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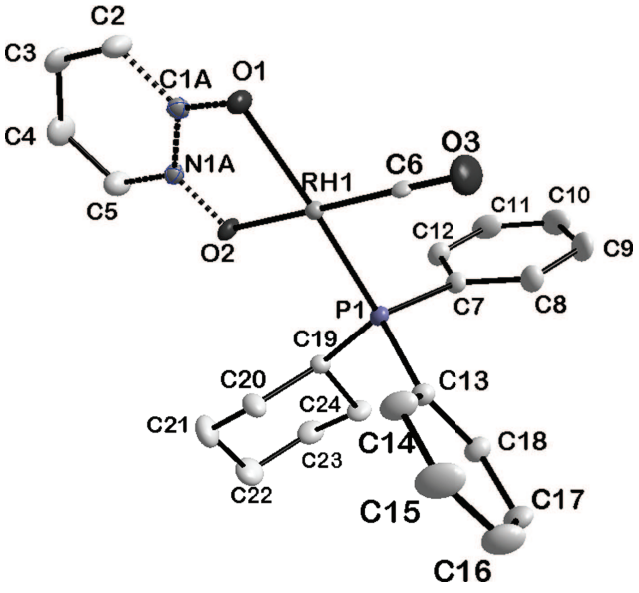
The crystal structure of carbonyl(2-oxopyridin-1(2*H*)-olato-$\kappa^2 O,O'$)-(diphenylcyclohexylphosphine-κP)rhodium(I), $C_{24}H_{25}NO_3PRh$



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Abstract

$C_{24}H_{25}NO_3PRh$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.5498(1)$ Å, $b = 13.4996(2)$ Å, $c = 17.428(3)$ Å, $V = 2246.7(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0163$, $wR_{ref}(F^2) = 0.0376$, $T = 100$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow cuboid
Size:	0.25 × 0.21 × 0.11 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	8.6 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	56°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	62189, 5394, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5214
$N(param)_{refined}$:	273
Programs:	SHELX [1], Bruker programs [2], DIAMOND [3], WinGX [4]

Source of materials

[Rh(hopo)(CO)$_2$] (hopo = 2-oxopyridine-*N*-oxide) was synthesized according to the method described previously [5]. [Rh(hopo)(CO)$_2$(PPh$_2$Cy)] was synthesized by dissolving [Rh(hopo)(CO)$_2$] (0.1001 g, 0.3721 mmol) in 5 cm^3 of acetone. Diphenylcyclohexylphosphine (PPh$_2$Cy) (0.1198 g, 0.4465 mmol) was added to the aforementioned solution with stirring. Some ice water was added dropwise to precipitate the product. Yellow cuboid crystals, suitable for X-ray diffraction were obtained from recrystallization in acetone and a few drops of water.

IR: ν_{CO} 1974 cm^{-1}. **^{1}H-NMR** (600 MHz, CD_2Cl_2) δ 8.06 (d, ^{1}J = 6.4 Hz, 1H), 7.90 – 7.77 (m, 10H), 7.74 (d, ^{1}J = 6.4 Hz, 10H), 7.47 (s, 1H), 7.31 (dd, ^{2}J = 14.6, ^{1}J = 7.0 Hz, 1H), 7.27 (t, ^{1}J = 7.6 Hz, 1H), 6.93 (d, ^{1}J = 8.6 Hz, 1H), 6.71 (d, ^{1}J = 8.4 Hz, 1H), 6.55 (t, ^{1}J = 6.5 Hz, 1H), 6.46 (t, ^{1}J = 6.5 Hz, 1H), 1.96 (dd, ^{2}J = 534.0, ^{1}J = 200.8 Hz, 22H).**^{13}C-NMR** (75 MHz, CD_2Cl_2) δ 191.41 – 188.70 (m), 162.69 (s), 133.57 (d, J = 10.4 Hz), 133.21 (s), 132.57 (s), 131.91 (s), 130.05 (s), 128.09 (d, J = 10.0 Hz), 116.07 (s), 109.89 (d, J = 67.7 Hz), 35.97 (s), 28.57 (s), 26.88 (d, J = 13.0 Hz), 26.18 (s). **^{31}P-NMR** (243 MHz, CD_2Cl_2) δ 54.07 (d, ^{1}J (PRh major isomer) = 175.3 Hz), 53.83 (d, ^{1}J (PRh minor isomer) = 166.8 Hz).

Experimental details

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
C18	0.20115(18)	0.35714(12)	0.21110(10)	0.0194(3)
H18	0.1819	0.3509	0.2644	0.023*
C19	−0.11103(18)	0.21929(12)	0.22526(9)	0.0166(3)
H19	−0.1653	0.1590	0.2403	0.020*
C8	0.29728(19)	0.14995(13)	0.28919(11)	0.0232(4)
H8	0.3478	0.1871	0.2521	0.028*
C9	0.3669(2)	0.11000(14)	0.35180(11)	0.0307(4)
H9	0.4645	0.1210	0.3578	0.037*
C24	−0.11277(19)	0.28726(12)	0.29514(10)	0.0205(4)
H24A	−0.0619	0.2553	0.3380	0.025*
H24B	−0.0645	0.3501	0.2827	0.025*
C12	0.08191(19)	0.07910(13)	0.33483(10)	0.0214(4)
H12	−0.0156	0.0675	0.3290	0.026*
C16	0.3001(2)	0.44907(14)	0.10631(11)	0.0325(4)
H16	0.3500	0.5051	0.0879	0.039*
C6	0.22432(18)	0.05540(13)	0.09787(10)	0.0203(3)
C17	0.27413(19)	0.43927(12)	0.18420(10)	0.0231(4)
H17	0.3060	0.4884	0.2191	0.028*
C13	0.15609(17)	0.28388(12)	0.16034(10)	0.0163(3)
C23	−0.2624(2)	0.30874(14)	0.31938(11)	0.0262(4)
H23A	−0.3075	0.2465	0.3364	0.031*
H23B	−0.2618	0.3552	0.3634	0.031*
C21	−0.3409(2)	0.29003(16)	0.18212(12)	0.0319(5)
H21A	−0.3924	0.2275	0.1911	0.038*
H21B	−0.3878	0.3256	0.1396	0.038*
C10	0.2951(2)	0.05411(15)	0.40569(10)	0.0325(4)
H10	0.3437	0.0261	0.4480	0.039*
C14	0.1805(2)	0.29567(13)	0.08229(11)	0.0257(4)
H14	0.1470	0.2475	0.0470	0.031*
C20	−0.19155(19)	0.26614(13)	0.15879(10)	0.0220(4)
H20A	−0.1437	0.3277	0.1424	0.026*
H20B	−0.1926	0.2199	0.1147	0.026*
C22	−0.3471(2)	0.35338(15)	0.25441(12)	0.0326(5)
H22A	−0.3108	0.4204	0.2428	0.039*
H22B	−0.4459	0.3603	0.2709	0.039*
C7	0.15315(17)	0.13577(12)	0.28049(9)	0.0166(3)
C15	0.2541(2)	0.37814(15)	0.05559(11)	0.0345(5)
H15	0.2725	0.3852	0.0023	0.041*
C11	0.1529(2)	0.03927(14)	0.39786(9)	0.0277(4)
H11	0.1033	0.0020	0.4353	0.033*
O1	−0.00822(11)	−0.08180(8)	0.05211(6)	0.0177(2)
O2	−0.17128(11)	0.03295(9)	0.13536(6)	0.0171(2)
O3	0.34334(13)	0.06222(11)	0.08705(9)	0.0361(4)
P1	0.06165(4)	0.17455(3)	0.19372(2)	0.01312(8)
Rh1	0.039656(12)	0.045707(8)	0.115510(7)	0.01218(3)
N1	−0.22715(14)	−0.04344(11)	0.09621(7)	0.0166(3)
C1	−0.14052(17)	−0.10247(11)	0.05412(9)	0.0127(3)
C5	−0.36880(18)	−0.05673(13)	0.09785(9)	0.0212(4)
H5	−0.4259	−0.0133	0.1272	0.025*
C2	−0.20179(19)	−0.18112(13)	0.01427(10)	0.0216(4)
H2	−0.1438	−0.2248	−0.0144	0.026*
C3	−0.3429(2)	−0.19665(13)	0.01551(11)	0.0239(4)
H3	−0.3827	−0.2506	−0.0118	0.029*
C4	−0.42852(19)	−0.13216(13)	0.05752(11)	0.0250(4)
H4	−0.5272	−0.1409	0.0579	0.030*

$U_{iso}(H) = 1.2U_{eq}$ ($C_{aromatic}$). The highest peak is located 1.18 Å from O3 and the deepest hole is situated 1.01 Å from Rh1. The C1 and N1 atoms are disordered in a 0.8/0.2 ratio with the higher occupancy attributed to the isomer with PPh_2Cy *cis* to N. Some unusual ellipsoids in the direct vicinity of the Rh metal are caused by some small problems with the absorption correction.

Comment

The oxidative addition of iodomethane to Rh(I) complexes to form alkyl and acyl product is an important step in the catalytic process and is used on a massive scale in industry to convert methanol and carbon monoxide to acetic acid in Monsanto process [6, 7]. In the precursor $[Rh(BID)(CO)_2]$ complexes (where BID represents different monoanionic bidentate ligands such as cupferrate and 2-oxopyridine *N*-oxide, etc.) one of the two carbonyl can be substituted by tertiary phosphine ligands (PR_3) to form $[Rh(BID)(CO)(PR_3)]$ complexes. These complexes have been intensively studied as possible candidates for catalytic processes [8–10]. In this study the complex [Rh(hopo)(CO)(PPh_2Cy)] (hopo = 2-oxopyridine *N*-oxide) has been synthesized to study the electronic and steric influence of the phosphine ligands on the oxidative addition of methyl iodide.

The complex has a distorted square planar geometry around the Rh centre indicated by the small bite angle of 78.7(1)° of the five membered ring. Two isomers are present in a 80/20 ratio, with the principal isomer PPh_2Cy *cis* to the N atom. This was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectra of the complex. The effective cone angle, θ_E [11], of 156.48(2)° is similar to related compounds angles which are in the range of 154–157° [12–15].

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