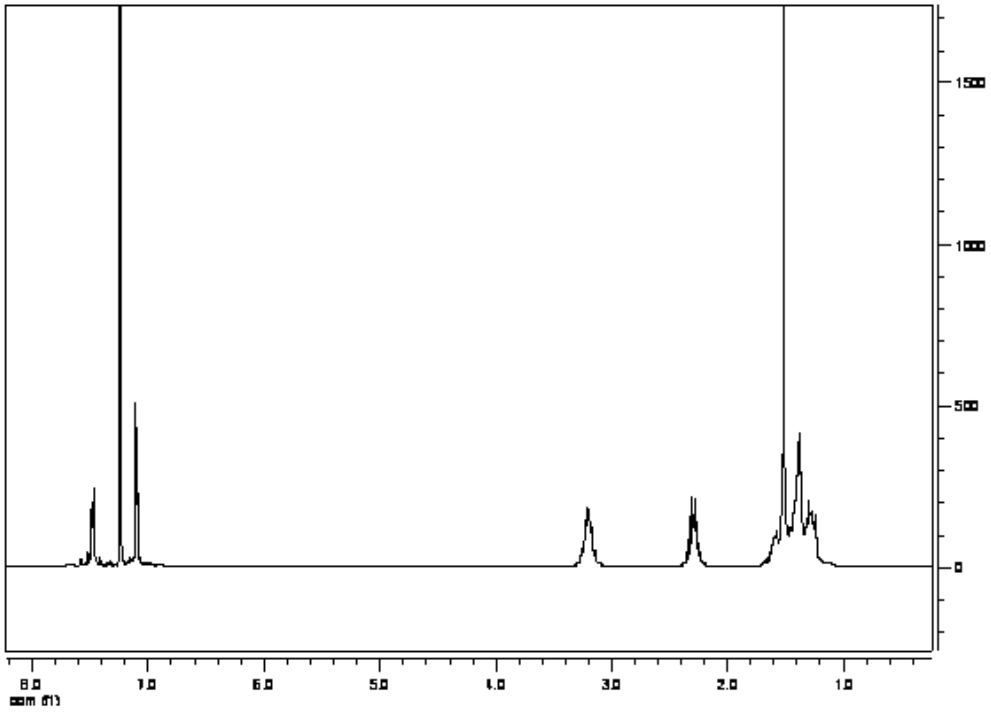


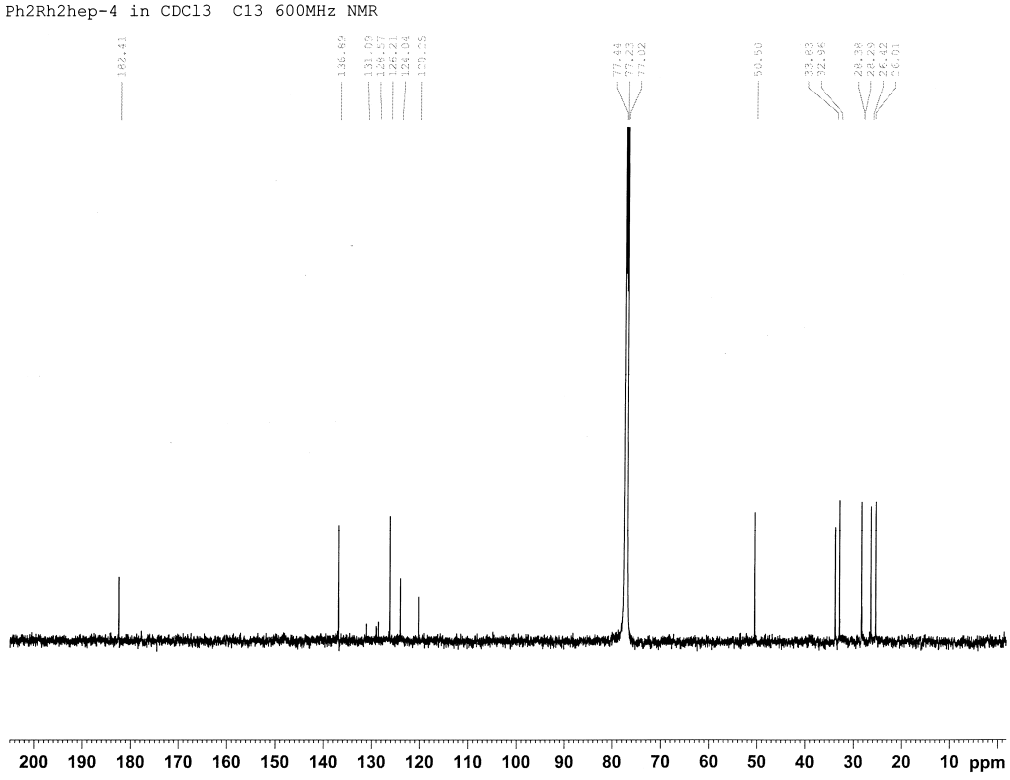
O: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.51–7.46 (comp, 4H), 7.19–7.14 (comp, 6H), 3.16–2.98 (comp, 5H), 2.98–2.93 (comp, 3H), 2.68–2.45 (comp, 4H), 2.38–2.31 (comp, 4H), 1.83–1.71 (comp, 4H), 1.68–1.32 (comp, 20H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 185.80, 185.68, 184.16, 183.84, 147.37 (d, $^{1}J_{C\text{-}Rh}$= 35.8 Hz), 144.58 (d, $^{1}J_{C\text{-}Rh}$= 34.3 Hz), 136.56, 134.28, 126.93, 126.85, 124.77, 124.73, 52.70, 51.06, 50.58, 38.65, 38.39, 38.27, 30.67, 30.53, 30.50, 29.64, 29.66, 29.00, 24.56, 24.40, 24.34, 24.21; UV/Visible (CH_2Cl_2): 430 nm (ε = 2580 $M^{-1}cm^{-1}$); IR (neat): cm^{-1}; HRMS (ESI): Calcd for $C_{36}H_{50}N_4O_4Rh_2$ (M^+): 808.1942; found: 808.1928.


7.459
7.451
7.445
7.169
7.162
3.138
3.120
3.079
2.957
2.939
2.917
2.521
2.515
2.379
2.305
2.287
2.284
1.598
1.580
1.497
1.482
1.477
7000
6000
5000
4000
3000
2000
1000
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
185.795
185.679
184.159
183.844
147.547
147.189
144.737
144.394
136.555
134.276
126.930
126.852
124.770
124.726
52.700
51.057
50.579
38.646
38.388
38.267
30.672
30.530
30.496
29.641
29.604
28.990
24.558
24.403
24.341
24.207
150
100
50
0
ppm (t1)

Synthesis of PhACO: To a dry flask was added 24.0 mg (30 μmol) $Rh_2(aco)_4(CH_3CN)_2$, 15 mg (0.15 mmol) of phenylboronic acid and 25.2 mg (0.30 mmol) of sodium bicarbonate, followed by 4.0 mL of dichloromethane (DCM), and the mixture was stirred at room temperature for a few minutes, after which 1.0 mL of a $CuSO_4.5H_2O$ solution (3 μmol/mL, 3 μmol) in MeOH was added. After stirring at room temperature for 20 h the solvents were removed under reduced pressure, and the residue was chromatographed on silica gel to yield 8.0 mg of **PhACO** (30.8 %).

PhACO: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.50 (comp, 4H), 7.08–7.11 (comp, 6H), 3.15–3.26 (comp, 8H), 2.24–2.36 (comp, 8H), 1.22–1.58 (comp, 32H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 182.41, 136.89, 131.09, 128.57 (d, $^1J_{C\text{-}Rh}$= 36.9 Hz), 126.21, 124.04, 120.26, 50.50, 33.83, 32.98, 28.30, 26.42, 25.41; UV/Visible (CH_2Cl_2): 435 nm (ε = 2084 $M^{-1}cm^{-1}$); HRMS (ESI): Calcd for $C_{40}H_{59}N_4O_4Rh_2$ $(M+H)^+$: 865.2646; found: 865.2652.





X-ray structural determinations of G, O, PhACO, and ACOBF4

Details of the x-ray structural analysis of G (CCDC#615577)**.** The crystal of **G** suitable X-ray analysis was obtained by evaporation of the solvents from the solution of **G** in chloroform and dichloromethane. A green prism of $C_{36}H_{50}N_4O_4Rh_2 \cdot 2CHCl_3$, approximate dimensions 0.08× 0.095× 0.21 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 150(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ= 0.71073 Å). The detector was placed at a distance of 5.200 cm from the crystal.

A total of 2130 frames was collected with a scan width of 0.5° in ω and an exposure time of 38 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 24 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a triclinic unit cell yielded a total of 13816 reflections to a maximum θ angle of 27.50°, of which 9901 were independent (completeness = 99.3%, R_{int} = 2.00%, R_{sig} = 3.07%) and 8334 were greater than 2σ(I). The final cell dimensions of a = 11.5388(8) Å, b = 11.6313(8) Å, c = 17.2249(12) Å, α= 82.9623(12)°, β= 78.2631(12)°, γ= 74.1013(13)°, V = 2171.4(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 14756 reflections with 2.3 < θ < 30.0° using Apex2. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.791 and 0.911.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group *P-1* with Z = 2 for the formula unit

$C_{36}H_{50}N_4O_4Rh_2 \cdot 2CHCl_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 487 variables converged at R_1=3.17 % for the observed data and wR_2=6.77 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 0.934 $\bar{e}/Å^3$ and the largest hole was -0.884 $\bar{e}/Å^3$. On the basis of the final model, the calculated density was 1.602 g/cm^3 and F(000), 1064 $\bar{e}$.

Details of the crystal data and structure refinement (Supplemental Table 1), atomic coordinates and equivalent isotropic atomic displacement parameters (Supplemental Table 2), anisotropic atomic displacement parameters (Supplemental Table 3), Hydrogen atom coordinates and isotropic atomic displacement parameters (Supplemental Table 4), bond lengths and angles (Supplemental Table 5), Torsion angles (Supplemental Table 6) are shown below.

Table 1. Crystal data and structure refinement for **G**.

Empirical formula	$C_{36}H_{50}N_4O_4Rh_2 \cdot 2CHCl_3$
Formula weight	1047.36
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal size	$0.21 \times 0.095 \times 0.08$ mm^3
Crystal habit	green prism
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.5388(8) Å α = 82.9623(12)°
	b = 11.6313(8) Å β = 78.2631(12)°
	c = 17.2249(12) Å γ = 74.1013(13)°
Volume	2171.4(3) Å^3
Z	2
Density, ρ_{calc}	1.602 g/cm^3
Absorption coefficient, μ	1.172 mm^{-1}
F(000)	1064 $\bar{e}$
Diffractometer	Bruker Smart Apex II CCD area detector
Radiation source	fine-focus sealed tube, MoKα
Detector distance	5.200 cm
Detector resolution	8.333 pixels/mm
Total frames	2130
Frame size	512 pixels
Frame width	0.5°
Exposure per frame	38 sec
Total measurement time	24 hours
Data collection method	ω and φ scans
θ range for data collection	1.83 to 27.50°
Index ranges	$-14 \le h \le 13$, $-15 \le k \le 12$, $-22 \le l \le 22$
Reflections collected	13816
Independent reflections	9901
Observed reflection, I>2σ(I)	8334
Coverage of independent reflections	99.3 %
Variation in check reflections	0 %
Absorption correction	Semi-empirical from equivalents
	SADABS (Sheldrick, 1996)
Max. and min. transmission	0.911 and 0.791
Structure solution technique	direct
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Refinement technique	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 1997)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	9901 / 0 / 487
Goodness-of-fit on F^2	1.000
Δ/σ_{max}	0.002

Final R indices:	R_1, I>2σ(I)	0.0317
	wR_2, all data	0.0677
	R_{int}	0.0200
	R_{sig}	0.0307
Weighting scheme		$w = 1/[\sigma^2(F_o^2)+(0.01P)^2+5.5P]$, $P = [\max(F_o^2,0)+2F_o^2]/3$
Largest diff. peak and hole		0.934 and -0.884 $\bar{e}/Å^3$

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$

Table 2. Atomic coordinates and equivalent* isotropic atomic displacement parameters ($Å^2$) for **G**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Rh1A	0.082005(18)	1.041271(18)	0.455103(11)	0.01524(5)
C1A	0.2514(2)	1.0367(2)	0.39700(16)	0.0189(5)
C2A	0.3406(2)	1.0515(3)	0.43615(17)	0.0231(6)
C3A	0.4594(3)	1.0435(3)	0.39510(18)	0.0268(6)
C4A	0.4912(3)	1.0193(3)	0.31569(19)	0.0305(7)
C5A	0.4028(3)	1.0038(3)	0.27680(18)	0.0286(6)
C6A	0.2839(3)	1.0115(3)	0.31742(16)	0.0233(6)
O1A	0.17365(17)	0.94459(19)	0.54474(11)	0.0262(4)
C11A	0.1339(2)	0.8832(3)	0.60734(16)	0.0219(6)
C12A	0.2257(3)	0.8332(3)	0.66239(17)	0.0284(7)
C13A	0.1863(3)	0.8894(3)	0.74218(18)	0.0294(7)
C14A	0.0961(3)	0.8324(3)	0.80069(17)	0.0301(7)
C15A	-0.0249(3)	0.8456(3)	0.77320(17)	0.0321(7)
C16A	-0.0136(3)	0.7930(3)	0.69429(16)	0.0241(6)
N1A	0.0231(2)	0.8689(2)	0.62374(13)	0.0190(5)
O2A	0.10303(17)	0.88660(17)	0.39946(11)	0.0236(4)
C21A	0.0443(3)	0.8051(3)	0.42207(16)	0.0214(5)
C22A	0.0811(3)	0.7024(3)	0.36857(18)	0.0280(6)
C23A	-0.0229(3)	0.6949(3)	0.3283(2)	0.0396(8)
C24A	-0.1104(4)	0.6286(4)	0.3812(2)	0.0544(11)
C25A	-0.1766(3)	0.6889(4)	0.4576(2)	0.0489(10)
C26A	-0.0964(3)	0.7094(3)	0.51059(19)	0.0323(7)
N2A	-0.0425(2)	0.8108(2)	0.48502(13)	0.0203(5)
Rh1B	0.420837(18)	0.537819(18)	-0.043874(11)	0.01472(5)
C1B	0.2915(2)	0.5250(2)	-0.10152(16)	0.0191(5)
C2B	0.3250(3)	0.4871(3)	-0.17811(17)	0.0266(6)
C3B	0.2362(3)	0.4758(3)	-0.2184(2)	0.0352(7)
C4B	0.1146(3)	0.4990(3)	-0.1821(2)	0.0336(7)
C5B	0.0815(3)	0.5334(3)	-0.10523(19)	0.0281(6)
C6B	0.1692(2)	0.5472(2)	-0.06441(17)	0.0218(6)
O1B	0.51586(18)	0.37488(17)	-0.09045(12)	0.0249(4)
C11B	0.6070(2)	0.2952(2)	-0.06755(16)	0.0207(5)
C12B	0.6585(3)	0.1896(3)	-0.11839(18)	0.0283(6)
C13B	0.7916(3)	0.1786(3)	-0.15836(19)	0.0343(7)
C14B	0.8833(3)	0.1154(3)	-0.1053(2)	0.0395(8)
C15B	0.8729(3)	0.1810(4)	-0.0322(2)	0.0423(9)
C16B	0.7486(3)	0.2063(3)	0.02161(18)	0.0283(6)
N1B	0.6544(2)	0.3059(2)	-0.00671(13)	0.0189(4)
O2B	0.32329(18)	0.45659(19)	0.05244(11)	0.0249(4)
C21B	0.3605(2)	0.4006(2)	0.11557(16)	0.0209(5)
C22B	0.2638(3)	0.3565(3)	0.17573(17)	0.0270(6)
C23B	0.2315(3)	0.4169(3)	0.25404(19)	0.0320(7)
C24B	0.3202(3)	0.3607(3)	0.31031(18)	0.0349(7)
C25B	0.4510(3)	0.3682(4)	0.27817(18)	0.0380(8)
C26B	0.5098(3)	0.3125(3)	0.19974(16)	0.0254(6)
N2B	0.4716(2)	0.3852(2)	0.12914(13)	0.0183(4)
C1	0.3742(3)	0.7173(3)	0.4466(2)	0.0424(8)
Cl11	0.49666(10)	0.72562(11)	0.48953(8)	0.0653(3)
Cl12	0.42543(12)	0.67570(13)	0.34864(8)	0.0753(4)
Cl13	0.29758(11)	0.61567(10)	0.50463(8)	0.0632(3)
C2	0.6956(3)	0.7848(3)	0.0391(2)	0.0444(9)
Cl21	0.84970(9)	0.77018(11)	-0.00131(7)	0.0632(3)

Cl22	0.60417(10)	0.86489(9)	-0.03093(8)	0.0607(3)
Cl23	0.65541(13)	0.85715(15)	0.12702(9)	0.0895(5)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic atomic displacement parameters* ($Å^2$) for **G**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1A	0.01323(10)	0.01872(11)	0.01437(10)	-0.00012(8)	-0.00175(7)	-0.00603(8)
C1A	0.0144(12)	0.0195(13)	0.0219(13)	0.0019(10)	-0.0013(10)	-0.0058(10)
C2A	0.0211(14)	0.0270(15)	0.0218(14)	0.0013(11)	-0.0052(11)	-0.0075(12)
C3A	0.0177(13)	0.0316(16)	0.0339(16)	0.0029(13)	-0.0081(12)	-0.0104(12)
C4A	0.0170(13)	0.0341(17)	0.0375(17)	0.0009(14)	0.0043(12)	-0.0098(13)
C5A	0.0254(15)	0.0312(16)	0.0257(15)	-0.0055(12)	0.0059(12)	-0.0079(13)
C6A	0.0202(13)	0.0269(15)	0.0235(14)	-0.0032(11)	-0.0021(11)	-0.0079(12)
O1A	0.0181(9)	0.0374(12)	0.0211(10)	0.0095(9)	-0.0054(8)	-0.0076(9)
C11A	0.0200(13)	0.0246(14)	0.0198(13)	0.0014(11)	-0.0040(10)	-0.0049(11)
C12A	0.0195(14)	0.0388(18)	0.0257(15)	0.0118(13)	-0.0080(11)	-0.0086(13)
C13A	0.0305(16)	0.0304(16)	0.0331(16)	0.0082(13)	-0.0196(13)	-0.0119(13)
C14A	0.0324(16)	0.0393(18)	0.0179(14)	0.0015(12)	-0.0094(12)	-0.0057(14)
C15A	0.0259(15)	0.047(2)	0.0219(15)	0.0019(13)	-0.0045(12)	-0.0086(14)
C16A	0.0233(14)	0.0263(15)	0.0240(14)	0.0059(11)	-0.0057(11)	-0.0108(12)
N1A	0.0191(11)	0.0217(12)	0.0171(11)	0.0015(9)	-0.0051(9)	-0.0068(9)
O2A	0.0217(10)	0.0230(10)	0.0264(10)	-0.0066(8)	0.0040(8)	-0.0100(8)
C21A	0.0221(13)	0.0226(14)	0.0211(13)	-0.0039(11)	-0.0038(10)	-0.0071(11)
C22A	0.0285(15)	0.0270(16)	0.0293(16)	-0.0110(12)	0.0022(12)	-0.0099(13)
C23A	0.0409(19)	0.047(2)	0.0343(18)	-0.0216(16)	-0.0047(15)	-0.0105(16)
C24A	0.047(2)	0.072(3)	0.060(3)	-0.037(2)	-0.0010(19)	-0.033(2)
C25A	0.0365(19)	0.065(3)	0.057(2)	-0.032(2)	0.0082(17)	-0.0334(19)
C26A	0.0365(17)	0.0297(17)	0.0329(17)	-0.0083(13)	0.0067(13)	-0.0188(14)
N2A	0.0215(11)	0.0222(12)	0.0192(11)	-0.0036(9)	-0.0022(9)	-0.0092(10)
Rh1B	0.01424(10)	0.01630(10)	0.01497(10)	0.00061(7)	-0.00448(7)	-0.00554(8)
C1B	0.0198(13)	0.0192(13)	0.0213(13)	0.0038(10)	-0.0099(10)	-0.0075(11)
C2B	0.0237(14)	0.0297(16)	0.0281(15)	-0.0050(12)	-0.0075(12)	-0.0063(12)
C3B	0.0367(18)	0.043(2)	0.0318(17)	-0.0104(14)	-0.0144(14)	-0.0107(15)
C4B	0.0327(17)	0.0372(18)	0.0404(18)	-0.0031(14)	-0.0226(14)	-0.0130(14)
C5B	0.0204(14)	0.0293(16)	0.0392(17)	0.0044(13)	-0.0125(12)	-0.0117(12)
C6B	0.0223(13)	0.0235(14)	0.0217(13)	0.0019(11)	-0.0069(11)	-0.0086(11)
O1B	0.0250(10)	0.0202(10)	0.0322(11)	-0.0070(8)	-0.0134(8)	-0.0021(8)
C11B	0.0210(13)	0.0190(13)	0.0234(14)	-0.0031(11)	-0.0044(11)	-0.0062(11)
C12B	0.0312(16)	0.0226(15)	0.0343(16)	-0.0096(12)	-0.0142(13)	-0.0025(12)
C13B	0.0422(19)	0.0324(17)	0.0256(16)	-0.0116(13)	-0.0001(13)	-0.0054(15)
C14B	0.0283(17)	0.045(2)	0.043(2)	-0.0209(16)	-0.0003(14)	-0.0017(15)
C15B	0.0244(16)	0.051(2)	0.050(2)	-0.0241(18)	-0.0120(15)	0.0060(15)
C16B	0.0306(16)	0.0262(15)	0.0254(15)	-0.0041(12)	-0.0114(12)	0.0027(13)
N1B	0.0160(11)	0.0208(12)	0.0198(11)	-0.0017(9)	-0.0039(8)	-0.0041(9)
O2B	0.0219(10)	0.0349(12)	0.0217(10)	0.0107(9)	-0.0090(8)	-0.0153(9)
C21B	0.0211(13)	0.0223(14)	0.0206(13)	0.0010(11)	-0.0038(10)	-0.0089(11)
C22B	0.0220(14)	0.0340(17)	0.0265(15)	0.0100(12)	-0.0053(11)	-0.0144(13)
C23B	0.0238(15)	0.0283(16)	0.0355(17)	0.0059(13)	0.0066(12)	-0.0049(13)
C24B	0.0364(18)	0.044(2)	0.0224(15)	-0.0022(14)	0.0044(13)	-0.0149(15)
C25B	0.0361(18)	0.061(2)	0.0207(15)	0.0026(15)	-0.0055(13)	-0.0218(17)
C26B	0.0226(14)	0.0282(15)	0.0229(14)	0.0071(12)	-0.0059(11)	-0.0050(12)
N2B	0.0193(11)	0.0200(11)	0.0151(10)	0.0029(9)	-0.0026(8)	-0.0066(9)
C1	0.0377(19)	0.0328(19)	0.058(2)	-0.0128(17)	-0.0137(17)	-0.0040(15)
Cl11	0.0466(6)	0.0634(7)	0.0958(9)	-0.0096(6)	-0.0308(6)	-0.0155(5)
Cl12	0.0703(8)	0.0799(9)	0.0726(8)	-0.0396(7)	0.0011(6)	-0.0095(7)
Cl13	0.0645(7)	0.0477(6)	0.0863(8)	0.0059(5)	-0.0271(6)	-0.0236(5)
C2	0.0340(19)	0.0351(19)	0.060(2)	-0.0102(17)	0.0102(16)	-0.0133(16)
Cl21	0.0356(5)	0.0625(7)	0.0794(8)	0.0037(6)	0.0100(5)	-0.0109(5)
Cl22	0.0532(6)	0.0373(5)	0.0865(8)	0.0029(5)	-0.0091(5)	-0.0088(5)
Cl23	0.0683(8)	0.1161(12)	0.0842(9)	-0.0592(9)	0.0088(7)	-0.0176(8)

* The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Table 4. Hydrogen atom coordinates and isotropic atomic displacement parameters ($Å^2$) for **G**.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H2A	0.3202	1.0671	0.4908	0.028
H3A	0.5193	1.0547	0.4219	0.032
H4A	0.5725	1.0134	0.2881	0.037
H5A	0.4236	0.9878	0.2222	0.034
H6A	0.2244	0.9994	0.2906	0.028
H12A	0.3058	0.8475	0.6363	0.034
H12B	0.2365	0.7455	0.6717	0.034
H13A	0.2597	0.8811	0.7658	0.035
H13B	0.1480	0.9760	0.7332	0.035
H14A	0.0787	0.8693	0.8520	0.036
H14B	0.1352	0.7461	0.8100	0.036
H15A	-0.0773	0.8065	0.8147	0.039
H15B	-0.0671	0.9320	0.7685	0.039
H16A	0.0474	0.7143	0.6933	0.029
H16B	-0.0934	0.7791	0.6912	0.029
H22A	0.1077	0.6263	0.4004	0.034
H22B	0.1518	0.7124	0.3272	0.034
H23A	-0.0694	0.7771	0.3136	0.048
H23B	0.0125	0.6534	0.2787	0.048
H24A	-0.0637	0.5462	0.3953	0.065
H24B	-0.1721	0.6221	0.3507	0.065
H25A	-0.2307	0.7674	0.4430	0.059
H25B	-0.2297	0.6392	0.4886	0.059
H26A	-0.1456	0.7217	0.5646	0.039
H26B	-0.0293	0.6359	0.5144	0.039
H2B	0.4087	0.4688	-0.2030	0.032
H3B	0.2593	0.4520	-0.2713	0.042
H4B	0.0543	0.4914	-0.2099	0.040
H5B	-0.0018	0.5479	-0.0798	0.034
H6B	0.1455	0.5715	-0.0116	0.026
H12C	0.6081	0.1979	-0.1598	0.034
H12D	0.6531	0.1152	-0.0848	0.034
H13C	0.8088	0.1343	-0.2067	0.041
H13D	0.8028	0.2599	-0.1753	0.041
H14C	0.9670	0.1056	-0.1367	0.047
H14D	0.8716	0.0343	-0.0880	0.047
H15C	0.9346	0.1329	-0.0006	0.051
H15D	0.8939	0.2582	-0.0498	0.051
H16C	0.7188	0.1329	0.0290	0.034
H16D	0.7589	0.2235	0.0743	0.034
H22C	0.2935	0.2689	0.1867	0.032
H22D	0.1888	0.3714	0.1525	0.032
H23C	0.2304	0.5027	0.2424	0.038
H23D	0.1481	0.4125	0.2806	0.038
H24C	0.3200	0.2753	0.3225	0.042
H24D	0.2908	0.4008	0.3607	0.042
H25C	0.4519	0.4538	0.2715	0.046
H25D	0.5021	0.3286	0.3184	0.046
H26C	0.5998	0.2968	0.1940	0.030
H26D	0.4904	0.2343	0.2017	0.030
H1	0.3154	0.7984	0.4457	0.051
H2	0.6813	0.7030	0.0510	0.053

Table 5. Bond lengths (Å) and angles (°) for **G**.

Rh1A-C1A	1.996(3)	Rh1A-N1A#1	2.009(2)
Rh1A-N2A#1	2.011(2)	Rh1A-O2A	2.0743(19)
Rh1A-O1A	2.0865(19)	Rh1A-Rh1A#1	2.5172(4)
C1A-C6A	1.391(4)	C1A-C2A	1.397(4)
C2A-C3A	1.393(4)	C3A-C4A	1.385(4)
C4A-C5A	1.390(4)	C5A-C6A	1.392(4)
O1A-C11A	1.293(3)	C11A-N1A	1.303(3)
C11A-C12A	1.516(4)	C12A-C13A	1.525(4)
C13A-C14A	1.525(4)	C14A-C15A	1.526(4)
C15A-C16A	1.526(4)	C16A-N1A	1.472(3)
N1A-Rh1A#1	2.009(2)	O2A-C21A	1.290(3)
C21A-N2A	1.313(3)	C21A-C22A	1.513(4)
C22A-C23A	1.530(4)	C23A-C24A	1.526(5)
C24A-C25A	1.527(5)	C25A-C26A	1.504(5)
C26A-N2A	1.462(3)	N2A-Rh1A#1	2.011(2)
Rh1B-C1B	1.999(2)	Rh1B-N1B#2	2.008(2)
Rh1B-N2B#2	2.011(2)	Rh1B-O1B	2.077(2)
Rh1B-O2B	2.0858(18)	Rh1B-Rh1B#2	2.5126(4)
C1B-C2B	1.388(4)	C1B-C6B	1.393(4)
C2B-C3B	1.390(4)	C3B-C4B	1.381(5)
C4B-C5B	1.378(5)	C5B-C6B	1.396(4)
O1B-C11B	1.290(3)	C11B-N1B	1.310(3)
C11B-C12B	1.510(4)	C12B-C13B	1.527(4)
C13B-C14B	1.516(5)0	C14B-C15B	1.520(4)
C15B-C16B	1.516(4)	C16B-N1B	1.466(4)0
N1B-Rh1B#2	2.008(2)	O2B-C21B	1.286(3)
C21B-N2B	1.310(3)	C21B-C22B	1.515(4)
C22B-C23B	1.529(4)	C23B-C24B	1.515(5)
C24B-C25B	1.521(4)	C25B-C26B	1.519(4)
C26B-N2B	1.466(3)	N2B-Rh1B#2	2.011(2)
C1-Cl12	1.752(4)	C1-Cl11	1.752(4)
C1-Cl13	1.762(4)	C2-Cl23	1.740(4)
C2-Cl21	1.742(4)	C2-Cl22	1.772(4)

C1A-Rh1A-N1A#1	103.00(10)	C1A-Rh1A-N2A#1	101.49(10)
N1A#1-Rh1A-N2A#1	90.50(9)	C1A-Rh1A-O2A	85.05(9)
N1A#1-Rh1A-O2A	88.07(9)	N2A#1-Rh1A-O2A	173.46(8)
C1A-Rh1A-O1A	83.25(9)	N1A#1-Rh1A-O1A	173.71(8)
N2A#1-Rh1A-O1A	88.94(9)	O2A-Rh1A-O1A	91.78(8)
C1A-Rh1A-Rh1A#1	155.57(8)	N1A#1-Rh1A-Rh1A#1	96.04(6)
N2A#1-Rh1A-Rh1A#1	93.42(6)	O2A-Rh1A-Rh1A#1	80.39(5)
O1A-Rh1A-Rh1A#1	77.74(5)	C6A-C1A-C2A	119.0(2)
C6A-C1A-Rh1A	119.82(19)	C2A-C1A-Rh1A	121.0(2)
C3A-C2A-C1A	120.0(3)	C4A-C3A-C2A	120.8(3)
C3A-C4A-C5A	119.3(3)	C4A-C5A-C6A	120.3(3)
C1A-C6A-C5A	120.6(3)	C11A-O1A-Rh1A	129.62(17)
O1A-C11A-N1A	123.4(2)	O1A-C11A-C12A	114.1(2)
N1A-C11A-C12A	122.4(2)	C11A-C12A-C13A	112.6(3)
C14A-C13A-C12A	113.0(2)	C13A-C14A-C15A	114.2(2)
C16A-C15A-C14A	115.2(3)	N1A-C16A-C15A	114.3(2)
C11A-N1A-C16A	120.2(2)	C11A-N1A-Rh1A#1	113.13(18)
C16A-N1A-Rh1A#1	126.71(17)	C21A-O2A-Rh1A	127.14(17)
O2A-C21A-N2A	123.5(2)	O2A-C21A-C22A	114.4(2)
N2A-C21A-C22A	122.1(2)	C21A-C22A-C23A	112.7(3)
C24A-C23A-C22A	112.7(3)	C23A-C24A-C25A	113.8(3)
C26A-C25A-C24A	116.1(3)	N2A-C26A-C25A	115.5(3)
C21A-N2A-C26A	119.8(2)	C21A-N2A-Rh1A#1	115.47(18)
C26A-N2A-Rh1A#1	124.52(18)	C1B-Rh1B-N1B#2	102.58(10)
C1B-Rh1B-N2B#2	101.94(10)	N1B#2-Rh1B-N2B#2	91.08(9)
C1B-Rh1B-O1B	83.92(9)	N1B#2-Rh1B-O1B	173.50(8)
N2B#2-Rh1B-O1B	87.40(9)	C1B-Rh1B-O2B	84.30(9)
N1B#2-Rh1B-O2B	88.01(9)	N2B#2-Rh1B-O2B	173.73(8)
O1B-Rh1B-O2B	92.81(8)	C1B-Rh1B-Rh1B#2	155.20(8)
N1B#2-Rh1B-Rh1B#2	95.11(6)	N2B#2-Rh1B-Rh1B#2	94.89(6)
O1B-Rh1B-Rh1B#2	78.74(5)	O2B-Rh1B-Rh1B#2	79.03(5)
C2B-C1B-C6B	119.5(2)	C2B-C1B-Rh1B	119.4(2)

C6B-C1B-Rh1B	121.0(2)	C1B-C2B-C3B	120.0(3)
C4B-C3B-C2B	120.6(3)	C5B-C4B-C3B	119.5(3)
C4B-C5B-C6B	120.6(3)	C1B-C6B-C5B	119.7(3)
C11B-O1B-Rh1B	128.94(17)	O1B-C11B-N1B	123.2(2)
O1B-C11B-C12B	114.7(2)	N1B-C11B-C12B	122.1(2)
C11B-C12B-C13B	112.9(2)	C14B-C13B-C12B	113.6(3)
C13B-C14B-C15B	113.8(3)	C16B-C15B-C14B	115.6(3)
N1B-C16B-C15B	115.5(3)	C11B-N1B-C16B	120.4(2)
C11B-N1B-Rh1B#2	113.89(18)	C16B-N1B-Rh1B#2	125.66(18)
C21B-O2B-Rh1B	128.34(17)	O2B-C21B-N2B	123.6(2)
O2B-C21B-C22B	114.7(2)	N2B-C21B-C22B	121.7(2)
C21B-C22B-C23B	113.2(2)	C24B-C23B-C22B	113.2(3)
C23B-C24B-C25B	114.1(3)	C26B-C25B-C24B	115.7(3)
N2B-C26B-C25B	115.0(3)	C21B-N2B-C26B	120.3(2)
C21B-N2B-Rh1B#2	114.10(17)	C26B-N2B-Rh1B#2	125.51(17)
Cl12-C1-Cl11	110.8(2)	Cl12-C1-Cl13	110.92(19)
Cl11-C1-Cl13	109.8(2)	Cl23-C2-Cl21	110.9(2)
Cl23-C2-Cl22	110.5(2)	Cl21-C2-Cl22	109.6(2)

Symmetry transformation codes:#1 -x,-y+2,-z+1 #2 -x+1,-y+1,-z

Table 6. Torsion angles (°) for **G**.

N1A#1-Rh1A-C1A-C6A	-43.1(2)	N2A#1-Rh1A-C1A-C6A	-136.3(2)
O2A-Rh1A-C1A-C6A	43.8(2)	O1A-Rh1A-C1A-C6A	136.2(2)
Rh1A#1-Rh1A-C1A-C6A	97.2(3)	N1A#1-Rh1A-C1A-C2A	140.8(2)
N2A#1-Rh1A-C1A-C2A	47.5(2)	O2A-Rh1A-C1A-C2A	-132.4(2)
O1A-Rh1A-C1A-C2A	-40.0(2)	Rh1A#1-Rh1A-C1A-C2A	-79.0(3)
C6A-C1A-C2A-C3A	1.3(4)	Rh1A-C1A-C2A-C3A	177.5(2)
C1A-C2A-C3A-C4A	-0.8(5)	C2A-C3A-C4A-C5A	0.4(5)
C3A-C4A-C5A-C6A	-0.5(5)	C2A-C1A-C6A-C5A	-1.5(4)
Rh1A-C1A-C6A-C5A	-177.7(2)	C4A-C5A-C6A-C1A	1.0(5)
C1A-Rh1A-O1A-C11A	-164.8(3)	N2A#1-Rh1A-O1A-C11A	93.5(3)
O2A-Rh1A-O1A-C11A	-80.0(2)	Rh1A#1-Rh1A-O1A-C11A	-0.2(2)
Rh1A-O1A-C11A-N1A	2.1(4)	Rh1A-O1A-C11A-C12A	-175.37(19)
O1A-C11A-C12A-C13A	113.4(3)	N1A-C11A-C12A-C13A	-64.2(4)
C11A-C12A-C13A-C14A	82.2(3)	C12A-C13A-C14A-C15A	-62.1(4)
C13A-C14A-C15A-C16A	58.4(4)	C14A-C15A-C16A-N1A	-78.7(3)
O1A-C11A-N1A-C16A	177.1(3)	C12A-C11A-N1A-C16A	-5.5(4)
O1A-C11A-N1A-Rh1A#1	-3.0(4)	C12A-C11A-N1A-Rh1A#1	174.4(2)
C15A-C16A-N1A-C11A	70.0(3)	C15A-C16A-N1A-Rh1A#1	-109.9(2)
C1A-Rh1A-O2A-C21A	157.6(2)	N1A#1-Rh1A-O2A-C21A	-99.2(2)
O1A-Rh1A-O2A-C21A	74.5(2)	Rh1A#1-Rh1A-O2A-C21A	-2.7(2)
Rh1A-O2A-C21A-N2A	1.8(4)	Rh1A-O2A-C21A-C22A	-179.78(18)
O2A-C21A-C22A-C23A	-115.6(3)	N2A-C21A-C22A-C23A	62.9(4)
C21A-C22A-C23A-C24A	-83.3(4)	C22A-C23A-C24A-C25A	62.2(5)
C23A-C24A-C25A-C26A	-56.9(5)	C24A-C25A-C26A-N2A	77.6(4)
O2A-C21A-N2A-C26A	-174.3(3)	C22A-C21A-N2A-C26A	7.4(4)
O2A-C21A-N2A-Rh1A#1	1.0(4)	C22A-C21A-N2A-Rh1A#1	-177.3(2)
C25A-C26A-N2A-C21A	-70.8(4)	C25A-C26A-N2A-Rh1A#1	114.4(3)
N1B#2-Rh1B-C1B-C2B	136.9(2)	N2B#2-Rh1B-C1B-C2B	43.1(2)
O1B-Rh1B-C1B-C2B	-42.9(2)	O2B-Rh1B-C1B-C2B	-136.4(2)
Rh1B#2-Rh1B-C1B-C2B	-88.6(3)	N1B#2-Rh1B-C1B-C6B	-46.7(2)
N2B#2-Rh1B-C1B-C6B	-140.5(2)	O1B-Rh1B-C1B-C6B	133.5(2)
O2B-Rh1B-C1B-C6B	40.0(2)	Rh1B#2-Rh1B-C1B-C6B	87.8(3)
C6B-C1B-C2B-C3B	2.5(4)	Rh1B-C1B-C2B-C3B	178.9(2)
C1B-C2B-C3B-C4B	-1.7(5)	C2B-C3B-C4B-C5B	-0.1(5)
C3B-C4B-C5B-C6B	1.2(5)	C2B-C1B-C6B-C5B	-1.3(4)
Rh1B-C1B-C6B-C5B	-177.7(2)	C4B-C5B-C6B-C1B	-0.5(4)
C1B-Rh1B-O1B-C11B	-160.9(2)	N2B#2-Rh1B-O1B-C11B	96.8(2)
O2B-Rh1B-O1B-C11B	-76.9(2)	Rh1B#2-Rh1B-O1B-C11B	1.3(2)
Rh1B-O1B-C11B-N1B	1.2(4)	Rh1B-O1B-C11B-C12B	-176.70(18)
O1B-C11B-C12B-C13B	117.5(3)	N1B-C11B-C12B-C13B	-60.4(4)
C11B-C12B-C13B-C14B	83.0(3)	C12B-C13B-C14B-C15B	-63.3(4)

C13B-C14B-C15B-C16B	57.0(4)	C14B-C15B-C16B-N1B	-76.8(4)
O1B-C11B-N1B-C16B	173.1(3)	C12B-C11B-N1B-C16B	-9.2(4)
O1B-C11B-N1B-Rh1B#2	-3.5(3)	C12B-C11B-N1B-Rh1B#2	174.2(2)
C15B-C16B-N1B-C11B	71.2(3)	C15B-C16B-N1B-Rh1B#2	-112.6(3)
C1B-Rh1B-O2B-C21B	160.3(3)	N1B#2-Rh1B-O2B-C21B	-96.8(2)
O1B-Rh1B-O2B-C21B	76.7(2)	Rh1B#2-Rh1B-O2B-C21B	-1.2(2)
Rh1B-O2B-C21B-N2B	-0.3(4)	Rh1B-O2B-C21B-C22B	177.62(19)
O2B-C21B-C22B-C23B	-115.1(3)	N2B-C21B-C22B-C23B	62.8(4)
C21B-C22B-C23B-C24B	-82.6(3)	C22B-C23B-C24B-C25B	62.0(4)
C23B-C24B-C25B-C26B	-57.5(4)	C24B-C25B-C26B-N2B	77.9(4)
O2B-C21B-N2B-C26B	-175.4(3)	C22B-C21B-N2B-C26B	6.9(4)
O2B-C21B-N2B-Rh1B#2	2.0(4)	C22B-C21B-N2B-Rh1B#2	-175.7(2)
C25B-C26B-N2B-C21B	-70.3(3)	C25B-C26B-N2B-Rh1B#2	112.6(2)

Symmetry transformation codes:#1 -x,-y+2,-z+1 #2 -x+1,-y+1,-z

Details of the x-ray structural analysis of O. The crystal of **O** suitable X-ray analysis was obtained by evaporation of the solvents from the solution of **O** in Et_2O and acetone. An orange/green prism of $C_{36}H_{50}N_4O_4Rh_2$, approximate dimensions $0.041 \times 0.092 \times 0.147$ mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 150(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ= 0.71073 Å). The detector was placed at a distance of 5.2 cm from the crystal.

A total of 1731 frames was collected with a scan width of 0.3° in ω and an exposure time of 30 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 21.9 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 12334 reflections to a maximum θ angle of 25.00°, of which 2923 were independent (completeness = 99.7%, R_{int} = 2.51%, R_{sig} = 2.02%) and 2684 were greater than 2σ(I). The final cell dimensions of a = 8.5366(8) Å, b = 20.8840(19) Å, c = 10.0597(9) Å, α= 90°, β= 111.8290(10)°, γ= 90°, V = 1664.8(3) Å^3, are based upon the refinement of the XYZ-centroids of 6253 reflections with 2.4 < θ < 28.9° using Apex2. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.813 and 0.958.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group $P2_1/c$ with Z = 2 for the formula unit $C_{36}H_{50}N_4O_4Rh_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 208 variables converged at R_1=5.17 % for the observed data and wR_2=11.76 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 0.600 $\bar{e}$/Å^3 and the largest hole was -0.983 $\bar{e}$/Å^3. On the basis of the final model, the calculated density was 1.613 g/cm^3 and F(000), 832 $\bar{e}$.

Details of the crystal data and structure refinement (Supplemental Table 7), atomic coordinates and equivalent isotropic atomic displacement parameters (Supplemental Table 8), anisotropic atomic displacement parameters (Supplemental Table 9), Hydrogen atom coordinates and isotropic atomic displacement parameters (Supplemental Table 10), bond lengths and angles (Supplemental Table 11) are shown below.

Table 7. Crystal data and structure refinement for **O**.

Empirical formula	$C_{36}H_{50}N_4O_4Rh_2$
Formula weight	808.62

Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	$0.147 \times 0.092 \times 0.041$ mm^3	
Crystal habit	orange/green prism	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.5366(8) Å	α = 90°
	b = 20.8840(19) Å	β = 111.8290(10)°
	c = 10.0597(9) Å	γ = 90°
Volume	1664.8(3) Å^3	
Z	2	
Density, ρ_{calc}	1.613 g/cm^3	
Absorption coefficient, μ	1.037 mm^{-1}	
F(000)	832 ē	
Diffractometer	Bruker Smart Apex II CCD area detector	
Radiation source	fine-focus sealed tube, MoKα	
Detector distance	5.2 cm	
Detector resolution	8.333 pixels/mm	
Total frames	1731	
Frame size	1024 pixels	
Frame width	0.3°	
Exposure per frame	30 sec	
Total measurement time	21.9 hours	
Data collection method	ω scans	
θ range for data collection	2.57 to 25.00°	
Index ranges	$-10 \le h \le 10$, $-24 \le k \le 24$, $-11 \le l \le 11$	
Reflections collected	12334	
Independent reflections	2923	
Observed reflection, I>2σ(I)	2684	
Coverage of independent reflections	99.7 %	
Variation in check reflections	0 %	
Absorption correction	Semi-empirical from equivalents	
	SADABS (Sheldrick, 1996)	
Max. and min. transmission	0.958 and 0.813	
Structure solution technique	direct	
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Refinement technique	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2923 / 0 / 208	
Goodness-of-fit on F^2	1.000	
Δ/σ_{max}	0.000	
Final R indices: R_1, I>2σ(I)	0.0517	
wR_2, all data	0.1176	
R_{int}	0.0251	
R_{sig}	0.0202	
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.P)^2+0.P]$, $P = [\max(F_o^2,0)+2F_o^2]/3$	
Correct the scheme as in	w=1/[^2^(Fo^2^)+(0.008P)^2^+17.6P], P=(max(Fo^2^,0)+2Fc^2^)/3	
Largest diff. peak and hole	0.600 and -0.983 ē/Å^3	

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$

Table 8. Atomic coordinates and equivalent* isotropic atomic displacement parameters (Å^2) for **O**.

Atom	***x/a***	***y/b***	***z/c***	**U_{eq}**
Rh1	1.02301(6)	0.05348(2)	0.45453(5)	0.03395(17)
C1	1.1472(8)	0.1238(3)	0.4038(7)	0.0372(14)
C2	1.2782(9)	0.1560(3)	0.5086(8)	0.0430(16)
C3	1.3566(10)	0.2070(3)	0.4725(9)	0.0512(18)
C4	1.3120(10)	0.2249(4)	0.3324(9)	0.056(2)

C5	1.1845(10)	0.1924(4)	0.2254(9)	0.0534(19)
C6	1.1034(9)	0.1413(3)	0.2623(7)	0.0412(15)
N1	0.7809(6)	0.0788(2)	0.3592(6)	0.0357(12)
O1	0.7328(5)	-0.0179(2)	0.4410(5)	0.0419(11)
C11	0.6798(8)	0.0350(3)	0.3730(7)	0.0371(14)
C12	0.4903(8)	0.0431(4)	0.3085(8)	0.0485(17)
C13	0.4203(11)	0.0388(4)	0.1472(9)	0.065(2)
C14	0.4438(11)	0.0987(4)	0.0713(10)	0.068(2)
C15	0.6248(11)	0.1214(4)	0.1133(10)	0.070(2)
C16	0.7117(10)	0.1367(4)	0.2727(10)	0.062(2)
N2	1.0208(7)	0.0928(2)	0.6376(6)	0.0386(13)
O2	0.9917(6)	-0.0050(2)	0.7265(5)	0.0409(11)
C21	1.0008(9)	0.0570(3)	0.7334(7)	0.0421(15)
C22	0.9844(11)	0.0849(4)	0.8652(8)	0.056(2)
C23	0.8116(15)	0.1150(5)	0.8402(12)	0.090(3)
C24	0.7940(13)	0.1837(5)	0.7813(10)	0.076(3)
C25	0.8183(12)	0.1886(5)	0.6385(10)	0.071(2)
C26	0.9930(13)	0.1646(4)	0.6464(11)	0.075(3)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 9. Anisotropic atomic displacement parameters* ($Å^2$) for **O**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	0.0377(3)	0.0281(3)	0.0404(3)	-0.0026(2)	0.0195(2)	-0.0022(2)
C1	0.043(4)	0.026(3)	0.051(4)	0.001(3)	0.027(3)	0.001(3)
C2	0.044(4)	0.038(4)	0.047(4)	0.000(3)	0.019(3)	-0.004(3)
C3	0.050(4)	0.042(4)	0.061(5)	0.001(4)	0.021(4)	-0.007(3)
C4	0.060(5)	0.041(4)	0.073(6)	0.009(4)	0.030(4)	-0.006(4)
C5	0.064(5)	0.049(4)	0.054(5)	0.012(4)	0.029(4)	0.002(4)
C6	0.042(4)	0.040(4)	0.043(4)	0.000(3)	0.018(3)	-0.002(3)
N1	0.030(3)	0.027(3)	0.050(3)	-0.002(2)	0.015(2)	0.005(2)
O1	0.030(2)	0.045(3)	0.051(3)	0.008(2)	0.016(2)	0.000(2)
C11	0.034(3)	0.034(3)	0.045(4)	-0.004(3)	0.017(3)	-0.001(3)
C12	0.039(4)	0.046(4)	0.063(5)	0.004(3)	0.022(3)	0.005(3)
C13	0.059(5)	0.062(5)	0.075(6)	0.000(4)	0.026(4)	0.001(4)
C14	0.067(6)	0.069(6)	0.072(6)	0.013(5)	0.030(5)	0.017(5)
C15	0.073(6)	0.062(5)	0.085(7)	0.018(5)	0.040(5)	0.016(5)
C16	0.049(5)	0.041(4)	0.103(7)	0.004(4)	0.035(5)	0.007(4)
N2	0.054(3)	0.028(3)	0.042(3)	-0.009(2)	0.027(3)	-0.011(2)
O2	0.054(3)	0.031(2)	0.041(3)	-0.0019(19)	0.022(2)	0.000(2)
C21	0.047(4)	0.038(4)	0.039(4)	-0.007(3)	0.013(3)	0.002(3)
C22	0.077(6)	0.044(4)	0.049(4)	-0.008(3)	0.026(4)	0.001(4)
C23	0.124(9)	0.077(7)	0.095(8)	-0.005(6)	0.072(7)	-0.003(6)
C24	0.083(7)	0.070(6)	0.078(6)	-0.005(5)	0.034(5)	0.012(5)
C25	0.077(6)	0.068(6)	0.072(6)	-0.002(5)	0.031(5)	0.007(5)
C26	0.087(7)	0.058(5)	0.092(7)	-0.010(5)	0.047(6)	-0.010(5)

* The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Table 10. Hydrogen atom coordinates and isotropic atomic displacement parameters ($Å^2$) for **O**.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H2	1.3138	0.1426	0.6056	0.052
H3	1.4422	0.2299	0.5454	0.061
H4	1.3683	0.2596	0.3081	0.068
H5	1.1529	0.2048	0.1281	0.064
H6	1.0175	0.1184	0.1895	0.049
H12A	0.4371	0.0096	0.3473	0.058
H12B	0.4602	0.0852	0.3374	0.058
H13A	0.2981	0.0293	0.1143	0.078
H13B	0.4752	0.0025	0.1184	0.078
H14A	0.3971	0.0906	-0.0332	0.082

H14B	0.3770	0.1338	0.0905	0.082
H15A	0.6260	0.1603	0.0573	0.084
H15B	0.6903	0.0879	0.0873	0.084
H16A	0.8045	0.1675	0.2859	0.075
H16B	0.6295	0.1572	0.3073	0.075
H22A	1.0725	0.1180	0.9048	0.067
H22B	1.0060	0.0507	0.9380	0.067
H23A	0.7935	0.1154	0.9319	0.108
H23B	0.7224	0.0880	0.7720	0.108
H24A	0.6805	0.2001	0.7686	0.091
H24B	0.8783	0.2113	0.8525	0.091
H25A	0.8042	0.2338	0.6068	0.086
H25B	0.7293	0.1632	0.5657	0.086
H26A	1.0175	0.1855	0.5679	0.090
H26B	1.0782	0.1803	0.7375	0.090

Table 11. Bond lengths (Å) and angles (°) for **O**.

Rh1-C1	1.986(6)	Rh1-N1	1.999(5)
Rh1-N2	2.023(5)	Rh1-O2#1	2.047(4)
Rh1-O1#1	2.091(4)	Rh1-Rh1#1	2.4994(10)
C1-C6	1.380(9)	C1-C2	1.391(9)
C2-C3	1.376(9)	C3-C4	1.369(11)
C4-C5	1.390(11)	C5-C6	1.396(10)
N1-C11	1.300(8)	N1-C16	1.478(9)
O1-C11	1.289(8)	O1-Rh1#1	2.091(4)
C11-C12	1.512(9)	C12-C13	1.509(11)
C13-C14	1.518(11)	C14-C15	1.518(12)
C15-C16	1.530(12)	N2-C21	1.281(8)
N2-C26	1.526(10)	O2-C21	1.296(8)
O2-Rh1#1	2.047(4)	C21-C22	1.502(9)
C22-C23	1.536(13)	C23-C24	1.538(13)
C24-C25	1.529(12)	C25-C26	1.547(12)
C1-Rh1-N1	103.7(2)	C1-Rh1-N2	96.9(2)
N1-Rh1-N2	88.4(2)	C1-Rh1-O2#1	90.0(2)
N1-Rh1-O2#1	89.6(2)	N2-Rh1-O2#1	173.13(19)
C1-Rh1-O1#1	82.2(2)	N1-Rh1-O1#1	174.05(19)
N2-Rh1-O1#1	91.8(2)	O2#1-Rh1-O1#1	89.50(19)
C1-Rh1-Rh1#1	157.90(19)	N1-Rh1-Rh1#1	97.86(15)
N2-Rh1-Rh1#1	88.51(15)	O2#1-Rh1-Rh1#1	85.26(12)
O1#1-Rh1-Rh1#1	76.21(12)	C6-C1-C2	119.2(6)
C6-C1-Rh1	119.6(5)	C2-C1-Rh1	121.2(5)
C3-C2-C1	120.5(7)	C4-C3-C2	120.4(7)
C3-C4-C5	120.1(7)	C4-C5-C6	119.4(7)
C1-C6-C5	120.4(7)	C11-N1-C16	120.2(6)
C11-N1-Rh1	111.8(4)	C16-N1-Rh1	127.9(4)
C11-O1-Rh1#1	131.2(4)	O1-C11-N1	122.9(6)
O1-C11-C12	115.6(6)	N1-C11-C12	121.5(6)
C13-C12-C11	112.8(6)	C12-C13-C14	114.8(7)
C15-C14-C13	115.4(7)	C14-C15-C16	113.8(7)
N1-C16-C15	112.3(7)	C21-N2-C26	117.6(6)
C21-N2-Rh1	119.7(4)	C26-N2-Rh1	120.4(5)
C21-O2-Rh1#1	121.6(4)	N2-C21-O2	124.4(6)
N2-C21-C22	121.3(6)	O2-C21-C22	114.3(6)
C21-C22-C23	114.4(7)	C22-C23-C24	113.3(8)
C25-C24-C23	113.4(8)	C24-C25-C26	113.3(8)
N2-C26-C25	118.9(7)		

Symmetry transformation codes:#1 -x+2,-y,-z+1

Details of the x-ray structural analysis of PhACO. A purple prism of $C_{40}H_{58}N_4O_4Rh_2 \cdot 2CH_2Cl_2$, approximate dimensions 0.275´ 0.33´ 0.42 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 200(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ= 0.71073 Å). The detector was placed at a distance of 5.0000 cm from the crystal.

A total of 2184 frames were collected with a scan width of -0.5° in ω and an exposure time of 13 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 11.5 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 22338 reflections to a maximum θ angle of 30.00°, of which 6347 were independent (completeness = 99.3%, R_{int} = 5.80%, R_{sig} = 3.28%) and 6166 were greater than 2σ(I). The final cell dimensions of *a* = 10.0542(3) Å, *b* = 11.0233(3) Å, *c* = 11.6576(3) Å, α= 88.0671(4)°, β= 65.9778(3)°, γ= 69.4042(4)°, *V* = 1095.59(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 21281 reflections with 2.3 < θ < 32.1° using Apex2. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.686 and 0.751.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group *P-1* with *Z* = 1 for the formula unit $C_{40}H_{58}N_4O_4Rh_2 \cdot 2CH_2Cl_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 290 variables converged at R_1=1.99 % for the observed data and wR_2=4.66 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 0.721`e/$Å^3$ and the largest hole was -0.704`e/$Å^3$. On the basis of the final model, the calculated density was 1.568 g/cm^3 and F(000), 532`e. Fifteen restraints were employed to restrain geometry and atomic displacement parameters of disordered ligand (C13 to C16) described as superposition of two alternative conformations.

Details of the crystal data and structure refinement (Supplemental Table 12), atomic coordinates and equivalent isotropic atomic displacement parameters (Supplemental Table 13), anisotropic atomic displacement parameters (Supplemental Table 14), Hydrogen atom coordinates and isotropic atomic displacement parameters (Supplemental Table 15), and bond lengths and angles (Supplemental Table 16) are shown below.

Table 12. Crystal data and structure refinement for **PhACO**.

Formula weight	1034.58	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal size	0.42 ´ 0.33 ´ 0.275 mm^3	
Crystal habit	purple prism	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0542(3) Å	a = 88.0671(4)°
	b = 11.0233(3) Å	b = 65.9778(3)°
	c = 11.6576(3) Å	g = 69.4042(4)°
Volume	1095.59(5) $Å^3$	
Z	1	
Density, r_{calc}	1.568 g/cm^3	
Absorption coefficient, m	1.043 mm^{-1}	
F(000)	532`e	
Diffractometer	Bruker Smart Apex II CCD area detector	
Radiation source	fine-focus sealed tube, MoKa	

Detector distance		5.0000 cm
Detector resolution		11.198 pixels/mm
Total frames		2184
Frame size		512 pixels
Frame width		-0.5°
Exposure per frame		13 sec
Total measurement time		11.5 hours
Data collection method		w and φ scans
q range for data collection		1.99 to 30.00°
Index ranges		-14 £ *h* £ 14, -15 £ *k* £ 15, -16 £ *l* £ 16
Reflections collected		22338
Independent reflections		6347
Observed reflection, I>2s(I)		6166
Coverage of independent reflections		99.3 %
Variation in check reflections		0 %
Absorption correction		Semi-empirical from equivalents SADABS (Sheldrick, 1996)
Max. and min. transmission		0.751 and 0.686
Structure solution technique		direct
Structure solution program		SHELXS-97 (Sheldrick, 1990)
Refinement technique		Full-matrix least-squares on F^2
Refinement program		SHELXL-97 (Sheldrick, 1997)
Function minimized		$Sw(F_o^2 - F_c^2)^2$
Data / restraints / parameters		6347 / 15 / 290
Goodness-of-fit on F^2		1.003
D/s_{max}		0.001
Final R indices:	R_1, I>2s(I)	0.0199
	wR_2, all data	0.0466
	R_{int}	0.0580
	R_{sig}	0.0328
Weighting scheme	$w = 1/[s^2(F_o^2)+(0.01P)^2+1.091P]$, $P = [max(F_o^2,0)+2F_o^2]/3$	
Largest diff. peak and hole	0.721 and -0.704`e/Å^3	

$R_1 = S||F_o|-|F_c||/S|F_o|$, $wR2 = [Sw(F_o^2 - F_c^2)^2/S\, w(F_o^2)^2]^{1/2}$

Table 13. Atomic coordinates and equivalent* isotropic atomic displacement parameters (Å^2) for **PhACO**.

Atom	***x/a***	***y/b***	***z/c***	**U_{eq}**
Rh1	0.430393(11)	0.421754(9)	0.043074(9)	0.01432(3)
N1	0.23041(13)	0.58538(10)	0.13268(10)	0.01771(19)
O1	0.35742(11)	0.72644(9)	0.04471(9)	0.02028(18)
C11	0.23351(15)	0.70314(12)	0.11439(12)	0.0180(2)
C12	0.08951(16)	0.82788(13)	0.17310(15)	0.0248(3)
C13	0.0728(2)	0.89071(16)	0.29485(17)	0.0349(3)
C14	0.0101(3)	0.8237(3)	0.4111(2)	0.0392(6)
C15	0.1205(3)	0.6848(3)	0.4067(2)	0.0421(7)
C16	0.0780(2)	0.57775(17)	0.36418(16)	0.0380(4)
C13A	0.0728(2)	0.89071(16)	0.29485(17)	0.0349(3)
C14A	0.1077(9)	0.7972(6)	0.3919(5)	0.0365(15)
C15A	-0.0007(7)	0.7209(5)	0.4394(5)	0.0344(14)
C16A	0.0780(2)	0.57775(17)	0.36418(16)	0.0380(4)
C17	0.08684(17)	0.57422(14)	0.23106(14)	0.0253(3)
N2	0.45856(13)	0.39575(11)	0.20473(10)	0.0183(2)
O2	0.56468(12)	0.55123(9)	0.13796(9)	0.02083(18)
C21	0.52397(15)	0.47414(12)	0.21950(12)	0.0182(2)
C22	0.55523(18)	0.48609(14)	0.33449(13)	0.0236(3)

C23	0.72368(19)	0.40451(16)	0.31396(15)	0.0296(3)
C24	0.7597(2)	0.25848(17)	0.31725(18)	0.0359(4)
C25	0.7477(2)	0.18945(16)	0.21132(17)	0.0332(3)
C26	0.5933(2)	0.16984(15)	0.24409(18)	0.0326(3)
C27	0.44272(18)	0.29270(14)	0.28619(14)	0.0245(3)
C31	0.31543(15)	0.30861(12)	0.03735(12)	0.0177(2)
C32	0.36004(17)	0.18097(13)	0.06540(14)	0.0228(3)
C33	0.27779(18)	0.10292(14)	0.06224(16)	0.0277(3)
C34	0.15270(18)	0.15130(15)	0.02954(16)	0.0283(3)
C35	0.10948(17)	0.27837(14)	-0.00078(15)	0.0256(3)
C36	0.19097(16)	0.35657(13)	0.00177(13)	0.0211(2)
C1	0.4672(2)	0.15378(18)	0.72168(18)	0.0388(4)
Cl1	0.64585(6)	0.03320(6)	0.62097(6)	0.05963(15)
Cl2	0.34564(7)	0.21663(6)	0.64222(6)	0.05770(14)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
** Occupation factors C13 – C16 = 0.718(5), C13A – C16A = 0.282(5) and the same for corresponding H atoms

Table 14. Anisotropic atomic displacement parameters* (Å^2) for **PhACO**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	0.01686(5)	0.01331(4)	0.01436(5)	0.00328(3)	-0.00728(3)	-0.00667(3)
N1	0.0175(5)	0.0171(5)	0.0175(5)	0.0020(4)	-0.0064(4)	-0.0065(4)
O1	0.0197(4)	0.0159(4)	0.0230(5)	0.0036(3)	-0.0073(4)	-0.0062(3)
C11	0.0193(5)	0.0170(5)	0.0180(5)	0.0014(4)	-0.0098(5)	-0.0047(4)
C12	0.0200(6)	0.0179(6)	0.0323(7)	0.0009(5)	-0.0110(5)	-0.0022(5)
C13	0.0344(8)	0.0245(7)	0.0398(9)	-0.0094(6)	-0.0135(7)	-0.0055(6)
C14	0.0325(14)	0.0424(13)	0.0300(12)	-0.0144(9)	-0.0130(10)	0.0020(10)
C15	0.0385(14)	0.0512(14)	0.0230(11)	-0.0048(10)	-0.0169(10)	0.0042(11)
C16	0.0411(9)	0.0349(8)	0.0225(7)	0.0093(6)	-0.0043(7)	-0.0079(7)
C13A	0.0344(8)	0.0245(7)	0.0398(9)	-0.0094(6)	-0.0135(7)	-0.0055(6)
C14A	0.046(4)	0.042(3)	0.025(3)	-0.003(2)	-0.016(3)	-0.017(3)
C15A	0.034(3)	0.040(3)	0.020(2)	-0.0021(19)	-0.007(2)	-0.008(2)
C16A	0.0411(9)	0.0349(8)	0.0225(7)	0.0093(6)	-0.0043(7)	-0.0079(7)
C17	0.0213(6)	0.0247(6)	0.0231(6)	0.0008(5)	-0.0018(5)	-0.0096(5)
N2	0.0216(5)	0.0184(5)	0.0165(5)	0.0057(4)	-0.0094(4)	-0.0079(4)
O2	0.0289(5)	0.0222(4)	0.0172(4)	0.0066(3)	-0.0121(4)	-0.0135(4)
C21	0.0201(5)	0.0187(5)	0.0150(5)	0.0028(4)	-0.0082(4)	-0.0056(4)
C22	0.0314(7)	0.0262(6)	0.0173(6)	0.0039(5)	-0.0137(5)	-0.0113(5)
C23	0.0324(7)	0.0353(8)	0.0292(7)	0.0059(6)	-0.0199(6)	-0.0135(6)
C24	0.0386(9)	0.0346(8)	0.0416(9)	0.0089(7)	-0.0278(8)	-0.0091(7)
C25	0.0319(8)	0.0283(7)	0.0396(9)	0.0029(6)	-0.0208(7)	-0.0044(6)
C26	0.0411(9)	0.0224(7)	0.0447(9)	0.0128(6)	-0.0284(8)	-0.0120(6)
C27	0.0317(7)	0.0246(6)	0.0234(6)	0.0117(5)	-0.0146(6)	-0.0149(6)
C31	0.0191(5)	0.0169(5)	0.0183(5)	0.0023(4)	-0.0071(5)	-0.0087(4)
C32	0.0243(6)	0.0186(6)	0.0290(7)	0.0063(5)	-0.0136(5)	-0.0093(5)
C33	0.0313(7)	0.0199(6)	0.0357(8)	0.0074(5)	-0.0147(6)	-0.0137(5)
C34	0.0287(7)	0.0260(7)	0.0355(8)	0.0035(6)	-0.0128(6)	-0.0169(6)
C35	0.0240(6)	0.0270(7)	0.0307(7)	0.0029(5)	-0.0142(6)	-0.0118(5)
C36	0.0224(6)	0.0187(5)	0.0239(6)	0.0032(5)	-0.0113(5)	-0.0077(5)
C1	0.0437(10)	0.0371(9)	0.0325(8)	-0.0003(7)	-0.0124(7)	-0.0153(8)
Cl1	0.0351(2)	0.0642(3)	0.0683(4)	-0.0157(3)	-0.0149(2)	-0.0117(2)
Cl2	0.0453(3)	0.0679(4)	0.0621(3)	0.0021(3)	-0.0276(3)	-0.0171(3)

* The anisotropic atomic displacement factor exponent takes the form: $-2p^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Table 15. Hydrogen atom coordinates and isotropic atomic displacement parameters ($Å^2$) for **PhACO**.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H12A	-0.0041	0.8081	0.1908	0.039(4)
H12B	0.0946	0.8908	0.1115	0.039(4)
H13A	0.0020	0.9823	0.3109	0.033(5)
H13B	0.1755	0.8894	0.2833	0.033(5)
H14A	-0.0110	0.8770	0.4866	0.046(6)
H14B	-0.0898	0.8207	0.4198	0.046(6)
H15A	0.1181	0.6725	0.4910	0.049(6)
H15B	0.2277	0.6745	0.3483	0.049(6)
H16A	0.1480	0.4926	0.3713	0.039(5)
H16B	-0.0290	0.5886	0.4237	0.039(5)
H13C	-0.0346	0.9545	0.3378	0.033(5)
H13D	0.1432	0.9392	0.2721	0.033(5)
H14C	0.2166	0.7355	0.3516	0.046(6)
H14D	0.0964	0.8490	0.4644	0.046(6)
H15C	-0.0977	0.7684	0.4300	0.049(6)
H15D	-0.0282	0.7145	0.5296	0.049(6)
H16C	0.1843	0.5372	0.3591	0.039(5)
H16D	0.0180	0.5253	0.4122	0.039(5)
H17A	0.0803	0.4920	0.2093	0.037(4)
H17B	-0.0043	0.6458	0.2303	0.037(4)
H22A	0.4829	0.4585	0.4060	0.030(3)
H22B	0.5334	0.5781	0.3571	0.030(3)
H23A	0.7955	0.4175	0.2318	0.031(3)
H23B	0.7447	0.4373	0.3794	0.031(3)
H24A	0.6872	0.2455	0.3991	0.045(4)
H24B	0.8660	0.2165	0.3118	0.045(4)
H25A	0.7656	0.2399	0.1394	0.037(4)
H25B	0.8328	0.1035	0.1832	0.037(4)
H26A	0.5796	0.1139	0.3118	0.042(4)
H26B	0.6040	0.1218	0.1696	0.042(4)
H27A	0.3578	0.2682	0.2866	0.028(3)
H27B	0.4132	0.3273	0.3730	0.028(3)
H32	0.4458	0.1471	0.0866	0.028(5)
H33	0.3076	0.0171	0.0824	0.038(5)
H34	0.0973	0.0987	0.0278	0.034(5)
H35	0.0247	0.3115	-0.0231	0.031(5)
H36	0.1625	0.4417	-0.0204	0.031(5)
H1A	0.4873	0.2248	0.7513	0.051(5)
H1B	0.4137	0.1163	0.7958	0.051(5)

Table 16. Bond lengths (Å), valence and torsion angles (°) for **PhACO**.

Rh1-C31	1.9947(12)	Rh1-N2	2.0137(11)	Rh1-O1#1	2.0373(9)
Rh1-N1	2.0623(11)	Rh1-O2#1	2.1043(9)	Rh1-Rh1#1	2.52606(19)
N1-C11	1.3175(16)	N1-C17	1.4770(17)	O1-C11	1.2903(16)
O1-Rh1#1	2.0373(9)	C11-C12	1.5204(18)	C12-C13	1.521(2)
C13-C14	1.531(3)	C14-C15	1.531(3)	C15-C16	1.545(3)
C16-C17	1.519(2)	C14A-C15A	1.525(7)	N2-C21	1.3079(17)
N2-C27	1.4659(16)	O2-C21	1.2911(15)	O2-Rh1#1	2.1043(9)
C21-C22	1.5157(18)	C22-C23	1.532(2)	C23-C24	1.523(2)
C24-C25	1.539(2)	C25-C26	1.533(2)	C26-C27	1.538(2)
C31-C32	1.3900(17)	C31-C36	1.3998(18)	C32-C33	1.3975(19)

C33-C34	1.384(2)	C34-C35	1.393(2)	C35-C36	1.3906(19)
C1-Cl1	1.7550(19)	C1-Cl2	1.765(2)		
C31-Rh1-N2	105.55(5)	C31-Rh1-O1#1	92.28(4)	N2-Rh1-O1#1	87.34(4)
C31-Rh1-N1	94.62(5)	N2-Rh1-N1	90.73(4)	O1#1-Rh1-N1	173.10(4)
C31-Rh1-O2#1	81.10(4)	N2-Rh1-O2#1	171.41(4)	O1#1-Rh1-O2#1	86.97(4)
N1-Rh1-O2#1	94.17(4)	C31-Rh1-Rh1#1	154.42(4)	N2-Rh1-Rh1#1	99.99(3)
O1#1-Rh1-Rh1#1	87.47(3)	N1-Rh1-Rh1#1	86.33(3)	O2#1-Rh1-Rh1#1	73.34(3)
C11-N1-C17	118.17(11)	C11-N1-Rh1	120.48(9)	C17-N1-Rh1	120.86(8)
C11-O1-Rh1#1	121.10(8)	O1-C11-N1	124.43(12)	O1-C11-C12	112.18(11)
N1-C11-C12	123.39(12)	C11-C12-C13	113.75(12)	C12-C13-C14	113.99(15)
C15-C14-C13	114.4(2)	C14-C15-C16	113.4(2)	C17-C16-C15	116.86(15)
N1-C17-C16	114.47(13)	C21-N2-C27	120.39(11)	C21-N2-Rh1	109.07(8)
C27-N2-Rh1	129.53(9)	C21-O2-Rh1#1	134.27(8)	O2-C21-N2	122.70(12)
O2-C21-C22	113.64(11)	N2-C21-C22	123.64(12)	C21-C22-C23	113.44(12)
C24-C23-C22	114.85(13)	C24C23-C24-C25	114.91(13)	C26-C25-C24	116.85(15)
C25-C26-C27	117.52(13)	N2-C27-C26	113.38(12)	C32-C31-C36	119.39(12)
C32-C31-Rh1	120.64(10)	C36-C31-Rh1	119.95(9)	C31-C32-C33	120.18(13)
C34-C33-C32	120.38(13)	C33-C34-C35	119.56(13)	C36-C35-C34	120.43(13)
C35-C36-C31	120.02(12)	Cl1-C1-Cl2	110.77(10)		

C31-Rh1-N1-C11	-150.74(10)	N2-Rh1-N1-C11	103.60(10)	O2#1-Rh1-N1-C11	-69.34(10)
Rh1#1-Rh1-N1-C11	3.64(10)	C31-Rh1-N1-C17	37.42(11)	N2-Rh1-N1-C17	-68.24(10)
O2#1-Rh1-N1-C17	118.81(10)	Rh1#1-Rh1-N1-C17	-168.21(10)	Rh1#1-O1-C11-N1	-1.86(18)
Rh1#1-O1-C11-C12	178.53(8)	C17-N1-C11-O1	170.03(12)	Rh1-N1-C11-O1	-2.03(18)
C17-N1-C11-C12	-10.40(19)	Rh1-N1-C11-C12	177.54(10)	O1-C11-C12-C13	-84.10(16)
N1-C11-C12-C13	96.29(16)	C11-C12-C13-C14	-77.72(19)	C12-C13-C14-C15	66.2(3)
C13-C14-C15-C16	-98.8(3)	C14-C15-C16-C17	62.9(3)	C11-N1-C17-C16	-84.17(16)
Rh1-N1-C17-C16	87.85(13)	C15-C16-C17-N1	46.0(2)	C31-Rh1-N2-C21	-175.67(9)
O1#1-Rh1-N2-C21	92.70(9)	N1-Rh1-N2-C21	-80.67(9)	Rh1#1-Rh1-N2-C21	5.73(9)
C31-Rh1-N2-C27	16.04(13)	O1#1-Rh1-N2-C27	-75.59(12)	N1-Rh1-N2-C27	111.04(12)
Rh1#1-Rh1-N2-C27	-162.55(11)	Rh1#1-O2-C21-N2	-6.2(2)	Rh1#1-O2-C21-C22	175.32(9)
	C27-N2-C21-O2	167.98(12)	Rh1-N2-C21-O2	-1.56(16)	C27-N2-C21-C22
-13.7(2)		Rh1-N2-C21-C22	176.75(10)	O2-C21-C22-C23	-83.94(15)
N2-C21-C22-C23	97.62(16)		C21-C22-C23-C24		-76.02(17)
C22-C23-C24-C25	63.9(2)	C23-C24-C25-C26	-96.66(18)		C24-C25-C26-C27
60.2(2)	C21-N2-C27-C26	-81.17(16)	Rh1-N2-C27-C26	85.98(15)	C25-
C26-C27-N2	46.73(19)	N2-Rh1-C31-C32	-45.27(12)	O1#1-Rh1-C31-C32	42.60(11)
N1-Rh1-C31-C32	-137.32(11)	O2#1-Rh1-C31-C32	129.17(12)	Rh1#1-Rh1-C31-C32	131.52(10)
N2-Rh1-C31-C36	136.32(11)	O1#1-Rh1-C31-C36	-135.82(11)	N1-Rh1-C31-C36	44.27(11)
O2#1-Rh1-C31-C36	-49.24(11)	Rh1#1-Rh1-C31-C36	-46.90(16)	C36-C31-C32-C33	-2.2(2)
Rh1-C31-C32-C33	179.41(11)	C31-C32-C33-C34	0.9(2)	C32-C33-C34-C35	0.3(2)
C33-C34-C35-C36	-0.1(2)	C34-C35-C36-C31	-1.2(2)	C32-C31-C36-C35	2.3(2)
Rh1-C31-C36-C35	-179.22(11)				

Symmetry transformation codes:#1: -x+1,-y+1,-z

Details of the x-ray structural analysis of ACOBF4. A purple needle of $C_{32}H_{54}N_6O_4Rh_2 \cdot BF_4 \cdot 2CH_3CN$, approximate dimensions 0.025x0.07x0.255 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 200(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ= 0.71073 Å). The detector was placed at a distance of 5.0000 cm from the crystal.

A total of 1818 frames were collected with a scan width of -0.5° in and an exposure time of 40 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 23.2 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of

the data using a Monoclinic unit cell yielded a total of 19810 reflections to a maximum □ angle of 25.00°, of which 3653 were independent (completeness = 99.8%, R_{int} = 3.72%, R_{sig} = 2.54%) and 3296 were greater than 2□(I). The final cell dimensions of *a* = 24.381(2) Å, *b* = 7.1609(6) Å, *c* = 24.440(2) Å, α= 90°, β= 103.4465(13)°, γ= 90°, *V* = 4150.0(6) Å^3, are based upon the refinement of the XYZ-centroids of 8249 reflections with 2.7 < θ < 30.7° using Apex2. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.856 and 0.979. Fifty restraints were employed to geometry and atomic displacement parameters of BF_4 ions disordered around inversion center in two alternative orientations.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group *C2/c* with *Z* = 4 for the formula unit $C_{32}H_{54}N_6O_4Rh_2 \cdot BF_4 \cdot 2CH_3CN$. The final anisotropic full-matrix least-squares refinement on F^2 with 274 variables converged at R_1=3.14 % for the observed data and wR_2=6.67 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 0.633ē/Å^3 and the largest hole was -0.753ē/Å^3. On the basis of the final model, the calculated density was 1.539 g/cm^3 and F(000), 1980ē.

Table 17. Crystal data and structure refinement for **ACOBF4**.

Empirical formula	$C_{32}H_{54}N_6O_4Rh_2 \cdot BF_4 \cdot 2CH_3CN$	
Formula weight	961.55	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal size	0.255 □ 0.07 □ 0.025 mm^3	
Crystal habit	purple needle	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.381(2) Å	α = 90°
	b = 7.1609(6) Å	β = 103.4465(13)°
	c = 24.440(2) Å	γ = 90°
Volume	4150.0(6) Å^3	
Z	4	
Density, □$_{calc}$	1.539 g/cm^3	
Absorption coefficient, □	0.861 mm^{-1}	
F(000)	1980□e	
Diffractometer	Bruker Smart Apex II CCD area detector	
Radiation source	fine-focus sealed tube, MoK□	
Detector distance	5.0000 cm	
Detector resolution	11.198 pixels/mm	
Total frames	1818	
Frame size	512 pixels	
Frame width	-0.5°	
Exposure per frame	40 sec	
Total measurement time	23.2 hours	
Data collection method	ω and φ scans	
θ range for data collection	1.71 to 25.00°	
Index ranges	$-28 \le h \le 28$, $-8 \le k \le 8$, $-29 \le l \le 29$	
Reflections collected	19810	
Independent reflections	3653	
Observed reflection, I>2□(I)	3296	
Coverage of independent reflections	99.8 %	
Variation in check reflections	0 %	
Absorption correction	Semi-empirical from equivalents SADABS (Sheldrick, 1996)	
Max. and min. transmission	0.979 and 0.856	
Structure solution technique	direct	

Structure solution program		SHELXS-97 (Sheldrick, 1990)
Refinement technique		Full-matrix least-squares on F^2
Refinement program		SHELXL-97 (Sheldrick, 1997)
Function minimized		$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters		3653 / 50 / 274
Goodness-of-fit on F^2		0.996
Δ/σ_{max}		0.001
Final R indices:	R_1, I>2σ(I)	0.0314
	wR_2, all data	0.0667
	R_{int}	0.0372
	R_{sig}	0.0254
Weighting scheme		$w = 1/[\sigma^2(F_o^2)+(0.015P)^2+25.96P]$, $P = [\max(F_o^2,0)+2F_o^2]/3$
Largest diff. peak and hole		0.633 and -0.753 ē/Å^3

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$

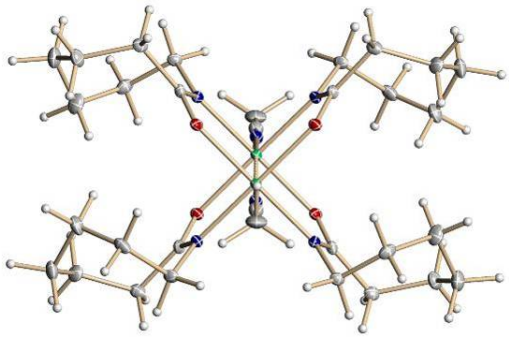


Figure S-2. Bisacetonitrile complex of dirhodium(II,III) tetrakis(1-aza-2-cyclooctanoate) = **ACOBF4;** view along the Rh-Rh bond axis with BF_4^- disordered and not shown. Bond lengths: Rh-Rh, 2.404 Å; Rh-N, 2.007 Å; Rh-O, 2.015 Å. Bond angles: AN-Rh-Rh, 174.1°; N-Rh-Rh, 88.5° and 88.5º; O-Rh-Rh, 87.8° and 87.9°.

Table 18. Atomic coordinates and equivalent* isotropic atomic displacement parameters (Å^2) for **ACOBF4**.

Atom	***x/a***	***y/b***	***z/c***	**U_{eq}**
Rh1	0.263738(10)	0.15140(3)	0.040695(10)	0.01643(8)
N1	0.28744(11)	-0.0587(4)	0.11101(11)	0.0238(6)
C1	0.29874(14)	-0.1656(5)	0.14581(15)	0.0289(8)
C2	0.31362(19)	-0.3003(6)	0.19135(18)	0.0534(12)
O11	0.19168(8)	0.5020(3)	0.00286(9)	0.0205(5)
N11	0.21831(10)	0.3154(3)	0.08007(10)	0.0184(5)
C11	0.19254(12)	0.4644(4)	0.05472(13)	0.0189(6)
C12	0.16195(14)	0.6062(4)	0.08260(14)	0.0252(7)
C13	0.10082(14)	0.5561(5)	0.08287(15)	0.0328(8)
C14	0.09149(15)	0.3973(5)	0.12148(17)	0.0385(9)
C15	0.10896(16)	0.2033(5)	0.10671(17)	0.0383(9)
C16	0.16694(15)	0.1375(5)	0.13908(14)	0.0311(8)
C17	0.21490(13)	0.2728(5)	0.13795(13)	0.0230(7)
O21	0.30393(8)	0.5088(3)	-0.00810(9)	0.0210(5)
N21	0.32969(10)	0.3215(4)	0.06888(10)	0.0187(5)
C21	0.33672(12)	0.4714(4)	0.04007(13)	0.0201(7)
C22	0.38305(13)	0.6141(4)	0.05949(14)	0.0250(7)
C23	0.43858(14)	0.5669(5)	0.04345(15)	0.0314(8)
C24	0.47266(14)	0.4048(5)	0.07499(17)	0.0352(9)
C25	0.44588(14)	0.2108(5)	0.06513(16)	0.0331(8)

C26	0.41625(14)	0.1420(5)	0.10960(15)	0.0323(8)
C27	0.37166(13)	0.2758(5)	0.12080(13)	0.0243(7)
N1A	0.18200(19)	0.7046(7)	0.23776(16)	0.0726(14)
C1A	0.1358(2)	0.7350(7)	0.23172(16)	0.0487(11)
C2A	0.0759(2)	0.7708(8)	0.2238(2)	0.0644(14)
B1**	0.4983(5)	0.7356(9)	0.2504(6)	0.052(2)
F1	0.5184(5)	0.9048(10)	0.2438(6)	0.135(4)
F2	0.4878(7)	0.642(2)	0.2024(6)	0.143(7)
F3	0.4503(3)	0.7518(15)	0.2667(5)	0.132(3)
F4	0.5358(6)	0.640(2)	0.2881(7)	0.126(6)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
** BF_4 is disordered around special site and occupation factor for all atoms (B1 – F4) was set to 0.5

Table 19. Anisotropic atomic displacement parameters* ($Å^2$) for **ACOBF4**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	0.01461(12)	0.01697(12)	0.01735(13)	0.00297(11)	0.00295(9)	0.00165(10)
N1	0.0195(14)	0.0241(15)	0.0272(15)	0.0028(13)	0.0045(11)	0.0015(12)
C1	0.0252(17)	0.0291(19)	0.0325(19)	0.0036(17)	0.0072(15)	0.0025(15)
C2	0.054(3)	0.056(3)	0.050(3)	0.032(2)	0.010(2)	0.011(2)
O11	0.0200(11)	0.0198(11)	0.0219(11)	0.0028(9)	0.0056(9)	0.0056(9)
N11	0.0181(13)	0.0177(14)	0.0195(13)	0.0015(11)	0.0048(10)	0.0010(10)
C11	0.0143(15)	0.0182(16)	0.0237(16)	-0.0007(13)	0.0035(12)	-0.0005(12)
C12	0.0289(18)	0.0207(17)	0.0262(18)	-0.0006(14)	0.0069(14)	0.0048(14)
C13	0.0243(18)	0.038(2)	0.037(2)	-0.0032(17)	0.0091(15)	0.0094(16)
C14	0.0254(19)	0.046(2)	0.047(2)	-0.0052(19)	0.0149(17)	-0.0014(17)
C15	0.033(2)	0.038(2)	0.045(2)	-0.0079(18)	0.0129(17)	-0.0150(17)
C16	0.042(2)	0.0289(19)	0.0268(18)	0.0003(16)	0.0163(16)	-0.0020(17)
C17	0.0269(17)	0.0234(17)	0.0183(16)	-0.0001(13)	0.0042(13)	0.0029(14)
O21	0.0184(11)	0.0211(11)	0.0217(11)	0.0030(9)	0.0014(9)	-0.0011(9)
N21	0.0146(12)	0.0208(14)	0.0194(13)	0.0018(11)	0.0015(10)	0.0008(11)
C21	0.0184(15)	0.0202(16)	0.0226(16)	-0.0010(13)	0.0064(13)	0.0009(13)
C22	0.0261(17)	0.0181(17)	0.0281(18)	0.0008(13)	0.0008(14)	-0.0027(13)
C23	0.0240(18)	0.034(2)	0.035(2)	0.0020(16)	0.0049(15)	-0.0106(16)
C24	0.0175(17)	0.041(2)	0.047(2)	-0.0004(18)	0.0069(16)	-0.0013(15)
C25	0.0210(17)	0.032(2)	0.045(2)	-0.0055(17)	0.0041(16)	0.0048(15)
C26	0.0231(17)	0.0282(19)	0.039(2)	0.0043(17)	-0.0064(15)	0.0001(15)
C27	0.0224(16)	0.0255(17)	0.0216(16)	0.0022(14)	-0.0019(13)	-0.0044(14)
N1A	0.058(3)	0.113(4)	0.042(2)	-0.016(2)	0.001(2)	-0.004(3)
C1A	0.064(3)	0.052(3)	0.027(2)	-0.0037(19)	0.003(2)	-0.002(2)
C2A	0.062(3)	0.079(4)	0.047(3)	-0.007(3)	0.002(2)	0.018(3)
B1	0.057(5)	0.047(5)	0.053(5)	-0.016(14)	0.016(4)	0.006(14)
F1	0.170(14)	0.072(5)	0.180(10)	0.009(7)	0.073(9)	-0.043(6)
F2	0.216(18)	0.135(11)	0.062(6)	-0.051(7)	0.002(8)	0.056(10)
F3	0.081(5)	0.154(9)	0.180(9)	-0.041(8)	0.067(6)	-0.002(6)
F4	0.119(9)	0.121(10)	0.109(10)	-0.011(7)	-0.034(7)	0.067(9)

* The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Table 20. Hydrogen atom coordinates and isotropic atomic displacement parameters ($Å^2$) for **ACOBF4**.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H2A	0.3530	-0.2820	0.2113	0.080
H2B	0.3087	-0.4271	0.1759	0.080
H2C	0.2892	-0.2826	0.2176	0.080
H12A	0.1620	0.7274	0.0632	0.030

H12B	0.1833	0.6230	0.1220	0.030
H13A	0.0825	0.6695	0.0934	0.039
H13B	0.0810	0.5234	0.0439	0.039
H14A	0.1125	0.4271	0.1603	0.046
H14B	0.0509	0.3939	0.1216	0.046
H15A	0.1082	0.2007	0.0660	0.046
H15B	0.0805	0.1128	0.1132	0.046
H16A	0.1656	0.1155	0.1787	0.037
H16B	0.1754	0.0165	0.1232	0.037
H17A	0.2089	0.3899	0.1573	0.028
H17B	0.2510	0.2174	0.1586	0.028
H22A	0.3904	0.6257	0.1009	0.030
H22B	0.3696	0.7369	0.0431	0.030
H23A	0.4300	0.5381	0.0027	0.038
H23B	0.4627	0.6798	0.0494	0.038
H24A	0.4803	0.4321	0.1158	0.042
H24B	0.5095	0.4007	0.0645	0.042
H25A	0.4182	0.2116	0.0284	0.040
H25B	0.4757	0.1200	0.0624	0.040
H26A	0.4448	0.1212	0.1452	0.039
H26B	0.3982	0.0203	0.0974	0.039
H27A	0.3524	0.2184	0.1481	0.029
H27B	0.3901	0.3920	0.1377	0.029
H2D	0.0609	0.8217	0.1860	0.097
H2E	0.0698	0.8609	0.2520	0.097
H2F	0.0564	0.6539	0.2280	0.097

Table 21. Bond lengths (Å), valence and torsion angles (°) for **ACOBF4**.

Rh1-N21	2.007(2)	Rh1-N11	2.007(2)	Rh1-O11#1	2.015(2)
Rh1-O21#1	2.015(2)	Rh1-N1	2.256(3)	Rh1-Rh1#1	2.4041(5)
N1-C1	1.130(4)	C1-C2	1.454(5)	O11-C11	1.291(4)
O11-Rh1#1	2.015(2)	N11-C11	1.317(4)	N11-C17	1.468(4)
C11-C12	1.513(4)	C12-C13	1.534(5)	C13-C14	1.528(5)
C14-C15	1.521(5)	C15-C16	1.525(5)	C16-C17	1.524(5)
O21-C21	1.288(4)	O21-Rh1#1	2.015(2)	N21-C21	1.317(4)
N21-C27	1.470(4)	C21-C22	1.515(4)	C22-C23	1.532(5)
C23-C24	1.528(5)	C24-C25	1.530(5)	C25-C26	1.520(5)
C26-C27	1.521(5)	N1A-C1A	1.122(6)	C1A-C2A	1.452(7)
B1-F2	1.326(9)	B1-F4	1.326(9)	B1-F3	1.326(9)
B1-F1	1.331(8)				

N21-Rh1-N11	88.15(10)	N21-Rh1-O11#1	91.41(9)	N11-Rh1-O11#1	176.44(9)
N21-Rh1-O21#1	176.38(9)	N11-Rh1-O21#1	91.74(9)	O11#1-Rh1-O21#1	88.47(8)
N21-Rh1-N1	95.76(10)	N11-Rh1-N1	95.58(10)	O11#1-Rh1-N1	87.98(9)
O21#1-Rh1-N1	87.85(9)	N21-Rh1-Rh1#1	88.53(7)	N11-Rh1-Rh1#1	88.53(7)
O11#1-Rh1-Rh1#1	87.93(6)	O21#1-Rh1-Rh1#1	87.84(6)	N1-Rh1-Rh1#1	174.14(7)
C1-N1-Rh1	179.0(3)	N1-C1-C2	178.9(4)	C11-O11-Rh1#1	121.13(19)
C11-N11-C17	119.6(3)	C11-N11-Rh1	120.3(2)	C17-N11-Rh1	120.09(19)
O11-C11-N11	121.9(3)	O11-C11-C12	113.9(3)	N11-C11-C12	124.3(3)
C11-C12-C13	115.2(3)	C14-C13-C12	117.4(3)	C15-C14-C13	116.3(3)
C14-C15-C16	115.9(3)	C17-C16-C15	114.6(3)	N11-C17-C16	111.4(3)
C21-O21-Rh1#1	121.33(19)	C21-N21-C27	119.5(3)	C21-N21-Rh1	120.3(2)
C27-N21-Rh1	120.2(2)	O21-C21-N21	121.9(3)	O21-C21-C22	113.9(3)
N21-C21-C22	124.2(3)	C21-C22-C23	114.2(3)	C24-C23-C22	116.6(3)
C23-C24-C25	116.6(3)	C26-C25-C24	116.0(3)	C25-C26-C27	113.8(3)
N21-C27-C26	111.6(3)	N1A-C1A-C2A	179.0(6)	F2-B1-F4	108.3(7)
F2-B1-F3	108.0(10)	F4-B1-F3	110.5(10)	F2-B1-F1	110.8(11)

F4-B1-F1	109.8(11)	F3-B1-F1	109.5(9)		
N21-Rh1-N11-C11	86.2(2)	O21#1-Rh1-N11-C11	-90.2(2)	N1-Rh1-N11-C11	-178.2(2)
Rh1#1-Rh1-N11-C11	-2.4(2)	N21-Rh1-N11-C17	-92.1(2)	O21#1-Rh1-N11-C17	91.5(2)
N1-Rh1-N11-C17	3.5(2)	Rh1#1-Rh1-N11-C17	179.3(2)	Rh1#1-O11-C11-N11	-6.1(4)
Rh1#1-O11-C11-C12	173.60(19)	C17-N11-C11-O11	-176.1(3)	Rh1-N11-C11-O11	5.6(4)
C17-N11-C11-C12	4.3(4)	Rh1-N11-C11-C12	-174.0(2)	O11-C11-C12-C13	96.0(3)
N11-C11-C12-C13	-84.4(4)	C11-C12-C13-C14	71.2(4)	C12-C13-C14-C15	-66.5(4)
C13-C14-C15-C16	97.4(4)	C14-C15-C16-C17	-52.3(4)	C11-N11-C17-C16	94.2(3)
Rh1-N11-C17-C16	-87.5(3)	C15-C16-C17-N11	-56.8(4)	N11-Rh1-N21-C21	-86.7(2)
O11#1-Rh1-N21-C21	89.8(2)	N1-Rh1-N21-C21	177.9(2)	Rh1#1-Rh1-N21-C21	1.9(2)
N11-Rh1-N21-C27	95.6(2)	O11#1-Rh1-N21-C27	-88.0(2)	N1-Rh1-N21-C27	0.1(2)
Rh1#1-Rh1-N21-C27	-175.9(2)	Rh1#1-O21-C21-N21	4.0(4)	Rh1#1-O21-C21-C22	-176.15(19)
C27-N21-C21-O21	173.8(3)	Rh1-N21-C21-O21	-3.9(4)	C27-N21-C21-C22	-6.0(4)
Rh1-N21-C21-C22	176.2(2)	O21-C21-C22-C23	-93.0(3)	N21-C21-C22-C23	86.9(4)
C21-C22-C23-C24	-71.5(4)	C22-C23-C24-C25	65.6(4)	C23-C24-C25-C26	-98.4(4)
C24-C25-C26-C27	54.3(4)	C21-N21-C27-C26	-93.5(3)	Rh1-N21-C27-C26	84.3(3)
C25-C26-C27-N21	55.1(4)				

Symmetry transformation codes:#1 -x+1/2,-y+1/2,-z

DFT Calculations. Optimization of the structures of **G** and **O** of bisphenyldirhodium(III) caprolactamate. The crystal structures were taken as the starting points for the optimizations. The optimized structures were verified using the normal mode analysis which indicated that all frequencies were in positive values. A comparison of the crystal and computational data in bond lengths and angles associated with the metal dirhodium(III) framework is given in Table S-1.

Table S-1. Experimental (Expt.) and calculated (Opt) data for selected bond lengths (in angstroms) and angles (in degrees) associated with the dirhodium(III) framework.

Properties	G (C_{2h})			O (Ci)		
	Expt.	Opt-g	Opt-s	Expt.	Opt-g	Opt-s
Rh-Rh	2.514	2.586	2.584	2.499	2.588	2.586
Rh-C	1.998	2.008	2.007	1.986	2.007	2.007
Rh-N	2.004	2.054	2.054	1.995	2.045	2.045
Rh-N	2.012	2.054	2.054	2.023	2.062	2.062
Rh-O	2.072	2.141	2.142	2.047	2.128	2.129
Rh-O	2.092	2.141	2.142	2.091	2.158	2.160
C-N_{amide}	1.304	1.322	1.321	1.280	1.321	1.320
C-N_{amide}	1.307	1.322	1.321	1.300	1.322	1.322
C-Rh-Rh	156.2	156.1	156.2	157.9	155.4	155.5
N-Rh-Rh	94.5	94.8	94.9	88.5	92.8	92.9
N-Rh-Rh	95.3	94.8	94.9	98.0	97.4	97.3
O-Rh-Rh	78.4	77.6	77.7	76.2	79.6	79.6
O-Rh-Rh	79.3	77.6	77.7	75.1	75.1	75.2
$\triangle E_{rel}$ (kJ/mol)	-	0.0	0.0	-	0.1	1.1

To investigate the origin of the conformational energies, conformation changes were calculated of the ligands only. The homologous compounds of 6- 7- and 8- member-rings (valarolactamate,

caprolactamate and 1-aza-2-cyclononanoate) were examined. The structural and energetic data are illustrated in the Figure S-3.

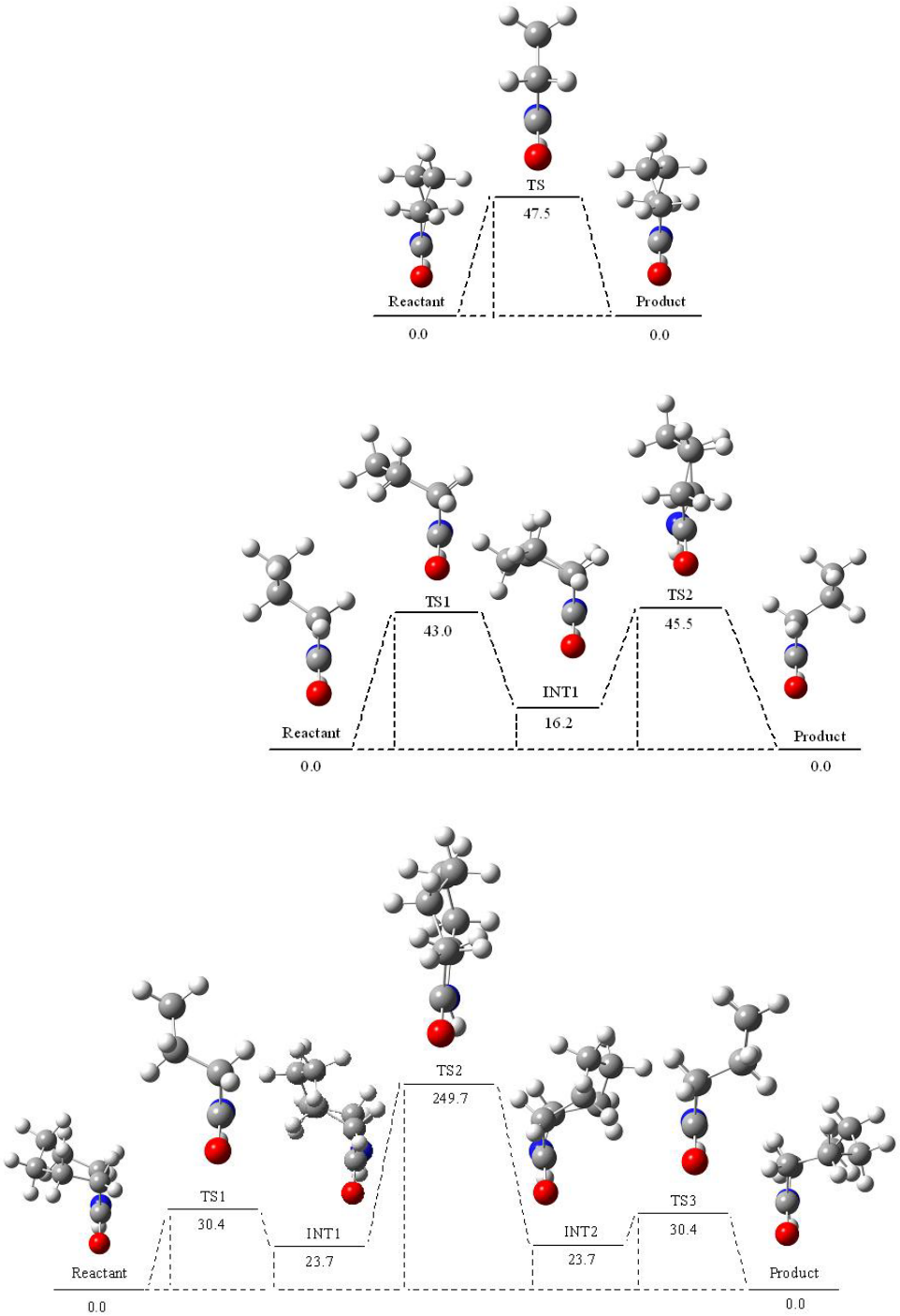


Figure S-3. The calculated energy pathways for 6-, 7-, 8-member-ring ligand molecules.

Table S-2. Experimental (Expt.) and calculated (Opt) data for selected bond lengths and angles associated with **PhACN**. The experimental data is based on the observed conformational orientation having a percentage of 78% of the propeller structure.

	Propeller			Biplanar
	Expt.	Opt 1	Opt 2	
Rh-Rh	2.526	2.526	2.526	2.526
Rh-C	1.995	2.017	2.015	2.039
Rh-N	2.014(2.062)	2.045(2.095)	2.041(2.096)	2.062(2.068)
Rh-O	2.037(2.104)	2.103(2.168)	2.099(2.177)	2.133(2.141)
C-Rh-Rh	154.4	153.1	152.7	151.9
N-Rh-Rh	86.3(100.0)	90.8(100.6)	89.9(101.7)	95.6(96.6)
O-Rh-Rh	73.3(87.5)	73.4(82.8)	72.3(83.7)	77.3(78.2)
$\triangle E_{rel}$		0.00	-0.74	9.42

Table S-3. Experimental (Expt.) and calculated (Opt) data for selected bond lengths and angles associated with **ACNBF4**. The experimental data is based on biplanar structure of **ACNBF4**.

	Biplanar		Propeller
	Expt	Opt	Opt
Rh-Rh	2.404	2.404	2.404
Rh-N	2.007	2.045(2.048)	2.052(2.054)
Rh-O	2.015	2.055(2.059)	2.049(2.051)
AN-Ru		2.365	2.364
AN-Rh-Rh	174.1	171.0	171.7
N-Rh-Rh	88.5	89.1(89.3)	88.3(88.4)
O-Rh-Rh	87.8	87.4(87.6)	88.2(88.3)
$\triangle E_{rel}$		0.00	-1.29