trans-Bis(6-methyl-2-pyridinolato)bis(triphenylphosphine)ruthenium(II)

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Abstract. $[Ru(C_6H_6NO)_2(C_{18}H_{15}P)_2]$, $C_{48}H_{42}N_2O_2P_2$-Ru, $M_r = 841.9$, monoclinic, $C2/c$, $a = 15.511$ (3), $b = 20.602$ (4), $c = 12.732$ (3) Å, $\beta = 103.00$ (2)°, $U = 3964.3$ Å^3, $Z = 4$, $D_x = 1.410$ Mg m^{-3}; final $R = 0.061$ for 2785 reflexions. The $[Ru(mhp)_2(PPh_3)_2]$ molecule (Hmhp = 6-methyl-2-pyridinol) is centrosymmetric. The Ru atom is coordinated in a distorted octahedral geometry by two PPh$_3$ ligands and by two chelating mhp ligands in an all-*trans* arrangement, with Ru–P 2.367 (2), Ru–N 2.092 (5) and Ru–O 2.151 (4) Å. The geometry of the mhp ligand binding differs considerably from that generally found when the ligand bridges a metal–metal bond, and indicates a predominance of one tautomeric form, with little C–O multiple-bond character.

Introduction. The compound was obtained from the reaction of $[Ru_2(CH_3CO_2)_4(PPh_3)_2]$ with Na(mhp) in methanol under reflux, and was recrystallized from a CH$_2$Cl$_2$/pentane mixture. Chemical analysis, NMR (^{1}H and ^{31}P) and mass spectroscopy support the suggested molecular formula $[Ru(mhp)_2(PPh_3)_2]$.

Crystals were yellow needles. One, of maximum dimension 0.47 mm, was sealed in a capillary tube and used for X-ray investigation. All crystallographic measurements were made with a Stoe–Siemens AED diffractometer and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Cell dimensions were obtained from 46 automatically centred reflexions. Intensities were measured by a profile-fitting method (Clegg, 1981) for reflexions with $7 < 2\theta < 50°$. Absorption corrections were not applied ($\mu = 0.51$ mm^{-1}). From 5272 measured intensities, including many equivalent reflexions, 3484 unique data were obtained, of which 2785 with $I > 2\sigma(I)$ were used for structure determination. The discrepancy index for equivalent reflexions was 0.039.

The location of the Ru atom on the centre of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$ was clear from the analysis of the intensity distribution, reflexions with $k + l$ even being on average rather more intense than those with $k + l$

odd. The position of the P atom was deduced from the Patterson synthesis, and the remaining atoms from subsequent difference syntheses. Refinement to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F_o) + 0.001F_o^2$] included H atoms with constraints on positions (C–H = 0.96 Å, H–C–H = 109.5° for methyl H, aromatic H on external bisector of C–C–C angle) and isotropic thermal parameters [U(H) = $1.2U_{effective}$(C)]; anisotropic thermal parameters were refined for all other atoms.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$)

$U = \frac{1}{3}$ of the trace of the orthogonalized U_{ij} matrix.

|	x	y	z	U
Ru	2500	2500	5000	313 (2)
O	1292 (3)	2787 (2)	3906 (4)	673 (19)
C(1)	1720 (5)	3136 (3)	3279 (5)	614 (27)
C(2)	1310 (6)	3464 (3)	2421 (6)	837 (34)
C(3)	1946 (7)	3792 (3)	1875 (7)	830 (38)
C(4)	2838 (6)	3772 (3)	2245 (5)	736 (35)
C(5)	3156 (5)	3391 (3)	3184 (6)	760 (33)
C(6)	4085 (5)	3383 (4)	3609 (8)	941 (41)
N	2586 (3)	3088 (2)	3688 (4)	364 (16)
P	2447 (1)	3439 (1)	6055 (1)	347 (5)
C(11)	1348 (4)	3791 (3)	6028 (4)	398 (19)
C(12)	1254 (4)	4422 (3)	6364 (5)	489 (23)
C(13)	424 (5)	4668 (3)	6343 (5)	612 (28)
C(14)	–306 (4)	4297 (4)	5999 (5)	632 (28)
C(15)	–225 (4)	3661 (3)	5681 (6)	665 (29)
C(16)	595 (4)	3421 (3)	5681 (5)	545 (24)
C(21)	2909 (4)	3312 (2)	7495 (4)	393 (19)
C(22)	2395 (4)	3332 (2)	8249 (5)	434 (21)
C(23)	2761 (4)	3190 (3)	9321 (5)	520 (24)
C(24)	3647 (4)	3030 (3)	9642 (5)	578 (26)
C(25)	4157 (4)	3002 (3)	8907 (5)	570 (25)
C(26)	3789 (4)	3139 (3)	7840 (5)	504 (22)
C(31)	3022 (4)	4160 (2)	5706 (5)	434 (21)
C(32)	3819 (4)	4400 (3)	6330 (6)	570 (26)
C(33)	4209 (5)	4931 (4)	5965 (7)	818 (36)
C(34)	3846 (5)	5244 (3)	5036 (7)	778 (37)
C(35)	3050 (5)	5016 (3)	4422 (6)	699 (32)
C(36)	2646 (4)	4477 (3)	4754 (5)	556 (26)

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Table 2. *Bond lengths* (Å) *and angles* (°)

Ru—O	2·151 (4)	C(11)—C(12)	1·385 (8)
Ru—N	2·092 (5)	C(11)—C(16)	1·381 (8)
Ru—P	2·367 (2)	C(12)—C(13)	1·379 (10)
		C(13)—C(14)	1·355 (10)
O—C(1)	1·354 (9)	C(14)—C(15)	1·384 (10)
C(1)—C(2)	1·321 (10)	C(15)—C(16)	1·364 (9)
C(1)—N	1·331 (8)	C(21)—C(22)	1·378 (9)
C(2)—C(3)	1·490 (14)	C(21)—C(26)	1·384 (8)
C(3)—C(4)	1·358 (14)	C(22)—C(23)	1·387 (8)
C(4)—C(5)	1·424 (10)	C(23)—C(24)	1·382 (9)
C(5)—C(6)	1·421 (11)	C(24)—C(25)	1·357 (10)
C(5)—N	1·355 (10)	C(25)—C(26)	1·379 (8)
		C(31)—C(32)	1·401 (8)
P—C(11)	1·846 (6)	C(31)—C(36)	1·384 (8)
P—C(21)	1·831 (6)	C(32)—C(33)	1·380 (10)
P—C(31)	1·838 (6)	C(33)—C(34)	1·354 (11)
		C(34)—C(35)	1·387 (10)
		C(35)—C(36)	1·387 (10)

O—Ru—N	61·8 (2)	P—C(11)—C(12)	121·5 (4)
O—Ru—P	90·4 (1)	P—C(11)—C(16)	120·0 (4)
N—Ru—P	89·8 (1)	C(12)—C(11)—C(16)	118·4 (5)
		C(11)—C(12)—C(13)	120·0 (5)
Ru—O—C(1)	93·2 (4)	C(12)—C(13)—C(14)	120·5 (6)
O—C(1)—C(2)	123·5 (7)	C(13)—C(14)—C(15)	120·2 (6)
O—C(1)—N	108·4 (5)	C(14)—C(15)—C(16)	119·3 (6)
C(2)—C(1)—N	128·1 (7)	C(11)—C(16)—C(15)	121·4 (6)
C(1)—C(2)—C(3)	111·8 (8)	P—C(21)—C(22)	122·4 (4)
C(2)—C(3)—C(4)	123·7 (7)	P—C(21)—C(26)	119·4 (5)
C(3)—C(4)—C(5)	116·1 (8)	C(22)—C(21)—C(26)	118·0 (5)
C(4)—C(5)—C(6)	117·1 (8)	C(21)—C(22)—C(23)	120·4 (5)
C(4)—C(5)—N	120·8 (7)	C(22)—C(23)—C(24)	120·1 (7)
C(6)—C(5)—N	121·9 (7)	C(23)—C(24)—C(25)	120·1 (6)
Ru—N—C(1)	96·6 (4)	C(24)—C(25)—C(26)	119·6 (6)
Ru—N—C(5)	144·1 (4)	C(21)—C(26)—C(25)	121·8 (6)
C(1)—N—C(5)	119·3 (5)	P—C(31)—C(32)	124·2 (4)
		P—C(31)—C(36)	117·5 (4)
Ru—P—C(11)	117·4 (2)	C(32)—C(31)—C(36)	118·3 (5)
Ru—P—C(21)	113·3 (2)	C(31)—C(32)—C(33)	119·1 (6)
C(11)—P—C(21)	103·1 (3)	C(32)—C(33)—C(34)	123·0 (7)
Ru—P—C(31)	116·3 (2)	C(33)—C(34)—C(35)	118·2 (7)
C(11)—P—C(31)	100·0 (3)	C(34)—C(35)—C(36)	120·4 (6)
C(21)—P—C(31)	104·8 (2)	C(31)—C(36)—C(35)	120·9 (6)

The final R is 0·061, with $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0·078$. Atom coordinates, bond lengths and angles are given in Tables 1 and 2.*

Discussion. The role of mhp as a bridging ligand in metal—metal bonded species is already well established. In particular, [M_2(mhp)₄] complexes have been crystallographically studied for $M = $ Cr, Mo, W (Cotton, Fanwick, Niswander & Sekutowski, 1978), for $M=$ Rh (Berry, Garner, Hillier, MacDowell & Clegg, 1980*a*; Clegg, 1980*a*), and for $M = $ Ru (Berry, Garner, Hillier, MacDowell & Clegg, 1980*b*; Clegg, 1980*b*).

* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35611 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure reported here (Fig. 1) appears to be the first in which mhp acts as a bidentate ligand coordinated to only one metal atom. This mode of coordination produces a four-membered RuOCN chelate ring with an O—Ru—N angle of only 61·8 (2)°. The reduction of the ring size from the five-membered Ru₂OCN in [Ru₂(mhp)₄] produces, as it must, smaller internal angles in this ring, but there are also considerable changes in bond lengths, Table 3. The Ru—N length is insignificantly different, but Ru—O is much longer for the mononuclear complex, as is C—O; the mean C—N, however, is slightly shorter. It has been argued that in [M_2(mhp)₄] complexes the mhp ligands can best be described in terms of a roughly equal mixture of the extreme tautomeric forms (1) and (2) (Cotton *et al.*, 1978). The very different ligand bond lengths for [Ru(mhp)₂(PPh₃)₂] indicate that, in this case, form (2) predominates.

(1)   (2)
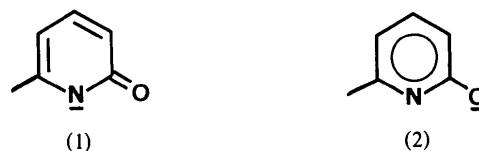
Highly anisotropic thermal motion of the mhp C atoms furthest from Ru renders bond lengths and angles

Table 3. *Comparison of some geometrical parameters in* [Ru₂(mhp)₄] *and* [Ru(mhp)₂(PPh₃)₂]

Distances are in Å, angles in degrees. Values for [Ru₂(mhp)₄] (Clegg, 1980*b*) are averaged over the four chemically equivalent ligands.

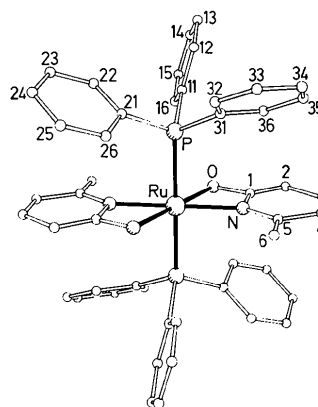|	[Ru₂(mhp)₄]	[Ru(mhp)₂(PPh₃)₂]
Ru—O	2·044 (10)	2·151 (4)
Ru—N	2·089 (5)	2·092 (5)
O—C	1·296 (8)	1·354 (9)
N—C(mean)	1·363 (8)	1·343 (12)
Ru—N—C(O)	119·1 (4)	96·6 (4)
Ru—O—C	119·8 (4)	93·2 (4)
N—C—O	119·4 (4)	108·4 (5)

Fig. 1. The [Ru(mhp)₂(PPh₃)₂] molecule, showing the atom labelling. C atoms are labelled by number only; H atoms are omitted.

involving these atoms unreliable for comparison with other structures. This motion is shown in Fig. 2; a considerable component of it is rocking of the mhp ligands in the equatorial plane, about the P—Ru—P′ axis.
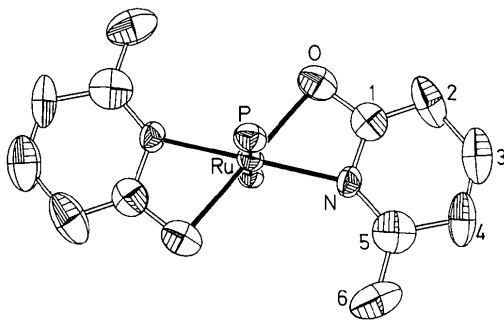

Fig. 2. Thermal motion depicted as 50% probability ellipsoids. Phenyl rings and H atoms are not included.

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Tetrakis[μ-(6-methyl-2-pyridinolato)]-diruthenium (Dichloromethane Solvate)

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Abstract. [Ru$_2$(C$_6$H$_6$NO)$_4$].CH$_2$Cl$_2$, C$_{24}$H$_{24}$N$_4$O$_4$Ru$_2$.-CH$_2$Cl$_2$, M_r = 719·6, monoclinic, $P2_1/n$, a = 12·775 (3), b = 17·155 (4), c = 12·834 (3) Å, β = 103·93 (2)°, U = 2729·9 Å^3, Z = 4, D_x = 1·752 Mg m^{-3}; final R = 0·045 for 3839 reflexions. The molecule, like those of other [M_2(mhp)$_4$] complexes (Hmhp = 6-methyl-2-pyridinol), has approximate $\bar{4}2m$ symmetry. The Ru—Ru length is 2·238 (1) Å.

Introduction. This compound has been prepared in the course of a study of complexes of the 6-methyl-2-pyridinolato (mhp) ligand. A preliminary description of the preparation, spectroscopic properties and crystal structure has already been given (Berry, Garner, Hillier, MacDowell & Clegg, 1980a).

A yellow crystal, 0·3 × 0·3 × 0·2 mm, sealed in a capillary tube, was used for crystallographic measurements performed with a Stoe–Siemens AED diffractometer controlled by a Data General S250 minicomputer (Clegg, 1981). Cell dimensions were obtained from 30 centred reflexions. Intensities were measured for all unique reflexions with 7 < 2θ < 50°

in a θ/ω scan mode, with graphite-monochromated Mo Kα radiation (λ = 0·71069 Å). Corrections were applied for absorption by an empirical method based on azimuthal-scan measurements (μ = 1·32 mm^{-1}), and for a gradual decay in the intensities of three standard reflexions, amounting to *ca* 18% by the end of the data collection. The discrepancy index for the 397 azimuthal-scan data was reduced from 0·021 to 0·012 by the absorption correction; transmission factors for the complete data set were 0·456–0·514. 3839 reflexions with $I > 2\sigma(I)$ were used for structure determination.

The structure was solved by conventional Patterson and Fourier techniques, and refined by minimization of $\sum w\Delta^2$ [Δ = |F_o| − |F_c|; w^{-1} = $\sigma^2(F_o)$ + 0·001F_o^2]. Constraints were applied for H atoms [C—H = 0·96 Å, H—C—H = 109·5° in methyl groups, aromatic H on C—C—C external bisector; U(H) = gU_{iso}(C), with g = 1·1 for aromatic and 1·2 for methyl H]. H atoms were not included for the CH$_2$Cl$_2$ solvent molecule, which displays high thermal motion. Anisotropic thermal parameters were refined for all other atoms.