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Enantiomorphs of a carbene–ruthenium(II)–porphyrin complex with four 'chiral pillars'

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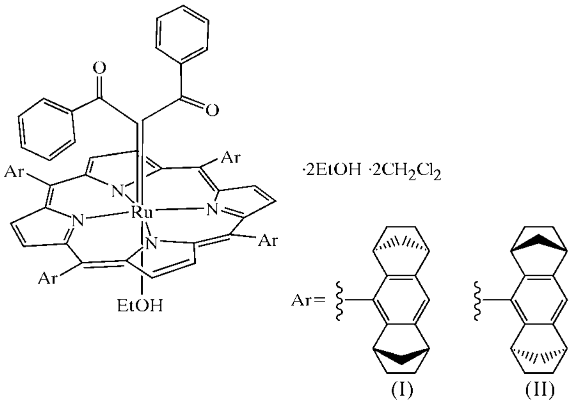
The chiral metalloporphyrin (dibenzoylmethylene-*κC*)(ethanol-*κO*){5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrinato-κ^4N}ruthenium(II)–ethanol–dichloromethane (1/2/2), $[\mathrm{Ru}(\mathrm{C_{84}H_{76}N_4})(\mathrm{C_{15}H_{10}O_2})(\mathrm{C_2H_6O})]\cdot 2\mathrm{C_2H_6O}\cdot 2\mathrm{CH_2Cl_2}$, and its enantiomorph were prepared from enantiomerically pure porphyrins. The enantiomers are potential versatile catalysts for asymmetric cyclopropanation, aziridination or epoxidation. In each compound, the rather large dibenzoylcarbene group is squeezed between four columnar 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl groups at the *meso* positions resulting in a doming deformation of the porphyrin core. The dibenzoylcarbene group has an *anti* conformation. The benzoyl O atoms make short van der Waals contacts (< 2.6 Å) with the methine groups of the chiral columnar substituents at the 10 and 20 positions of the porphyrin rings. A hydrogen-bonded supramolecular chain is formed parallel to the *b* axis by interactions between the benzoyl O atom and the hydroxy groups of the coordinated and uncoordinated ethanol molecules.

Comment

In recent decades, highly efficient and stereoselective catalytic systems have been developed with metalloporphyrins for epoxidation and cyclopropanation of alkenes (Che & Huang, 2002). Halterman and co-workers synthesized the first chiral tetraarylporphyrin, 5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrin, $\mathrm{H_2por^*(+)}$, and demonstrated the asymmetric epoxidation with a manganese chloride complex of the porphyrin as a chiral catalyst (Halterman & Jan, 1991; Halterman *et al.*, 1997). Che and co-workers reported the asymmetric cyclopropanation by using carbonyl or carbene ruthenium complexes of the Halterman porphyrin (Lo *et al.*, 1997; Che *et al.*, 2001). The groups of Halterman and Che have prepared only one enantiomer of an enantiomeric aldehyde, (1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carbaldehyde, for synthesis of the porphyrin catalysts, but have not isolated the opposite enantiomer. We have obtained both enantiomers of the aldehyde by resolving a racemic mixture with (*S*,*S*)-hydrobenzoin as well as with the *R*,*R* isomer, thereby yielding a chiral pair of the porphyrins, $\mathrm{H_2por^*(-)}$ and $\mathrm{H_2por^*(+)}$. Initially, we prepared dibenzoylcarbene ruthenium complexes of both enantiomeric porphyrins, $[\mathrm{Ru\{por^*(+)\}\{{=}C(COPh)_2\}}]$ and $[\mathrm{Ru\{por^*(-)\}\{{=}C(COPh)_2\}}]$, and confirmed that the complexes induced optically active products. Through the cyclopropanation of styrene with methyl diazoacetate, the enantiomeric porphyrins commonly afforded methyl 2-phenylcyclopropanecarboxylate with *trans*/*cis* ratios of 3:1 and turnovers of up to 3×10^4. In addition, the $[\mathrm{Ru\{por^*(+)\}\{{=}C(COPh)_2\}}]$ catalyst enantioselectively afforded the 1*S*,2*S* product in 75% ee, whereas its enantiomer gave the 1*R*,2*R* isomer in 72% ee (Hirasawa *et al.*, 2007). We describe here structural features of the ruthenium carbene complexes of the chiral porphyrin $[\mathrm{Ru\{por^*(+)\}\{{=}C(COPh)_2\}(EtOH)}]\cdot 2\mathrm{EtOH}\cdot 2\mathrm{CH_2Cl_2}$, (I), and its enantiomorph $[\mathrm{Ru\{por^*(-)\}\{{=}C(COPh)_2\}(EtOH)}]\cdot 2\mathrm{EtOH}\cdot 2\mathrm{CH_2Cl_2}$, (II).



The circular dichroism spectra of $[\mathrm{Ru\{por^*(+)\}\{{=}C(COPh)_2\}}]$ and $[\mathrm{Ru\{por^*(-)\}\{{=}C(COPh)_2\}}]$ in chloroform solution appear as mirror images of each other (Fig. 1), so they have enantiomeric structures in chloroform solutions. The crystal structures of (I) and (II) are enantiomorphs in the space group $P2_12_12_1$ and their absolute configurations were

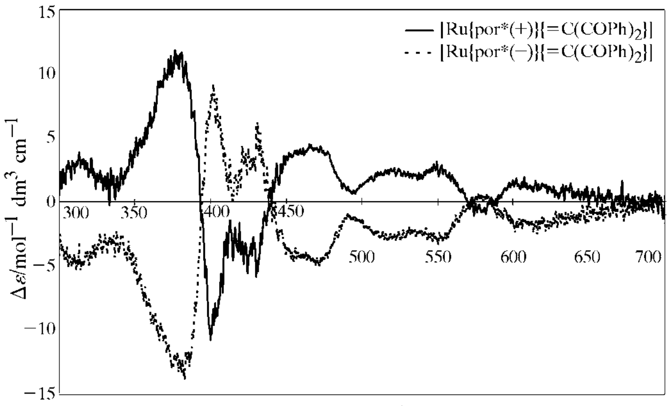


Figure 1
Circular dichroism spectra for $[\mathrm{Ru\{por^*(+)\}\{{=}C(COPh)_2\}}]$ and $[\mathrm{Ru\{por^*(-)\}\{{=}C(COPh)_2\}}]$ in chloroform solution.

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determined clearly by the diffraction experiments. The absolute configuration of the porphyrinate ligand in (I) agrees with those in [Fe{por*(+)}Cl] (Halterman *et al.*, 1997) and [Ru{por*(+)}(CO)(EtOH)] (Lo *et al.*, 1997). Each asymmetric unit in (I) and (II) includes one metalloporphyrin molecule and two molecules each of the dichloromethane and ethanol solvents, as shown in Figs. 2 and 3. There seems to be no remarkable difference between (I) and (II) in terms of bond lengths and angles. The angles about the carbene C85 atoms (Tables 1 and 3) are significantly smaller than those in the analogous carbene–ruthenium–porphyrins reported so far (Che & Huang, 2002; Li *et al.*, 2004), which lie in the range *ca* 111–117°, except for a value of 108.0 (3)° in [Ru(tpfpp)-{C(Ph)$CO_2CH_2CH{=}CH_2$}(MeOH)], where tpfpp is the tetrakis(pentafluorophenyl)porphyrinate dianion. The ketone groups in (I) and (II) are oriented perpendicular to the carbene group and *anti* to one another, as indicated by the Ru1—C85—C86—O1 and Ru1—C85—C93—O2 torsion

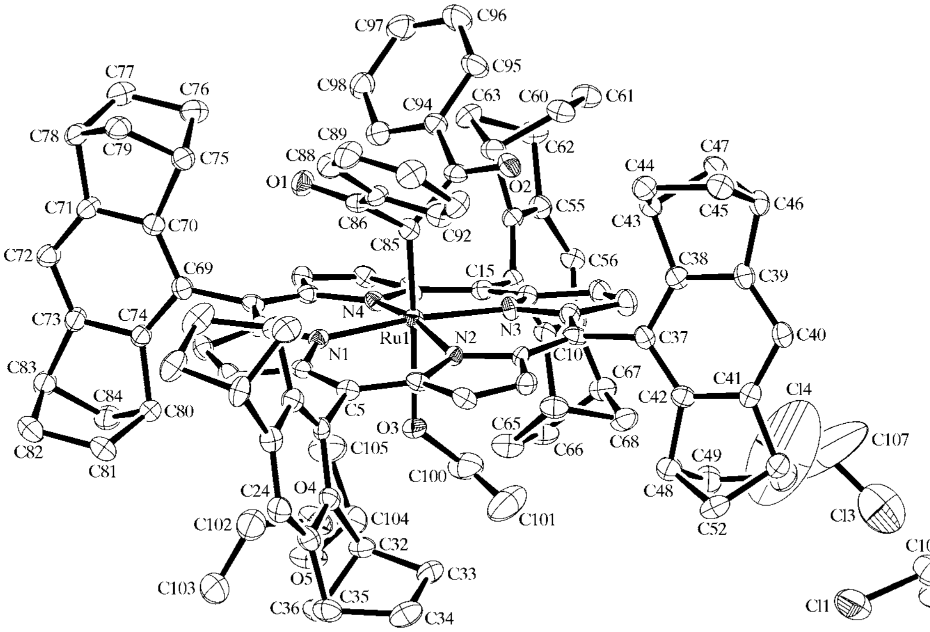

Figure 2
The asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. The minor fragment of the coordinated ethanol molecule is disordered.

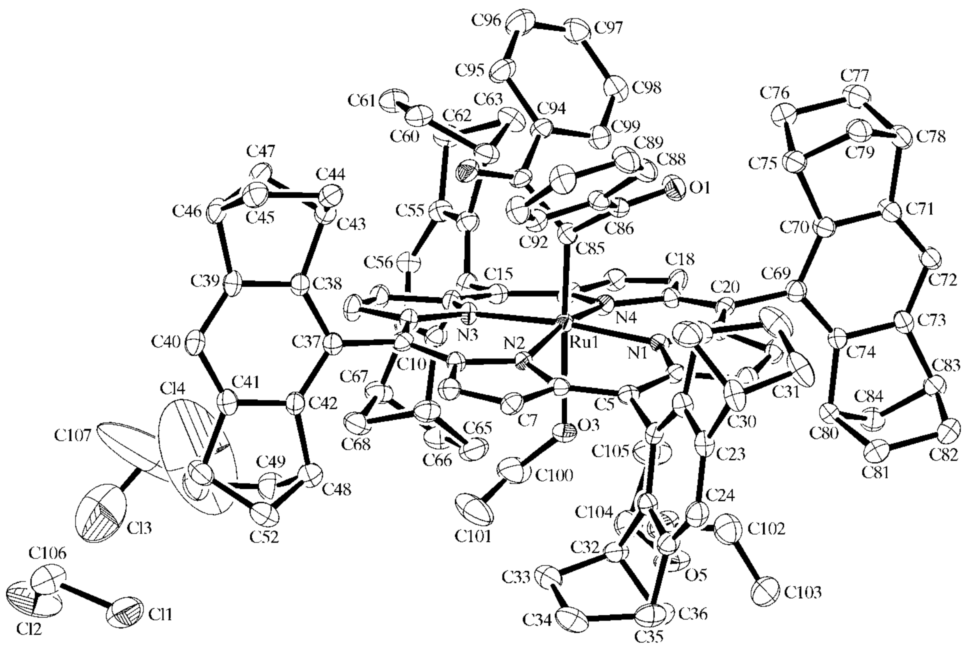

Figure 3
The asymmetric unit of (II), showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. The minor fragment of the coordinated ethanol molecule is disordered.

angles (Tables 1 and 3), so that the ketone and carbene groups are not conjugated; this is similar to the case of [Ru(ttp){$=$C(COPh)$_2$}(py)], where ttp is the tetra-*p*-tolylporphyrinate dianion (Harada *et al.*, 2003).

In each of (I) and (II), the rather large dibenzoylcarbene group is squeezed between four 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl groups, which act like chiral pillars to cause doming deformation of the porphyrin core, with maximum and minimum deviations from the $C_{20}N_4$ least-squares plane of 0.222 (3) and −0.235 (4) Å for atoms C20 and C15 in (I), and 0.230 (3) and −0.227 (3) Å for atoms C20 and C15 in (II), respectively. The Ru atoms are displaced out of the $C_{20}N_4$ least-squares planes toward the carbene C85 atoms by 0.2257 (7) and 0.2249 (6) Å in (I) and (II), respectively. The benzoyl O atoms, O1 and O2, are close to the methine groups, C75—H61 and C43—H27, respectively, of the chiral columnar substituents at the 10 and 20 positions of the porphyrin rings, lying within the van der Waals contact distance (2.6 Å), as indicated in Tables 2 and 4. These close approaches suggest steric interactions between the benzoyl O atoms and the methine groups of the chiral pillars, which constrain the configuration of the dibenzoylcarbene group. Intermolecular hydrogen bonds involving the benzoyl O atom and the hydroxy groups of the coordinated and uncoordinated ethanol molecules form a supramolecular O3—H87$\cdots$O4—H93$\cdots$O5—H99$\cdots$O2^i chain parallel to the *b* axis [symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; Tables 2 and 4, and Fig. 4]. One of the two dichloromethane solvent molecules also interacts with the benzoyl group through a C106—H105$\cdots$O1^{ii} interaction [symmetry code: (ii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$].

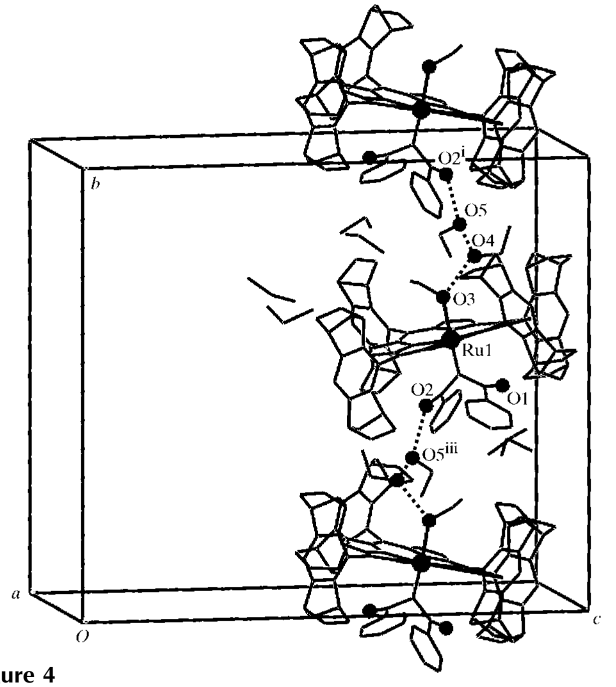

Figure 4
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain parallel to the *b* axis. Hydrogen bonds are represented by dashed lines. The Ru and O atoms are indicated by solid circles and uninvolved H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.]

Experimental

The chiral tetraarylporphyrins H$_2$por*(+) and H$_2$por*(−), and their ruthenium carbonyl complexes [Ru{por*(+)}(CO)] and [Ru{por*(−)}(CO)] were prepared according to the procedures of Halterman *et al.* (1997) and Lo *et al.* (1997). A solution of [Ru{por*(+)}(CO)] (170 mg, 0.134 mmol) and $N_2$$=$C(COPh)$_2$ (390 mg, 1.558 mmol) in octane (500 ml) was refluxed under a nitrogen atmosphere for 7 h. After removal of the volatiles *in vacuo*, the residue was chromatographed on silica (benzene/hexane, 4:1 *v*/*v*), then on alumina (dichloromethane/hexane, 1:4 *v*/*v*). An intense red eluant was collected and evaporated to dryness. Recrystallization from a dichloromethane/ethanol solution gave air-stable dark-red crystals of (I) (yield 66 mg, 0.0449 mmol, 33%). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.37 (*dd*, *J* = 37.5 and 4.8 Hz, 8H), 7.29 (*s*, 4H), 6.89 (*t*, *J* = 7.3 Hz, 2H), 6.56 (*d*, *J* = 7.9 Hz, 4H), 4.87 (*m*, 4H), 3.55 (*d*, *J* = 2.8 Hz, 4H), 3.46 (*d*, *J* = 2.7 Hz, 4H), 2.75 (*d*, *J* = 2.7 Hz, 4H), 2.21 (*d*, *J* = 2.9 Hz, 4H), 1.96 (*d*, *J* = 7.9 Hz, 4H), 1.91 (*m*, 4H), 1.79 (*d*, *J* = 7.9 Hz, 4H), 1.75 (*m*, 4H), 1.49 (*m*, 4H), 1.38 (*m*, 8H), 1.26 (*m*, 8H), 1.20 (*d*, *J* = 7.9 Hz, 4H), 1.12 (*m*, 4H), 0.82 (*m*, 4H). UV/vis (CHCl$_3$): λ_{max} (log ε) 406 (5.05), 536 (4.03). Preparation of enantiomer (II) was carried out with [Ru{por*(−)}(CO)] (345 mg, 0.272 mmol) and $N_2$$=$C(COPh)$_2$ (983 mg, 3.928 mmol) (yield 151 mg, 0.1027 mmol, 38%). The ^{1}H NMR and UV/vis spectra of (II) correspond to those of (I). Up to 573 K, the compounds [Ru{por*(+)}{$=$C(COPh)$_2$}] and [Ru{por*(−)}{$=$C(COPh)$_2$}] do not decompose, melt or sublime.

Compound (I)

Crystal data

[Ru($C_{84}H_{76}N_4$)($C_{15}H_{10}O_2$)(C_2H_6O)]·$2C_2H_6O$·$2CH_2Cl_2$
M_r = 1772.85
Orthorhombic, $P2_12_12_1$
a = 13.7461 (18) Å
b = 23.674 (3) Å
c = 26.781 (3) Å
V = 8715.2 (19) Å^3
Z = 4
Mo *K*α radiation
μ = 0.36 mm^{-1}
T = 120 (1) K
0.27 × 0.25 × 0.23 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: numerical (*NUMABS*; Rigaku, 2005)
T_{min} = 0.910, T_{max} = 0.920
68148 measured reflections
19645 independent reflections
17526 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.134
S = 1.10
19645 reflections
1095 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}
Absolute structure: Flack (1983), 8928 Friedel pairs
Flack parameter: 0.01 (2)

Compound (II)

Crystal data

[Ru($C_{84}H_{76}N_4$)($C_{15}H_{10}O_2$)(C_2H_6O)]·$2C_2H_6O$·$2CH_2Cl_2$
M_r = 1772.85
Orthorhombic, $P2_12_12_1$
a = 13.7694 (15) Å
b = 23.691 (3) Å
c = 26.794 (3) Å
V = 8740.5 (18) Å^3
Z = 4
Mo *K*α radiation
μ = 0.36 mm^{-1}
T = 120 (1) K
0.33 × 0.22 × 0.18 mm

Table 1
Selected geometric parameters (Å, °) for (I).

Ru1—C85	1.866 (3)	Ru1—N2	2.048 (3)
Ru1—N4	2.044 (3)	Ru1—N3	2.061 (3)
Ru1—N1	2.044 (3)	Ru1—O3	2.260 (2)
C85—Ru1—N1	92.26 (14)	N3—Ru1—N4	90.27 (12)
C85—Ru1—N2	95.76 (14)	C85—Ru1—O3	177.01 (14)
C85—Ru1—N3	93.91 (14)	N1—Ru1—O3	84.78 (11)
C85—Ru1—N4	95.75 (14)	N2—Ru1—O3	83.87 (12)
N1—Ru1—N2	90.54 (12)	N3—Ru1—O3	89.05 (11)
N1—Ru1—N3	173.83 (12)	N4—Ru1—O3	84.64 (11)
N1—Ru1—N4	89.15 (12)	C86—C85—C93	109.8 (3)
N2—Ru1—N3	88.80 (11)	Ru1—C85—C86	124.5 (3)
N2—Ru1—N4	168.49 (12)	Ru1—C85—C93	125.7 (3)
N4—Ru1—C85—C86	106.1 (3)	Ru1—C85—C86—O1	−87.0 (4)
N3—Ru1—C85—C93	14.6 (3)	Ru1—C85—C93—O2	−85.5 (4)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H87···O4	0.84	1.87	2.686 (4)	162
O4—H93···O5	0.84	1.95	2.785 (5)	173
O5—H99···O2^{i}	0.84	2.00	2.828 (4)	169
C106—H105···O1^{ii}	0.99	2.45	3.314 (6)	145
C75—H61···O1	1.00	2.29	3.285 (5)	172
C43—H27···O2	1.00	2.31	3.307 (5)	172

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$.

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: numerical (*NUMABS*; Rigaku, 2005)
$T_{\min} = 0.891$, $T_{\max} = 0.938$
68786 measured reflections
20000 independent reflections
18189 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.123$
$S = 1.10$
20000 reflections
1095 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.06$ e Å^{-3}
$\Delta\rho_{\min} = -0.98$ e Å^{-3}
Absolute structure: Flack (1983), 9149 Friedel pairs
Flack parameter: −0.046 (19)

The methyl C atoms of the coordinated ethanol ligands are disordered over two positions as C101 and C108, with corresponding site-occupancy factors of 0.68 (4) and 0.32 (4) for (I), and 0.64 (3) and 0.36 (3) for (II). Atoms C101 were refined anisotropically, and atoms C108 were treated isotropically. One of the two dichloromethane solvent molecules (Cl3, Cl4 and C107) has large displacement parameters; some disordered models over two or more sites were tried, but the refinements did not converge well. The hydroxy H atoms were found in a difference Fourier map, but their positions were subsequently optimized geometrically. The other H atoms were placed in geometrically idealized positions. All H atoms were constrained to ride on their parent atoms, with O—H bond lengths of 0.84 Å, C—H bond lengths of 0.98, 0.99, 1.00 and 0.95 Å for CH$_3$, CH$_2$, methine CH and aromatic CH groups, respectively, and $U_{\rm iso}$(H) values of $1.5U_{\rm eq}$(O or methyl C) or $1.2U_{\rm eq}$(methylene, methine or aromatic C).

Table 3
Selected geometric parameters (Å, °) for (II).

Ru1—C85	1.869 (3)	Ru1—N3	2.056 (3)
Ru1—N1	2.049 (3)	Ru1—N4	2.052 (3)
Ru1—N2	2.054 (3)	Ru1—O3	2.261 (2)
C85—Ru1—N1	92.59 (12)	N3—Ru1—N4	90.16 (11)
C85—Ru1—N2	95.65 (13)	C85—Ru1—O3	177.46 (12)
C85—Ru1—N3	93.48 (12)	N1—Ru1—O3	84.89 (10)
C85—Ru1—N4	95.80 (13)	N2—Ru1—O3	84.09 (10)
N1—Ru1—N2	90.53 (10)	N3—Ru1—O3	89.05 (10)
N1—Ru1—N3	173.93 (11)	N4—Ru1—O3	84.48 (10)
N1—Ru1—N4	89.12 (11)	C93—C85—C86	109.9 (3)
N2—Ru1—N3	88.98 (10)	Ru1—C85—C86	123.8 (2)
N2—Ru1—N4	168.55 (11)	Ru1—C85—C93	126.3 (2)
N3—Ru1—C85—C93	−14.6 (3)	Ru1—C85—C86—O1	86.6 (4)
N1—Ru1—C85—C86	−16.1 (3)	Ru1—C85—C93—O2	85.3 (4)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H87···O4	0.84	1.91	2.684 (4)	153
O4—H93···O5	0.84	1.94	2.780 (4)	176
O5—H99···O2^{i}	0.84	1.99	2.827 (4)	176
C106—H105···O1^{ii}	0.99	2.46	3.329 (5)	146
C75—H61···O1	1.00	2.30	3.290 (4)	172
C43—H27···O2	1.00	2.32	3.316 (4)	172

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$.

For both compounds, data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3081). Services for accessing these data are described at the back of the journal.

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