Supporting Information

Stable Ruthenium Nitrosyl Porphyrins with Axial O-Bonded Ligands; Preparation and Redox Behavior

Dennis Awasabisah,[a] Nan Xu,[a] Krishna P. Sharmah Gautam,[b] Douglas R. Powell,[a] Michael J. Shaw[b] and George B. Richter-Addo*[a]

CONTENTS

Experimental Section

General: All reactions were performed under N_2 using standard Schlenk glassware and/or in an Innovative Technology Labmaster 100 Dry Box. Solvents required for reactions were collected under a nitrogen atmosphere from a solvent distillation system (Innovative Technology, Inc. Newburyport, MA, USA, PS-400-5MD). Glass syringes were dried and purged with nitrogen gas before use. (T(*p*-OMe)PP)Ru(NO)(O-*i*-C_5H_{11}) was prepared as reported in literature.[1] Chloroform-*d* ($CDCl_3$, 99.96 atom %D), 2,3,5,6-tetrafluorophenol (HOC_6HF_4, 97%), trifluoroacetic acid ($CF_3C(=O)OH$, 99%), ferrocene (Fc, 98%) and tetrabutylammonium hexafluorophosphate (NBu_4PF_6, ≥99%) were purchased from Aldrich Chemical Co. Dichloromethane for electrochemical studies was purchased from Aldrich Chemical Company and distilled from CaH_2 under N_2 prior to use.

Instrumentation/Spectroscopy: IR spectra were recorded on a Bio-Rad FT-155 FTIR spectrometer. ^{1}H NMR spectroscopy data were obtained from a Varian 300 MHz spectrometer at 20 °C and the signals referenced to the residual signal of the solvent

employed ($CHCl_3$ at 7.24 ppm). ^{19}F NMR spectral signals referenced to $C_6H_5CF_3$ set to -63.72 ppm\. Coupling constants are reported in Hz. ESI mass spectra were obtained on a Micromass Q-TOF mass spectrometer.

Cyclic voltammetric measurements were performed using a BAS CV50W instrument (Bioanalytical Systems, West Lafayette, IN). A three-electrode cell was utilized and consisted of a 3.0-mm diameter Pt disk working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. Solutions were deaerated before electrochemical experiments by passing a stream of N_2 gas through the solution for a minimum of 10 min. A blanket of N_2 was maintained over the solution while performing the experiments. The electrochemical experiments were performed in solutions containing 0.1 M NBu_4PF_6 at room temperature. A Bruker Vector 22 FTIR spectrometer equipped with a mid-IR fiber-optic dip probe and liquid nitrogen cooled MCT detector (RemSpec Corporation, Sturbridge, MA, USA) was used for spectroelectrochemistry. Ferrocene was used as standard for the electrochemical experiments, and potentials were referenced to the Fc/Fc^+ couple set at 0.00 V. X-ray diffraction data was collected using a diffractometer with a Bruker APEX ccd area detector[2, 3] and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).

Synthesis of Compounds:

(T(*p*-OMe)PP)Ru(NO)(OC_6HF_4) (1). To a stirred 10 mL solution of (T(*p*-OMe)PP)Ru(NO)(O-*i*-C_5H_{11}) (50 mg, 0.053 mmol) at room temperature was added excess 2,3,5,6-tetrafluorophenol (45.7 mg, 0.284 mmol). The color of the solution changed from red to green on stirring for 30 min. After 1 h of stirring, the volume of the solvent was reduced in vacuo to 2 mL, then 10 mL of hexane was added to aid precipitation of a solid. The supernatant was discarded, and the resulting solid washed with methanol (3 x 15 mL) and the supernatant discarded each time. The solid was dried overnight in vacuo. Further purification of the solid was accomplished as follows: The solid was dissolved in a minimum amount of CH_2Cl_2 and applied on a neutral alumina (in hexane) column. The column was first eluted with hexane to remove trace unreacted species and byproducts. A green band was then eluted with CH_2Cl_2; this green band was collected and taken to dryness overnight in vacuo to afford (T(*p*-OMe)PP)Ru(NO)(OC_6HF_4) (**1**; 43.6 mg, 80% yield). IR (CH_2Cl_2, cm^-

^{1}): υ_{NO} = 1850 s. IR (KBr, cm^{-1}): υ_{NO} = 1844 s; also 1735 w, 1685 w, 1654 m, 1636 m, 1606 m, 1559 m, 1540 w, 1507 s, 1501 s, 1472 s, 1458 m, 1438 w, 1349 m, 1305 w, 1288 m, 1245 s, 1176 s, 1093 s, 1019 s, 1010 m, 932 m, 848 w, 901 s, 718 m, 607 w. ^{19}F NMR (282 MHz, $CDCl_3$, 20 °C): δ −146.7 (m, 2F) and δ −162.2 (m, 2F). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 9.01 (s, 8H, *pyrrole*-H of T(*p*-OMe)PP), 8.17 (d, $^{3}J_{H-H}$ = 7.2 Hz, 4H, *o*-H of (T(*p*-OMe)PP), 8.08 (d, $^{3}J_{H-H}$ = 7.5 Hz, 4H, *o′*-H of (T(*p*-OMe)PP), 7.30 (*app* t (overlapping d's), 8H, *m*/ *m′*-H of (T(*p*-OMe)PP)), 5.29 (m, 1H, *H*-C_6F_4), 4.10 (s, 12H, OCH_3). The ESI mass spectrum (TOF) of **1** shows peaks at *m/z* = 864.3 and *m/z* = 1052.3 representing [(T(*p*-OMe)PP)Ru(NO)]$^{+}$ (100%) and [M + Na^{+}] respectively. Anal. Calc. ($C_{54}H_{37}N_5O_6F_4Ru$•CH_3OH): C, 62.26; H, 3.89; N, 6.60 %. Found: C, 62.29; H, 3.61, N 6.74 %.

(T(*p*-OMe)PP)Ru(NO)(OC(=O)CF_3) (2). A stirred CH_2Cl_2 (10 mL) solution of (T(*p*-OMe)PP)Ru(NO)(O-*i*-C_5H_{11}) (50 mg, 0.053 mmol) was treated with excess trifluoroacetic acid (~0.2 mL, ~3 mmol). After stirring for 1 h, the color of the solution changed from red to green. The volume of the solution was reduced to 2 mL in vacuo, and 10 mL hexane was added to aid precipitation of a solid. The supernatant was discarded and the resulting solid was washed with methanol (3 x 15 mL) and the supernatant discarded each time. The crude solid was dried overnight in vacuo. Further purification of the crude solid was accomplished by dissolving it in a minimum amount of CH_2Cl_2 and applying it on a neutral alumina (in hexane) column. The column was first eluted with hexane to remove trace unreacted species and byproducts, and then CH_2Cl_2 was then used to elute a green band which was collected and dried overnight under vacuum to afford (T(*p*-OMe)PP)Ru(NO)(OC(=O)CF_3) (**2**; 44.0 mg, 85% yield). IR (CH_2Cl_2, cm^{-1}): υ_{NO} = 1866 s; υ_{CO} = 1717 m. IR (KBr, cm^{-1}): υ_{NO} = 1861 s, υ_{CO} = 1719 m; also 1606 s, 1512 s, 1493 w, 1463 w, 1348 m, 1245 s, 1175 s, 1020 s, 1009 m, 810 m, 800 m, 713 w.). IR (CH_2Cl_2, cm^{-1}): υ_{NO} = 1866 s; υ_{CO} = 1717 m. IR (KBr, cm^{-1}): υ_{NO} = 1861 s, υ_{CO} = 1719 m; also 1606 s, 1512 s, 1493 w, 1463 w, 1348 m, 1245 s, 1175 s, 1020 s, 1009 m, 810 m, 800 m, 713 w. ^{19}F NMR (282 MHz, $CDCl_3$, 20 °C): δ = −78.1 (s, 3F, CF_3). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) : δ = 9.04 (s, 8H, *pyrrole*-H of T(*p*-OMe)PP), 8.20 (d, $^{3}J_{H-H}$ = 7.8 Hz , 4H, *o*-H of (T(*p*-

OMe)PP), 8.10 (d, $^{3}J_{H\text{-}H}$ = 8.1 Hz, 4H, *o′*-H of (T(*p*-OMe)PP), 7.30 (*app* d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 8H, *m*/ *m′*-H of (T(*p*-OMe)PP), 4.10 (s, 12H, OCH_3). The ESI mass spectrum (TOF) of **2** shows peaks at *m/z* = 864.1 and *m/z* = 1000.1 representing [(T(*p*-OMe)PP)Ru(NO)]$^{+}$ (100%) and [M + Na^{+}] respectively. Anal. Calc. ($C_{50}H_{36}N_5O_7F_3Ru{\bullet}CH_2Cl_2$): C, 57.69; H, 3.61; N, 6.60 %. Found: C, 57.62; H, 3.34; N, 6.60 %.

B. Crystallography

(i) (T(*p*-OMe)PP)Ru(NO)(OC_6HF_4) (**1**)

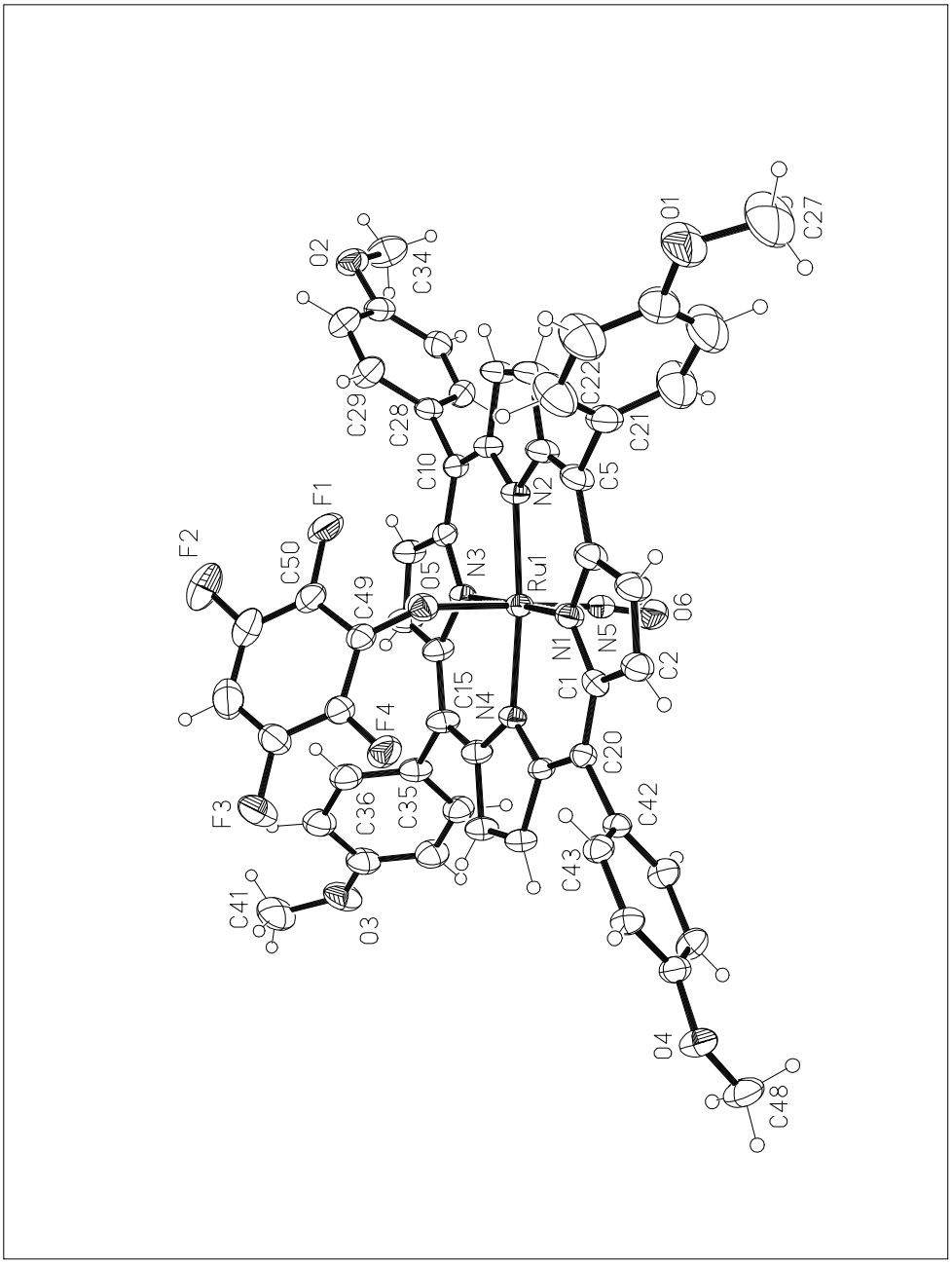

Fig. S1. Thermal Ellipsoid plot of (T(*p*-OMe)PP)Ru(NO)(OC_6HF_4) (**1**). The C_6H_{14} solvate is not shown.

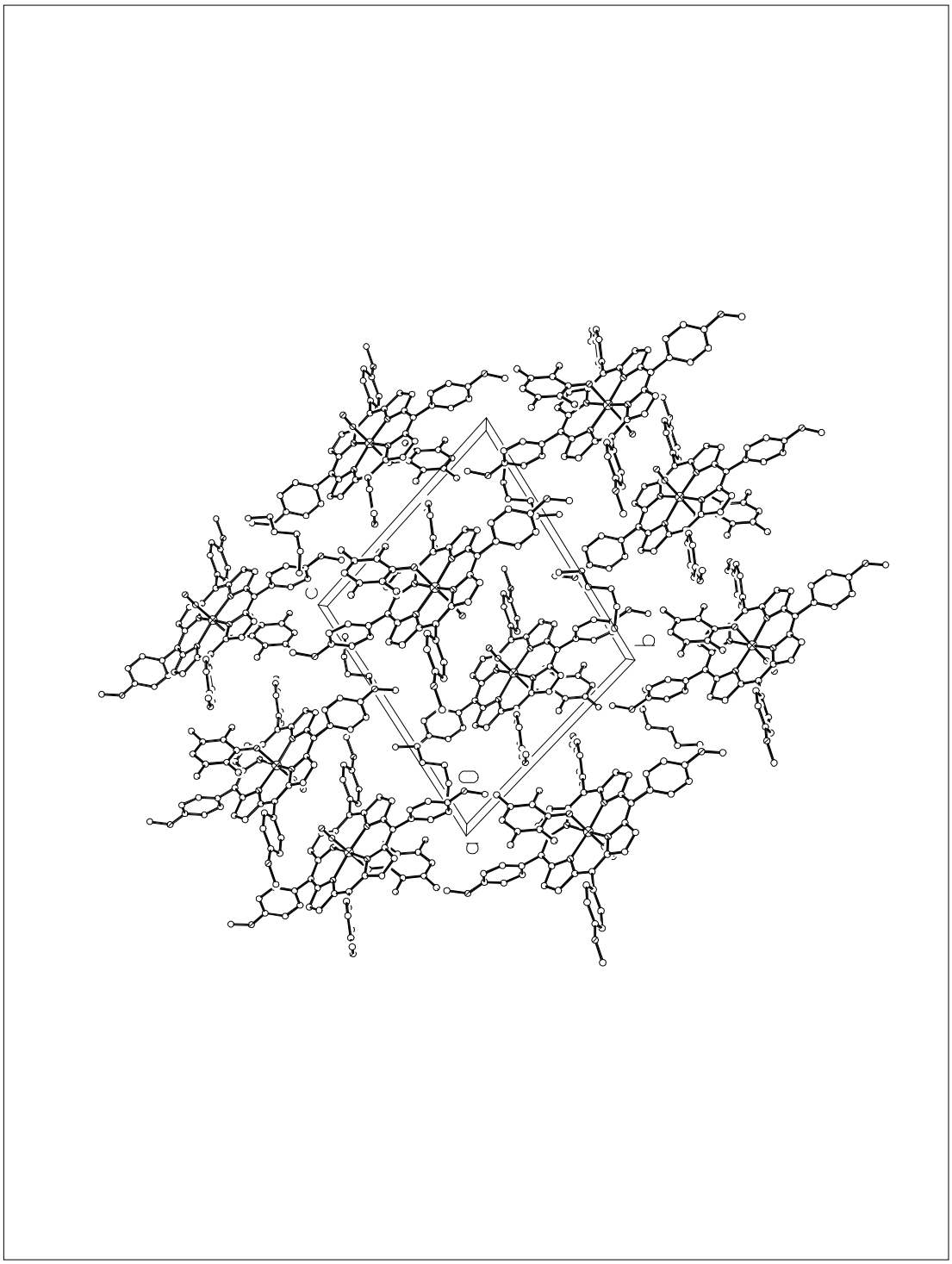

Fig. S2. Unit cell and packing diagram of (T(*p*-OMe)PP)Ru(NO)(OC_6HF_4) (**1**). The C_6H_{14} solvate is not shown.

Comment

One *p*-methoxyphenyl group was disordered. The occupancies for atoms O3, C35-C41 refined to 0.444(6), 0.349(6), and 0.207(4) for the unprimed, primed and double-primed atoms, respectively. One end of the *n*-hexane was disordered. The occupancies for atom C6S refined to 0.792(15) and 0.208(15) for the unprimed and primed atoms. Restriants on the positional and displacement parameters of all disordered atoms were required. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A purple block-shaped crystal of dimensions 0.380 x 0.260 x 0.080 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector[2] and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear least squares fit of 6753 peaks in the range 2.27 < θ < 28.31°. A total of 41662 data were measured in the range 1.196 < θ < 28.334° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical from equivalents method[3] giving minimum and maximum transmission factors of 0.867 and 0.970. The data were merged to form a set of 12434 independent data with R(int) = 0.0439 and a coverage of 100.0 %.

The triclinic space group $P\bar{1}$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[3] The positions of hydrogens bonded to carbons were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 842 parameters were refined against 910 restraints and 12434 data to give wR(F^2) = 0.1954 and S = 1.005 for weights of w = 1/[σ^2 (F^2) + (0.1260 P)^2 + 3.2000 P], where P = [F_o^2 + 2F_c^2] / 3. The final R(F) was 0.0617 for the 9328 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 2.519 and -1.193 e/Å^3, respectively.

Table S1. Crystal data and structure refinement for (T(*p*-OMe)PP)Ru(NO)(OC_6HF_4) ·(C_6H_{12}) (**1**·C_6H_{14}).

Empirical formula	(C_{54} H_{37} F_4 N_5 O_6 Ru) · (C_6 H_{14})	
	C_{60} H_{51} F_4 N_5 O_6 Ru	
Formula weight	1115.12	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	*a* = 9.4322(6) Å	α= 72.590(2)°
	b = 16.2330(11) Å	β= 78.034(2)°
	c = 18.0081(12) Å	γ= 74.000(3)°
Volume	2505.5(3) $Å^3$	
Z, *Z*'	2, 1	
Density (calculated)	1.478 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1148	
Absorption coefficient	0.388 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.970 and 0.867	
Theta range for data collection	1.196 to 28.334°	
Reflections collected	41662	
Independent reflections	12434 [R(int) = 0.0439]	
Data / restraints / parameters	12434 / 910 / 842	
wR(F^2 all data)	*wR*2 = 0.1954	
R(*F* obsd data)	*R*1 = 0.0617	
Goodness-of-fit on F^2	1.005	
Observed data [I > 2σ(I)]	9328	
Extinction coefficient	n/a	
Largest and mean shift / s.u.	0.001and 0.000	
Largest diff. peak and hole	2.519 and -1.193 e/$Å^3$	

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

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table S2. Bond lengths (Å) and angles (°) for (T(*p*-OMe)PP)Ru(NO)(OC_6HF_4)·(C_6H_{14}) (**1**·C_6H_{14}).

Ru(1)-N(5)	1.739(3)	C(5)-C(21)	1.511(5)
Ru(1)-O(5)	2.000(3)	C(6)-C(7)	1.441(5)
Ru(1)-N(3)	2.055(3)	C(7)-C(8)	1.357(6)
Ru(1)-N(4)	2.059(3)	C(7)-H(7)	0.9500
Ru(1)-N(2)	2.061(3)	C(8)-C(9)	1.446(5)
Ru(1)-N(1)	2.064(3)	C(8)-H(8)	0.9500
F(1)-C(50)	1.351(5)	C(9)-C(10)	1.391(5)
F(2)-C(51)	1.353(5)	C(10)-C(11)	1.394(5)
F(3)-C(53)	1.353(5)	C(10)-C(28)	1.506(5)
F(4)-C(54)	1.338(5)	C(11)-C(12)	1.440(5)
O(1)-C(24)	1.391(6)	C(12)-C(13)	1.353(5)
O(1)-C(27)	1.398(7)	C(12)-H(12)	0.9500
O(2)-C(31)	1.375(5)	C(13)-C(14)	1.438(5)
O(2)-C(34)	1.437(6)	C(13)-H(13)	0.9500
O(3)-C(38)	1.383(8)	C(14)-C(15)	1.406(5)
O(3)-C(41)	1.413(10)	C(15)-C(16)	1.393(5)
O(3')-C(38')	1.384(8)	C(15)-C(35)	1.516(6)
O(3')-C(41')	1.417(10)	C(15)-C(35')	1.519(6)
O(3")-C(38")	1.389(9)	C(15)-C(35")	1.540(7)
O(3")-C(41")	1.418(11)	C(16)-C(17)	1.442(5)
O(4)-C(45)	1.364(4)	C(17)-C(18)	1.356(5)
O(4)-C(48)	1.429(5)	C(17)-H(17)	0.9500
O(5)-C(49)	1.316(5)	C(18)-C(19)	1.442(5)
O(6)-N(5)	1.156(4)	C(18)-H(18)	0.9500
N(1)-C(4)	1.374(5)	C(19)-C(20)	1.400(5)
N(1)-C(1)	1.377(5)	C(20)-C(42)	1.500(5)
N(2)-C(9)	1.371(5)	C(21)-C(26)	1.354(7)
N(2)-C(6)	1.376(5)	C(21)-C(22)	1.378(7)
N(3)-C(11)	1.373(4)	C(22)-C(23)	1.388(7)
N(3)-C(14)	1.377(5)	C(22)-H(22)	0.9500
N(4)-C(19)	1.364(4)	C(23)-C(24)	1.348(7)
N(4)-C(16)	1.374(5)	C(23)-H(23)	0.9500
C(1)-C(20)	1.405(5)	C(24)-C(25)	1.351(8)
C(1)-C(2)	1.442(5)	C(25)-C(26)	1.418(7)
C(2)-C(3)	1.366(5)	C(25)-H(25)	0.9500
C(2)-H(2)	0.9500	C(26)-H(26)	0.9500
C(3)-C(4)	1.443(5)	C(27)-H(27A)	0.9800
C(3)-H(3)	0.9500	C(27)-H(27B)	0.9801
C(4)-C(5)	1.405(5)	C(27)-H(27C)	0.9800
C(5)-C(6)	1.394(6)	C(28)-C(29)	1.378(5)

C(28)-C(33)	1.395(5)	C(39")-C(40")	1.389(8)
C(29)-C(30)	1.396(6)	C(39")-H(39")	0.9500
C(29)-H(29)	0.9500	C(40")-H(40")	0.9500
C(30)-C(31)	1.375(6)	C(41")-H(41G)	0.9800
C(30)-H(30)	0.9500	C(41")-H(41H)	0.9800
C(31)-C(32)	1.392(6)	C(41")-H(41I)	0.9800
C(32)-C(33)	1.397(6)	C(42)-C(47)	1.392(5)
C(32)-H(32)	0.9500	C(42)-C(43)	1.396(5)
C(33)-H(33)	0.9500	C(43)-C(44)	1.386(5)
C(34)-H(34A)	0.9800	C(43)-H(43)	0.9500
C(34)-H(34B)	0.9800	C(44)-C(45)	1.402(5)
C(34)-H(34C)	0.9800	C(44)-H(44)	0.9500
C(35)-C(36)	1.375(6)	C(45)-C(46)	1.382(5)
C(35)-C(40)	1.380(6)	C(46)-C(47)	1.393(5)
C(36)-C(37)	1.390(7)	C(46)-H(46)	0.9500
C(36)-H(36)	0.9500	C(47)-H(47)	0.9500
C(37)-C(38)	1.393(5)	C(48)-H(48A)	0.9801
C(37)-H(37)	0.9500	C(48)-H(48B)	0.9799
C(38)-C(39)	1.396(5)	C(48)-H(48C)	0.9801
C(39)-C(40)	1.391(7)	C(49)-C(54)	1.399(5)
C(39)-H(39)	0.9500	C(49)-C(50)	1.403(5)
C(40)-H(40)	0.9500	C(50)-C(51)	1.367(7)
C(41)-H(41A)	0.9800	C(51)-C(52)	1.386(7)
C(41)-H(41B)	0.9800	C(52)-C(53)	1.377(7)
C(41)-H(41C)	0.9800	C(52)-H(52)	0.9500
C(35')-C(36')	1.379(7)	C(53)-C(54)	1.373(6)
C(35')-C(40')	1.380(6)	C(1S)-C(2S)	1.508(5)
C(36')-C(37')	1.390(7)	C(1S)-H(1S1)	0.9800
C(36')-H(36')	0.9500	C(1S)-H(1S2)	0.9800
C(37')-C(38')	1.393(6)	C(1S)-H(1S3)	0.9800
C(37')-H(37')	0.9500	C(2S)-C(3S)	1.491(5)
C(38')-C(39')	1.393(6)	C(2S)-H(2S1)	0.9900
C(39')-C(40')	1.391(7)	C(2S)-H(2S2)	0.9900
C(39')-H(39')	0.9500	C(3S)-C(4S)	1.490(5)
C(40')-H(40')	0.9500	C(3S)-H(3S1)	0.9900
C(41')-H(41D)	0.9799	C(3S)-H(3S2)	0.9900
C(41')-H(41E)	0.9801	C(4S)-C(5S)	1.518(5)
C(41')-H(41F)	0.9800	C(4S)-H(4S1)	0.9900
C(35")-C(40")	1.379(7)	C(4S)-H(4S2)	0.9900
C(35")-C(36")	1.381(7)	C(5S)-C(6S)	1.518(6)
C(36")-C(37")	1.387(8)	C(5S)-C(6S')	1.523(6)
C(36")-H(36")	0.9500	C(5S)-H(5S1)	0.9900
C(37")-C(38")	1.400(6)	C(5S)-H(5S2)	0.9900
C(37")-H(37")	0.9500	C(5S)-H(5S3)	0.9900
C(38")-C(39")	1.399(6)	C(5S)-H(5S4)	0.9900

C(6S)-H(6S1)	0.9799	C(6S')-H(6S4)	0.9800
C(6S)-H(6S2)	0.9800	C(6S')-H(6S5)	0.9799
C(6S)-H(6S3)	0.9800	C(6S')-H(6S6)	0.9799

N(5)-Ru(1)-O(5)	177.85(12)	C(2)-C(3)-C(4)	107.3(3)
N(5)-Ru(1)-N(3)	92.56(13)	C(2)-C(3)-H(3)	126.3
O(5)-Ru(1)-N(3)	88.77(11)	C(4)-C(3)-H(3)	126.3
N(5)-Ru(1)-N(4)	90.34(13)	N(1)-C(4)-C(5)	126.6(4)
O(5)-Ru(1)-N(4)	87.98(11)	N(1)-C(4)-C(3)	108.8(3)
N(3)-Ru(1)-N(4)	90.12(12)	C(5)-C(4)-C(3)	124.5(4)
N(5)-Ru(1)-N(2)	95.91(13)	C(6)-C(5)-C(4)	124.7(4)
O(5)-Ru(1)-N(2)	85.77(11)	C(6)-C(5)-C(21)	118.7(3)
N(3)-Ru(1)-N(2)	89.74(12)	C(4)-C(5)-C(21)	116.6(4)
N(4)-Ru(1)-N(2)	173.75(11)	N(2)-C(6)-C(5)	126.6(3)
N(5)-Ru(1)-N(1)	93.57(13)	N(2)-C(6)-C(7)	108.8(3)
O(5)-Ru(1)-N(1)	85.09(12)	C(5)-C(6)-C(7)	124.6(4)
N(3)-Ru(1)-N(1)	173.86(12)	C(8)-C(7)-C(6)	107.1(3)
N(4)-Ru(1)-N(1)	89.74(12)	C(8)-C(7)-H(7)	126.4
N(2)-Ru(1)-N(1)	89.73(12)	C(6)-C(7)-H(7)	126.4
C(24)-O(1)-C(27)	117.8(4)	C(7)-C(8)-C(9)	107.8(3)
C(31)-O(2)-C(34)	115.9(3)	C(7)-C(8)-H(8)	126.1
C(38)-O(3)-C(41)	118.6(7)	C(9)-C(8)-H(8)	126.1
C(38')-O(3')-C(41')	117.5(8)	N(2)-C(9)-C(10)	126.4(3)
C(38")-O(3")-C(41")	116.9(9)	N(2)-C(9)-C(8)	108.3(3)
C(45)-O(4)-C(48)	116.6(3)	C(10)-C(9)-C(8)	125.2(3)
C(49)-O(5)-Ru(1)	127.5(2)	C(9)-C(10)-C(11)	125.5(3)
C(4)-N(1)-C(1)	107.8(3)	C(9)-C(10)-C(28)	117.6(3)
C(4)-N(1)-Ru(1)	126.0(2)	C(11)-C(10)-C(28)	116.9(3)
C(1)-N(1)-Ru(1)	126.0(2)	N(3)-C(11)-C(10)	126.0(3)
C(9)-N(2)-C(6)	108.0(3)	N(3)-C(11)-C(12)	108.7(3)
C(9)-N(2)-Ru(1)	125.8(2)	C(10)-C(11)-C(12)	125.1(3)
C(6)-N(2)-Ru(1)	126.2(2)	C(13)-C(12)-C(11)	107.5(3)
C(11)-N(3)-C(14)	107.6(3)	C(13)-C(12)-H(12)	126.2
C(11)-N(3)-Ru(1)	126.1(2)	C(11)-C(12)-H(12)	126.2
C(14)-N(3)-Ru(1)	126.3(2)	C(12)-C(13)-C(14)	107.5(3)
C(19)-N(4)-C(16)	108.3(3)	C(12)-C(13)-H(13)	126.3
C(19)-N(4)-Ru(1)	126.1(2)	C(14)-C(13)-H(13)	126.3
C(16)-N(4)-Ru(1)	125.6(2)	N(3)-C(14)-C(15)	125.9(3)
O(6)-N(5)-Ru(1)	173.1(3)	N(3)-C(14)-C(13)	108.7(3)
N(1)-C(1)-C(20)	125.5(3)	C(15)-C(14)-C(13)	125.4(4)
N(1)-C(1)-C(2)	108.9(3)	C(16)-C(15)-C(14)	125.0(4)
C(20)-C(1)-C(2)	125.6(3)	C(16)-C(15)-C(35)	116.8(9)
C(3)-C(2)-C(1)	107.2(3)	C(14)-C(15)-C(35)	117.9(9)
C(3)-C(2)-H(2)	126.4	C(16)-C(15)-C(35')	117.8(12)
C(1)-C(2)-H(2)	126.4	C(14)-C(15)-C(35')	117.1(12)

C(16)-C(15)-C(35")	113.9(9)	C(28)-C(29)-H(29)	119.7
C(14)-C(15)-C(35")	118.9(10)	C(30)-C(29)-H(29)	119.7
N(4)-C(16)-C(15)	127.0(3)	C(31)-C(30)-C(29)	120.8(4)
N(4)-C(16)-C(17)	108.3(3)	C(31)-C(30)-H(30)	119.6
C(15)-C(16)-C(17)	124.8(3)	C(29)-C(30)-H(30)	119.6
C(18)-C(17)-C(16)	107.5(3)	O(2)-C(31)-C(30)	116.3(4)
C(18)-C(17)-H(17)	126.3	O(2)-C(31)-C(32)	123.8(4)
C(16)-C(17)-H(17)	126.3	C(30)-C(31)-C(32)	119.9(4)
C(17)-C(18)-C(19)	107.3(3)	C(31)-C(32)-C(33)	118.7(4)
C(17)-C(18)-H(18)	126.3	C(31)-C(32)-H(32)	120.7
C(19)-C(18)-H(18)	126.3	C(33)-C(32)-H(32)	120.7
N(4)-C(19)-C(20)	126.5(3)	C(28)-C(33)-C(32)	121.7(4)
N(4)-C(19)-C(18)	108.6(3)	C(28)-C(33)-H(33)	119.1
C(20)-C(19)-C(18)	124.8(3)	C(32)-C(33)-H(33)	119.1
C(19)-C(20)-C(1)	125.3(3)	O(2)-C(34)-H(34A)	109.5
C(19)-C(20)-C(42)	116.2(3)	O(2)-C(34)-H(34B)	109.5
C(1)-C(20)-C(42)	118.5(3)	H(34A)-C(34)-H(34B)	109.5
C(26)-C(21)-C(22)	117.2(4)	O(2)-C(34)-H(34C)	109.5
C(26)-C(21)-C(5)	121.8(4)	H(34A)-C(34)-H(34C)	109.5
C(22)-C(21)-C(5)	121.0(4)	H(34B)-C(34)-H(34C)	109.5
C(21)-C(22)-C(23)	121.0(5)	C(36)-C(35)-C(40)	119.3(6)
C(21)-C(22)-H(22)	119.5	C(36)-C(35)-C(15)	118.8(6)
C(23)-C(22)-H(22)	119.5	C(40)-C(35)-C(15)	121.7(6)
C(24)-C(23)-C(22)	120.9(5)	C(35)-C(36)-C(37)	122.0(7)
C(24)-C(23)-H(23)	119.6	C(35)-C(36)-H(36)	119.0
C(22)-C(23)-H(23)	119.6	C(37)-C(36)-H(36)	119.0
C(23)-C(24)-C(25)	120.0(5)	C(36)-C(37)-C(38)	118.5(6)
C(23)-C(24)-O(1)	117.0(5)	C(36)-C(37)-H(37)	120.7
C(25)-C(24)-O(1)	123.0(5)	C(38)-C(37)-H(37)	120.7
C(24)-C(25)-C(26)	118.9(5)	O(3)-C(38)-C(37)	122.4(8)
C(24)-C(25)-H(25)	120.5	O(3)-C(38)-C(39)	116.6(7)
C(26)-C(25)-H(25)	120.5	C(37)-C(38)-C(39)	119.8(7)
C(21)-C(26)-C(25)	122.0(5)	C(40)-C(39)-C(38)	120.2(6)
C(21)-C(26)-H(26)	119.0	C(40)-C(39)-H(39)	119.9
C(25)-C(26)-H(26)	119.0	C(38)-C(39)-H(39)	119.9
O(1)-C(27)-H(27A)	109.5	C(35)-C(40)-C(39)	120.1(7)
O(1)-C(27)-H(27B)	109.5	C(35)-C(40)-H(40)	120.0
H(27A)-C(27)-H(27B)	109.5	C(39)-C(40)-H(40)	120.0
O(1)-C(27)-H(27C)	109.5	O(3)-C(41)-H(41A)	109.5
H(27A)-C(27)-H(27C)	109.5	O(3)-C(41)-H(41B)	109.5
H(27B)-C(27)-H(27C)	109.5	H(41A)-C(41)-H(41B)	109.5
C(29)-C(28)-C(33)	118.3(4)	O(3)-C(41)-H(41C)	109.5
C(29)-C(28)-C(10)	121.1(3)	H(41A)-C(41)-H(41C)	109.5
C(33)-C(28)-C(10)	120.5(3)	H(41B)-C(41)-H(41C)	109.5
C(28)-C(29)-C(30)	120.5(4)	C(36')-C(35')-C(40')	119.6(7)

C(36')-C(35')-C(15)	118.1(7)	H(41G)-C(41")-H(41I)	109.5
C(40')-C(35')-C(15)	122.1(7)	H(41H)-C(41")-H(41I)	109.5
C(35')-C(36')-C(37')	121.3(8)	C(47)-C(42)-C(43)	118.0(3)
C(35')-C(36')-H(36')	119.4	C(47)-C(42)-C(20)	119.7(3)
C(37')-C(36')-H(36')	119.4	C(43)-C(42)-C(20)	122.1(3)
C(36')-C(37')-C(38')	118.5(7)	C(44)-C(43)-C(42)	120.9(3)
C(36')-C(37')-H(37')	120.8	C(44)-C(43)-H(43)	119.5
C(38')-C(37')-H(37')	120.8	C(42)-C(43)-H(43)	119.5
O(3')-C(38')-C(37')	119.9(10)	C(43)-C(44)-C(45)	120.0(3)
O(3')-C(38')-C(39')	116.5(9)	C(43)-C(44)-H(44)	120.0
C(37')-C(38')-C(39')	120.9(8)	C(45)-C(44)-H(44)	120.0
C(40')-C(39')-C(38')	119.0(7)	O(4)-C(45)-C(46)	124.7(3)
C(40')-C(39')-H(39')	120.5	O(4)-C(45)-C(44)	115.5(3)
C(38')-C(39')-H(39')	120.5	C(46)-C(45)-C(44)	119.7(3)
C(35')-C(40')-C(39')	120.7(7)	C(45)-C(46)-C(47)	119.5(3)
C(35')-C(40')-H(40')	119.7	C(45)-C(46)-H(46)	120.2
C(39')-C(40')-H(40')	119.7	C(47)-C(46)-H(46)	120.2
O(3')-C(41')-H(41D)	109.5	C(42)-C(47)-C(46)	121.7(3)
O(3')-C(41')-H(41E)	109.5	C(42)-C(47)-H(47)	119.1
H(41D)-C(41')-H(41E)	109.5	C(46)-C(47)-H(47)	119.1
O(3')-C(41')-H(41F)	109.5	O(4)-C(48)-H(48A)	109.5
H(41D)-C(41')-H(41F)	109.5	O(4)-C(48)-H(48B)	109.5
H(41E)-C(41')-H(41F)	109.5	H(48A)-C(48)-H(48B)	109.5
C(40")-C(35")-C(36")	115.7(8)	O(4)-C(48)-H(48C)	109.5
C(40")-C(35")-C(15)	118.7(10)	H(48A)-C(48)-H(48C)	109.5
C(36")-C(35")-C(15)	125.6(10)	H(48B)-C(48)-H(48C)	109.5
C(35")-C(36")-C(37")	123.4(9)	O(5)-C(49)-C(54)	122.2(4)
C(35")-C(36")-H(36")	118.3	O(5)-C(49)-C(50)	122.3(3)
C(37")-C(36")-H(36")	118.3	C(54)-C(49)-C(50)	115.4(4)
C(36")-C(37")-C(38")	119.9(8)	F(1)-C(50)-C(51)	119.0(4)
C(36")-C(37")-H(37")	120.1	F(1)-C(50)-C(49)	118.8(4)
C(38")-C(37")-H(37")	120.1	C(51)-C(50)-C(49)	122.2(4)
O(3")-C(38")-C(39")	123.2(10)	F(2)-C(51)-C(50)	118.3(4)
O(3")-C(38")-C(37")	119.0(11)	F(2)-C(51)-C(52)	120.1(5)
C(39")-C(38")-C(37")	117.8(8)	C(50)-C(51)-C(52)	121.6(4)
C(40")-C(39")-C(38")	119.8(8)	C(53)-C(52)-C(51)	117.0(4)
C(40")-C(39")-H(39")	120.1	C(53)-C(52)-H(52)	121.5
C(38")-C(39")-H(39")	120.1	C(51)-C(52)-H(52)	121.5
C(35")-C(40")-C(39")	123.4(9)	F(3)-C(53)-C(54)	118.0(4)
C(35")-C(40")-H(40")	118.3	F(3)-C(53)-C(52)	120.0(4)
C(39")-C(40")-H(40")	118.3	C(54)-C(53)-C(52)	121.9(4)
O(3")-C(41")-H(41G)	109.4	F(4)-C(54)-C(53)	119.4(4)
O(3")-C(41")-H(41H)	109.5	F(4)-C(54)-C(49)	118.7(4)
H(41G)-C(41")-H(41H)	109.5	C(53)-C(54)-C(49)	121.9(4)
O(3")-C(41")-H(41I)	109.5	C(2S)-C(1S)-H(1S1)	109.5

C(2S)-C(1S)-H(1S2)	109.5	H(6S4)-C(6S')-H(6S6)	109.5
H(1S1)-C(1S)-H(1S2)	109.5	H(6S5)-C(6S')-H(6S6)	109.5
C(2S)-C(1S)-H(1S3)	109.4		
H(1S1)-C(1S)-H(1S3)	109.5		
H(1S2)-C(1S)-H(1S3)	109.5		
C(3S)-C(2S)-C(1S)	113.2(6)		
C(3S)-C(2S)-H(2S1)	108.9		
C(1S)-C(2S)-H(2S1)	108.9		
C(3S)-C(2S)-H(2S2)	108.9		
C(1S)-C(2S)-H(2S2)	108.9		
H(2S1)-C(2S)-H(2S2)	107.7		
C(4S)-C(3S)-C(2S)	116.6(6)		
C(4S)-C(3S)-H(3S1)	108.1		
C(2S)-C(3S)-H(3S1)	108.1		
C(4S)-C(3S)-H(3S2)	108.1		
C(2S)-C(3S)-H(3S2)	108.1		
H(3S1)-C(3S)-H(3S2)	107.3		
C(3S)-C(4S)-C(5S)	113.1(5)		
C(3S)-C(4S)-H(4S1)	109.0		
C(5S)-C(4S)-H(4S1)	109.0		
C(3S)-C(4S)-H(4S2)	109.0		
C(5S)-C(4S)-H(4S2)	109.0		
H(4S1)-C(4S)-H(4S2)	107.8		
C(6S)-C(5S)-C(4S)	112.0(6)		
C(4S)-C(5S)-C(6S')	111.6(7)		
C(6S)-C(5S)-H(5S1)	109.2		
C(4S)-C(5S)-H(5S1)	109.2		
C(6S)-C(5S)-H(5S2)	109.2		
C(4S)-C(5S)-H(5S2)	109.2		
H(5S1)-C(5S)-H(5S2)	107.9		
C(4S)-C(5S)-H(5S3)	109.3		
C(6S')-C(5S)-H(5S3)	109.3		
C(4S)-C(5S)-H(5S4)	109.3		
C(6S')-C(5S)-H(5S4)	109.3		
H(5S3)-C(5S)-H(5S4)	108.0		
C(5S)-C(6S)-H(6S1)	109.6		
C(5S)-C(6S)-H(6S2)	109.6		
H(6S1)-C(6S)-H(6S2)	109.5		
C(5S)-C(6S)-H(6S3)	109.3		
H(6S1)-C(6S)-H(6S3)	109.5		
H(6S2)-C(6S)-H(6S3)	109.5		
C(5S)-C(6S')-H(6S4)	111.4		
C(5S)-C(6S')-H(6S5)	108.6		
H(6S4)-C(6S')-H(6S5)	109.5		
C(5S)-C(6S')-H(6S6)	108.4		

(ii) (T(*p*-OMe)PP)Ru(NO)(OC(=O)CF_3) (**2**)

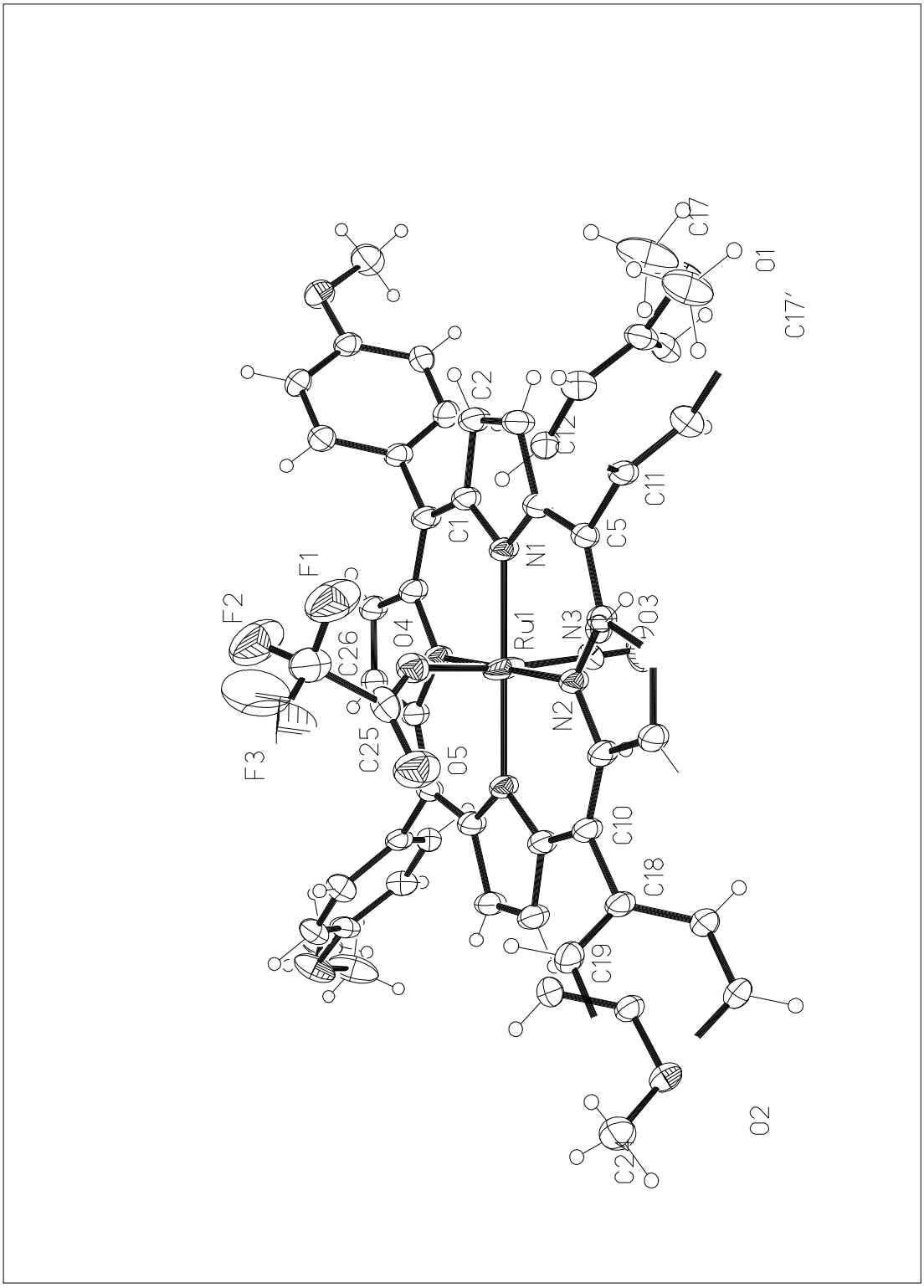

Fig. S3. Thermal ellipsoid plot of (T(*p*-OMe)PP)Ru(NO)(OC(=O)CF_3) (**2**)

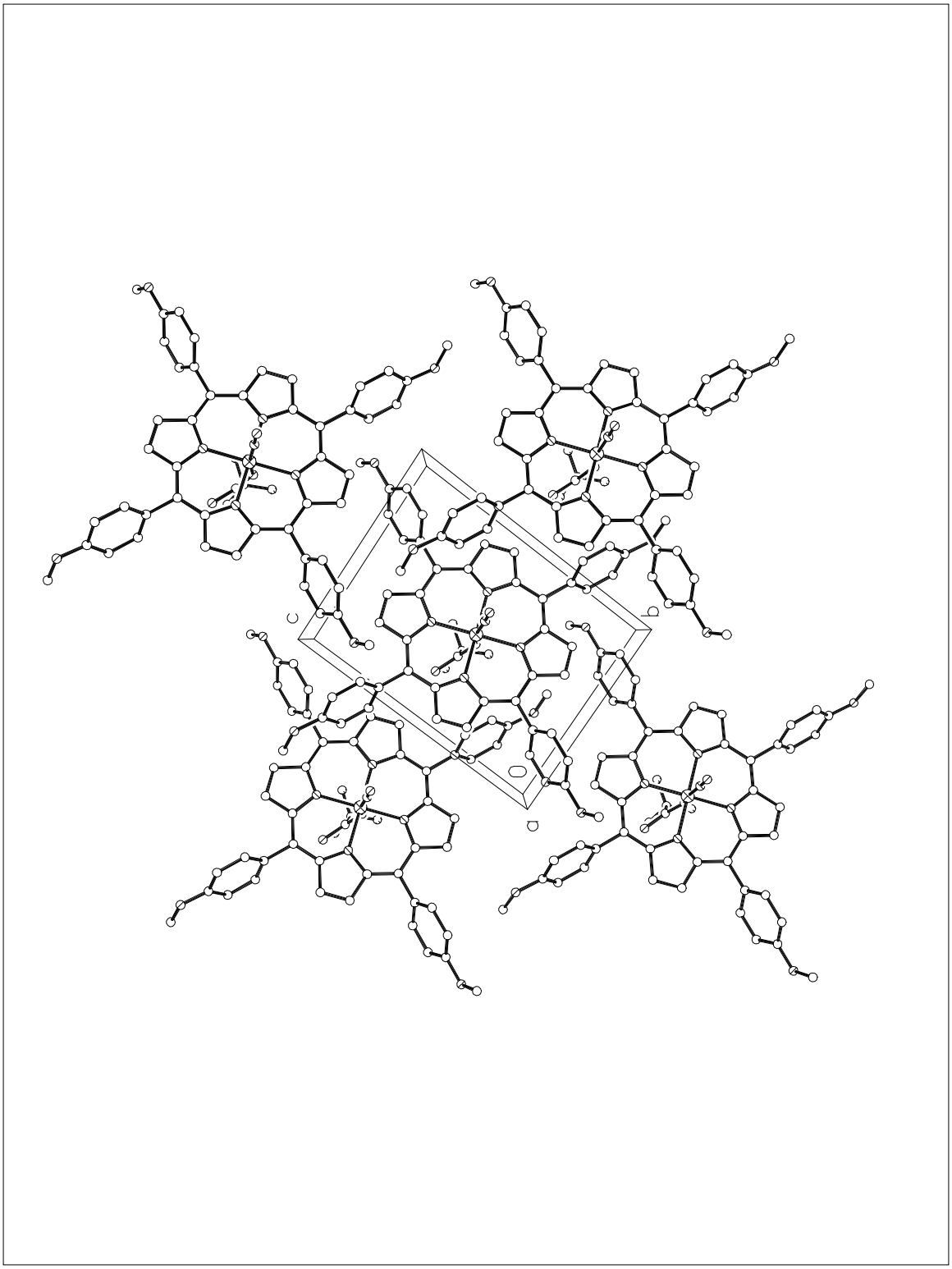

Fig. S4 Unit cell and packing diagram of (T(*p*-OMe)PP)Ru(NO)(OC(=O)CF_3) (**2**)

Comment

The molecule was found to sit on a crystallographic center of symmetry; thus, the NO and the trifluoroacetate were disordered 50:50 across the porphyrin plane. One methyl group was disordered. The occupancies for C17 refined to 0.56(2) and 0.44(2) for the unprimed and primed atoms. Restraints on the positional and displacement parameters of the disordered atoms were required. Also the displacement parameters of O4 and N3 were required. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A red block-shaped crystal of dimensions 0.500 x 0.440 x 0.150 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector[2] and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear least squares fit of 7226 peaks in the range 2.18 < θ < 28.30°. A total of 20468 data were measured in the range 1.680 < θ < 28.295° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method[3] giving minimum and maximum transmission factors of 0.812 and 0.938. The data were merged to form a set of 5377 independent data with R(int) = 0.0176 and a coverage of 100.0 %.

The triclinic space group $P\bar{1}$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[3] The positions of hydrogens bonded to carbons were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 350 parameters were refined against 22 restraints and 5377 data to give wR(F^2) = 0.1928 and S = 1.084 for weights of w = 1/[σ^2 (F^2) + (0.0800 P)^2 + 4.6000 P], where P = [F_o^2 + 2F_c^2] / 3. The final R(F) was 0.0691 for the 5330 observed, [F > 4σ(F)], data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 1.476 and -2.081 e/Å^3, respectively.

Table S3. Crystal data and structure refinement for (T(*p*-OMe)PP)Ru(NO)-(OC(=O)CF_3) (**2**).

Empirical formula	C_{50} H_{36} F_3 N_5 O_7 Ru	
Formula weight	976.91	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	*a* = 9.5563(4) Å	α= 83.241(2)°
	b = 9.6307(4) Å	β= 74.191(2)°
	c = 12.6223(5) Å	γ= 76.385(3)°
Volume	1084.55(8) $Å^3$	
Z, Z'	1, 0.5	
Density (calculated)	1.496 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	498	
Absorption coefficient	0.435 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.938 and 0.812	
Theta range for data collection	1.680 to 28.295°	
Reflections collected	20468	
Independent reflections	5377 [R(int) = 0.0176]	
Data / restraints / parameters	5377 / 22 / 350	
wR(F^2 all data)	*wR*2 = 0.1928	
R(*F* obsd data)	*R*1 = 0.0691	
Goodness-of-fit on F^2	1.084	
Observed data [I > 2σ(I)]	5330	
Extinction coefficient	n/a	
Largest and mean shift / s.u.	0.001and 0.000	
Largest diff. peak and hole	1.476 and -2.081 e/$Å^3$	

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

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table S4. Bond lengths (Å) and angles (°)for (T(*p*-OMe)PP)Ru(NO)(OC(=O)CF_3) (**2**).

Ru(1)-O(4)	1.773(11)	C(9)-C(10)	1.402(5)
Ru(1)-N(3)	1.986(11)	C(10)-C(18)	1.499(5)
Ru(1)-N(1)	2.052(3)	C(11)-C(12)	1.385(6)
Ru(1)-N(2)	2.056(3)	C(11)-C(16)	1.396(5)
F(1)-C(26)	1.325(11)	C(12)-C(13)	1.393(5)
F(2)-C(26)	1.302(12)	C(12)-H(12)	0.9500
F(3)-C(26)	1.280(13)	C(13)-C(14)	1.383(6)
O(1)-C(14)	1.373(4)	C(13)-H(13)	0.9500
O(1)-C(17')	1.461(7)	C(14)-C(15)	1.393(6)
O(1)-C(17)	1.466(7)	C(15)-C(16)	1.385(5)
O(2)-C(21)	1.374(4)	C(15)-H(15)	0.9500
O(2)-C(24)	1.426(5)	C(16)-H(16)	0.9500
O(3)-N(3)	1.172(14)	C(17)-H(17A)	0.9800
O(4)-C(25)	1.225(13)	C(17)-H(17B)	0.9800
O(5)-C(25)	1.272(13)	C(17)-H(17C)	0.9800
N(1)-C(1)	1.375(5)	C(17')-H(17D)	0.9800
N(1)-C(4)	1.375(5)	C(17')-H(17E)	0.9800
N(2)-C(9)	1.376(5)	C(17')-H(17F)	0.9800
N(2)-C(6)	1.377(5)	C(18)-C(19)	1.364(6)
C(1)-C(10)#1	1.399(5)	C(18)-C(23)	1.411(5)
C(1)-C(2)	1.444(5)	C(19)-C(20)	1.402(5)
C(2)-C(3)	1.358(5)	C(19)-H(19)	0.9500
C(2)-H(2)	0.9500	C(20)-C(21)	1.395(5)
C(3)-C(4)	1.444(5)	C(20)-H(20)	0.9500
C(3)-H(3)	0.9500	C(21)-C(22)	1.381(6)
C(4)-C(5)	1.401(5)	C(22)-C(23)	1.391(5)
C(5)-C(6)	1.402(5)	C(22)-H(22)	0.9500
C(5)-C(11)	1.501(5)	C(23)-H(23)	0.9500
C(6)-C(7)	1.443(5)	C(24)-H(24A)	0.9800
C(7)-C(8)	1.357(5)	C(24)-H(24B)	0.9800
C(7)-H(7)	0.9500	C(24)-H(24C)	0.9800
C(8)-C(9)	1.439(5)	C(25)-C(26)	1.551(15)
C(8)-H(8)	0.9500		

O(4)-Ru(1)-N(3)	168.7(4)	N(1)-Ru(1)-N(2)	89.87(12)
O(4)-Ru(1)-N(1)	86.1(3)	N(1)#1-Ru(1)-N(2)	90.13(12)
N(3)-Ru(1)-N(1)	88.4(3)	O(4)-Ru(1)-N(2)#1	85.4(3)
O(4)-Ru(1)-N(1)#1	93.8(3)	N(3)-Ru(1)-N(2)#1	84.7(3)
N(3)-Ru(1)-N(1)#1	91.6(3)	N(1)-Ru(1)-N(2)#1	90.13(12)
N(1)-Ru(1)-N(1)#1	180.0	N(1)#1-Ru(1)-N(2)#1	89.87(12)
O(4)-Ru(1)-N(2)	94.6(3)	N(2)-Ru(1)-N(2)#1	180.0
N(3)-Ru(1)-N(2)	95.3(3)	C(14)-O(1)-C(17')	116.6(5)

C(14)-O(1)-C(17)	114.2(4)	C(13)-C(12)-H(12)	119.5
C(21)-O(2)-C(24)	117.0(3)	C(14)-C(13)-C(12)	119.7(4)
C(25)-O(4)-Ru(1)	134.0(9)	C(14)-C(13)-H(13)	120.1
C(1)-N(1)-C(4)	107.5(3)	C(12)-C(13)-H(13)	120.1
C(1)-N(1)-Ru(1)	126.1(2)	O(1)-C(14)-C(13)	123.8(4)
C(4)-N(1)-Ru(1)	126.3(2)	O(1)-C(14)-C(15)	116.1(3)
C(9)-N(2)-C(6)	107.6(3)	C(13)-C(14)-C(15)	120.1(3)
C(9)-N(2)-Ru(1)	126.1(2)	C(16)-C(15)-C(14)	119.6(3)
C(6)-N(2)-Ru(1)	126.3(2)	C(16)-C(15)-H(15)	120.2
O(3)-N(3)-Ru(1)	178.3(9)	C(14)-C(15)-H(15)	120.2
N(1)-C(1)-C(10)#1	126.4(3)	C(15)-C(16)-C(11)	121.1(4)
N(1)-C(1)-C(2)	108.9(3)	C(15)-C(16)-H(16)	119.5
C(10)#1-C(1)-C(2)	124.7(3)	C(11)-C(16)-H(16)	119.5
C(3)-C(2)-C(1)	107.4(3)	O(1)-C(17)-H(17A)	109.5
C(3)-C(2)-H(2)	126.3	O(1)-C(17)-H(17B)	109.5
C(1)-C(2)-H(2)	126.3	H(17A)-C(17)-H(17B)	109.5
C(2)-C(3)-C(4)	107.2(3)	O(1)-C(17)-H(17C)	109.5
C(2)-C(3)-H(3)	126.4	H(17A)-C(17)-H(17C)	109.5
C(4)-C(3)-H(3)	126.4	H(17B)-C(17)-H(17C)	109.5
N(1)-C(4)-C(5)	126.4(3)	O(1)-C(17')-H(17D)	109.5
N(1)-C(4)-C(3)	109.0(3)	O(1)-C(17')-H(17E)	109.5
C(5)-C(4)-C(3)	124.6(3)	H(17D)-C(17')-H(17E)	109.5
C(4)-C(5)-C(6)	124.8(3)	O(1)-C(17')-H(17F)	109.5
C(4)-C(5)-C(11)	117.3(3)	H(17D)-C(17')-H(17F)	109.5
C(6)-C(5)-C(11)	117.9(3)	H(17E)-C(17')-H(17F)	109.5
N(2)-C(6)-C(5)	126.2(3)	C(19)-C(18)-C(23)	119.0(3)
N(2)-C(6)-C(7)	108.7(3)	C(19)-C(18)-C(10)	120.8(3)
C(5)-C(6)-C(7)	125.1(3)	C(23)-C(18)-C(10)	120.1(4)
C(8)-C(7)-C(6)	107.4(3)	C(18)-C(19)-C(20)	121.7(3)
C(8)-C(7)-H(7)	126.3	C(18)-C(19)-H(19)	119.2
C(6)-C(7)-H(7)	126.3	C(20)-C(19)-H(19)	119.2
C(7)-C(8)-C(9)	107.5(3)	C(21)-C(20)-C(19)	118.9(4)
C(7)-C(8)-H(8)	126.2	C(21)-C(20)-H(20)	120.6
C(9)-C(8)-H(8)	126.2	C(19)-C(20)-H(20)	120.6
N(2)-C(9)-C(10)	126.2(3)	O(2)-C(21)-C(22)	116.1(3)
N(2)-C(9)-C(8)	108.8(3)	O(2)-C(21)-C(20)	123.8(4)
C(10)-C(9)-C(8)	125.0(3)	C(22)-C(21)-C(20)	120.1(3)
C(1)#1-C(10)-C(9)	125.0(3)	C(21)-C(22)-C(23)	120.4(4)
C(1)#1-C(10)-C(18)	117.3(3)	C(21)-C(22)-H(22)	119.8
C(9)-C(10)-C(18)	117.7(3)	C(23)-C(22)-H(22)	119.8
C(12)-C(11)-C(16)	118.5(3)	C(22)-C(23)-C(18)	119.8(4)
C(12)-C(11)-C(5)	120.7(3)	C(22)-C(23)-H(23)	120.1
C(16)-C(11)-C(5)	120.8(4)	C(18)-C(23)-H(23)	120.1
C(11)-C(12)-C(13)	121.0(3)	O(2)-C(24)-H(24A)	109.5
C(11)-C(12)-H(12)	119.5	O(2)-C(24)-H(24B)	109.5

H(24A)-C(24)-H(24B)	109.5
O(2)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
O(4)-C(25)-O(5)	123.7(11)
O(4)-C(25)-C(26)	116.2(10)
O(5)-C(25)-C(26)	119.9(10)
F(3)-C(26)-F(2)	110.5(11)
F(3)-C(26)-F(1)	106.7(10)
F(2)-C(26)-F(1)	110.4(8)
F(3)-C(26)-C(25)	106.5(10)
F(2)-C(26)-C(25)	112.0(9)
F(1)-C(26)-C(25)	110.5(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+1

References

1. G.-B. Yi, M. A. Khan and G. B. Richter-Addo, *Inorg. Chem.*, 1997, **36**, 3876-3885.
2. (a) Data Collection: Bruker (2007). SMART Bruker AXS Inc., Madison, Wisconsin, USA. (b) Data Reduction: Bruker (2007). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
3. Bruker (2002). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
4. G. Sheldrick, *Acta Cryst. Sec. A*, 2008, **64**, 112-122.