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Bis(μ-pyridinyl-1-oxide)-1κO^1:2κC^2;1κC^2:2κO^1-bis[(η^4-cycloocta-1,5-diene)rhodium(I)]

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Key indicators

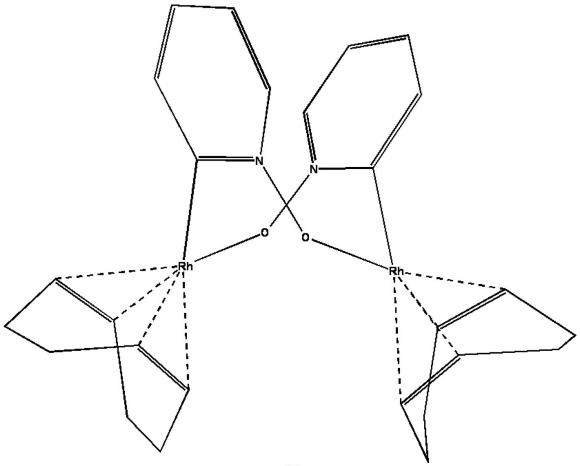
Single-crystal X-ray study
T = 146 K
Mean σ(C–C) = 0.006 Å
R factor = 0.032
wR factor = 0.082
Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Rh_2(C_5H_4N)_2(C_8H_{12})_2]$, the two rhodium(I) centres are coordinated by one η^4-cycloocta-1,5-diene ligand, and by a pyridinyl 1-oxide *ortho*-C atom from one bridging pyridinyl 1-oxide group and by a pyridinyl 1-oxide O atom from the other. The molecule has approximate C_2 symmetry, with the pseudo-C_2 axis perpendicular to the Rh$\cdots$Rh vector.

Comment

The title compound, $[Rh(COD)(\mu\text{-pyNO})]_2$ (COD is cycloocta-1,5-diene and pyNO is pyridinyl-1-oxide), (I), crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. A diagram of (I), with the atomic labelling scheme, is presented in Fig. 1. Important bond distances and angles are listed in Table 1.



(I)

The molecule of (I) has approximate C_2 symmetry, with the pseudo-C_2 axis perpendicular to the Rh$\cdots$Rh vector, which interconverts the two pyridinyl-1-oxide ligands bisecting the Rh$\cdots$Rh vector. The complex is chiral, and both enantiomers are present in the centrosymmetric crystal structure. Its chirality is reflected in its solution ^{1}H NMR spectrum.

The coordination environment at each Rh^I centre consists of a chelating η^4-COD ligand, and a pyridinyl-1-oxide *ortho*-C atom from one bridging pyNO group and a pyridinyl-1-oxide O atom from the other. The structural elements are similar to those in $[Rh(COD)(\mu\text{-mhp})]_2$ (mhp is 6-methyl-2-hydroxypyridinate; Rodman & Mann, 1988), where the Rh$\cdots$Rh distance is 3.367 (1) Å.

The eight-membered $(RhONC)_2$ ring adopts a twisted 'tub' conformation, in which the Rh centres are separated by

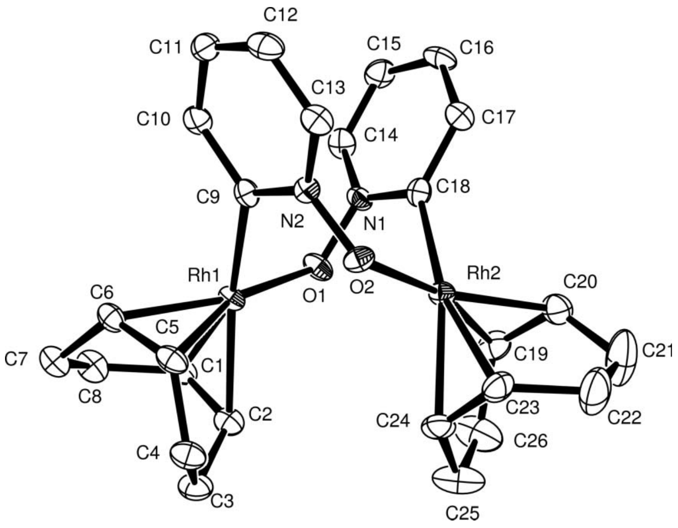


Figure 1
A view of the structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

3.4740 (4) Å. This value is longer than in related weakly interacting d^8–d^8 systems. For example, in two prototypical complexes of this type, $[Rh_2(1,3\text{-diisocyanopropane})_4]^{2+}$ (face-to-face geometry; Mann *et al.*, 1980) and [Rh(COD)(μ-pz)]$_2$ (open-book geometry; Beveridge *et al.*, 1983), the $M\cdots M$ distances are 3.246 (1) and 3.267 (2) Å, respectively. This difference can be explained by the increased flexibility of the eight-membered (RhONC)$_2$ bridging framework compared with that of the six-membered (RhNN)$_2$ unit found in bis-(pyrazolyl-bridged) complexes. The relative orientation of the two $M^{\rm I}$ square planes is significantly different from that found in either the face-to-face geometry, common for d^8–d^8 complexes with four bridging ligands, or in the open-book geometry found in [Ir(COD)(μ-pz)]$_2$ (Beveridge *et al.*, 1983). The dihedral angle formed by the intersection of the two square planes is 59.2 (3)° and there is a twist about the Rh$\cdots$Rh vector away from the eclipsed conformation.

The twist angle of 27° is the pseudo-torsion angle *Cg*1—Rh1$\cdots$Rh2—*Cg*2, where *Cg*1 and *Cg*2 are the centroids of the four olefinic C atoms (C1/C2/C5/C6 and C19/C20/C23/C24, respectively) relative to the Rh$\cdots$Rh vector. Both values are similar to those found in [Rh(COD)(μ-mhp)]$_2$ (57 and 27°, respectively; Rodman & Mann, 1988).

Each Rh$^{\rm I}$ centre exhibits an almost perfect square-planar geometry and the bond angles are close to 90°. The average Rh—C distance is 2.029 (3) Å, while the average Rh—O distance of 2.080 (2) Å is slighly longer. The average Rh—*x*1/*x*3 and Rh—*x*2/*x*4 distances (*x*1, *x*3, *x*2 and *x*4 are the centres of the C1—C2, C23—C24, C5—C6 and C19—C20 bonds, respectively) of 2.08 and 1.97 Å, respectively, indicate a stronger *trans*-influence of C *versus* O.

Experimental

A solution of {Ce[(NSiMe$_3$)$_2$]$_3$} (0.184 g, 0.30 mmol) in toluene (*ca* 10 ml) was added to [Rh(OH)(COD)]$_2$ (0.203 g, 0.44 mmol). After stirring at room temperature for 10 min, a solution of pyridine *N*-oxide (0.084 g, 0.88 mmol) in toluene (*ca* 10 ml) was added. Filtration and slow diffusion of pentane into the toluene solution afforded 0.105 g (37%) of orange–red crystals of (I). A new crop of the crystalline compound could be obtained by partial evaporation of the solvent and cooling to 253 K over 4 d (0.054 g, 19%). Spectroscopic analysis: ^{1}H NMR (C$_6$D$_6$, room temperature, δ, p.p.m.): 7.67 (*m*, 2H, Ar), 7.57 (*m*, 2H, Ar), 6.14 (*m*, 2H, Ar), 5.75 (*m*, 2H, Ar), 5.63 (*s*, 2H, COD), 5.40 (*s*, 2H, COD), 3.86 (*m*, 2H, COD), 3.27 (*m*, 2H, COD), 3.02 (*m*, 2H, COD), 2.69 (*m*, 4H, COD), 2.35 (*m*, 2H, COD), 2.11 (*m*, 4H, COD), 1.90 (*m*, 2H, COD), 1.82 (*m*, 2H, COD); ^{13}C{^{1}H}NMR (C$_6$D$_6$, room temperature, δ, p.p.m.): 196.7 [*d*, ^{1}J(Rh—C) = 46.1 Hz, CO], 137.5 (*s*, Ar), 137.4 (*s*, Ar), 125.6 (*s*, Ar), 117.1 (*s*, Ar), 97.4 [*d*, ^{1}J(Rh—C)= 8.3 Hz, COD], 91.3 [*d*, ^{1}J(Rh—C) = 7.1 Hz, COD], 67.3 [*d*, ^{1}J(Rh—C) = 15.7 Hz, COD], 63.2 [*d*, ^{1}J(Rh—C) = 14.29 Hz, COD], 34.6 (*s*, COD), 32.3 (*s*, COD), 30.0 (*s*, COD), 28.0 (*s*, COD). Analysis, calculated for C$_{26}$H$_{32}$N$_2$O$_2$Rh$_2$: C 51.16, H 5.28, N 4.59%; found: C 51.14, H 5.30, N 4.54%. The crystal was handled under a nitrogen atmosphere, mounted on a glass fibre with Paratone-*N* hydrocarbon oil and cooled to 146 (2) K for data collection.

Crystal data

[Rh$_2$(C$_5$H$_4$N)$_2$(C$_8$H$_{12}$)$_2$]
M_r = 610.36
Monoclinic, $P2_1/c$
a = 13.9304 (7) Å
b = 12.0102 (6) Å
c = 14.1320 (7) Å
β = 101.015 (1)°
V = 2320.8 (2) Å^3
Z = 4
D_x = 1.747 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6511 reflections
θ = 2.2–24.7°
μ = 1.45 mm^{-1}
T = 146 (2) K
Block, orange-red
0.33 × 0.19 × 0.16 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Sheldrick, 1996)
$T_{\rm min}$ = 0.647, $T_{\rm max}$ = 0.801
10107 measured reflections
3802 independent reflections
3334 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.068
$\theta_{\rm max}$ = 24.7°
$h = -16 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.082$
S = 1.00
3802 reflections
321 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh1—Rh2	3.4740 (4)	Rh2—C18	2.032 (3)
Rh1—C9	2.026 (3)	Rh2—O2	2.078 (2)
Rh1—O1	2.082 (2)	Rh2—C19	2.086 (4)
Rh1—C5	2.093 (3)	Rh2—C20	2.093 (4)
Rh1—C6	2.104 (4)	Rh2—C24	2.180 (4)
Rh1—C1	2.192 (3)	Rh2—C23	2.188 (4)
Rh1—C2	2.210 (4)		
C9—Rh1—O1	94.94 (12)	O1—N1—C18	118.7 (3)
C18—Rh2—O2	95.01 (11)	O2—N2—C9	119.5 (3)

H atoms on the py-NO (CH) and COD (CH_2) ligands were included in the refinement in calculated positions using a riding model. The methyne H atoms on the COD ligands (H1, H2, H5, H6, H19, H20, H23 and H24) were located using standard least-squares and difference Fourier techniques and were refined isotropically, with refined C—H distances in the range 0.89 (4)–0.98 (4) Å. Due to the crystal quality, diffraction was observed only out to θ_{max} = 24.7° with 0.96 data completeness, but the data were virtually complete up to θ = 23.0°. The deepest hole in the final difference Fourier map is located 0.94 Å from atom Rh1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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