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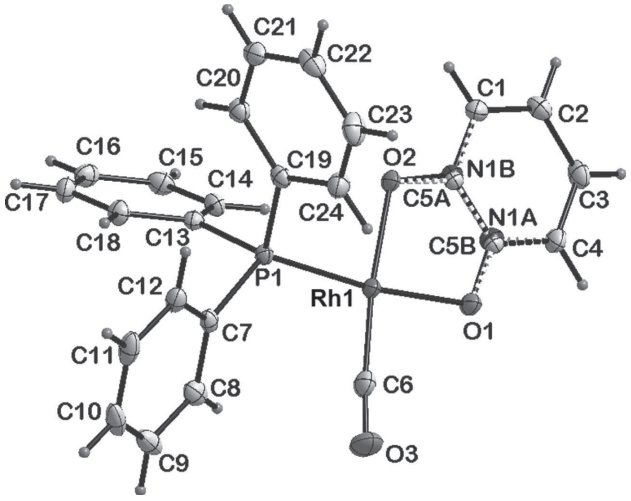
Crystal structure of carbonyl(2-oxopyridin-1(2*H*)-olato-κ^2*O*, *O*′)(triphenylphosphine-κ*P*)rhodium(I), $C_{24}H_{19}NO_3PRh$



DOI 10.1515/ncrs-2015-0266
Received November 23, 2015; accepted March 10, 2016; available online April 1, 2016

Abstract

$C_{24}H_{19}NO_3PRh$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1734(16)$ Å, $b = 9.5433(18)$ Å, $c = 12.342(2)$ Å, $\alpha = 92.400(6)°$, $\beta = 105.460(5)°$, $\gamma = 99.472(5)°$, $V = 1023$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0236$, $wR_{ref}(F^2) = 0.0597$, $T = 100$ K.

CCDC no.: 1463131

The figure shows the asymmetric unit of the title structure. Tables 1–3 contain details of the methods used and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow, cuboid, size 0.107×0.245×0.309 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.39 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω scans
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17984, 4923
$N(param)_{refined}$:	272
Programs:	SHELX [17], Bruker programs [18], Diamond [19], WinGX [20]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.4083	0.6079	0.5388	0.025
H(2)	2*i*	0.2496	0.7667	0.5577	0.026
H(3)	2*i*	0.2380	0.9629	0.4481	0.024
H(4)	2*i*	0.3959	1.0011	0.3294	0.022
H(8)	2*i*	1.0901	0.6518	0.2925	0.025
H(9)	2*i*	1.2812	0.5607	0.2345	0.033
H(10)	2*i*	1.2947	0.5736	0.0495	0.035
H(11)	2*i*	1.1129	0.6710	−0.0807	0.031
H(12)	2*i*	0.9184	0.7585	−0.0244	0.023
H(14)	2*i*	0.8599	0.9921	0.3788	0.021
H(15)	2*i*	1.0154	1.2075	0.4657	0.025
H(16)	2*i*	1.2042	1.3213	0.3878	0.024
H(17)	2*i*	1.2384	1.2181	0.2234	0.024
H(18)	2*i*	1.0884	0.9987	0.1392	0.021
H(20)	2*i*	0.7908	1.0411	0.0525	0.021
H(21)	2*i*	0.6108	1.0689	−0.1157	0.025
H(22)	2*i*	0.4253	0.8748	−0.2114	0.029
H(23)	2*i*	0.4176	0.6521	−0.1385	0.031
H(24)	2*i*	0.5932	0.6260	0.0319	0.026

Source of material

$[RhCl(CO)_2]_2$ was synthesized by refluxing hydrated $RhCl_3$ (0.1002 g, 0.480 mmol) in 6 cm^3 DMF for approximately 30 minutes. 2-Hydroxypyridine *N*-oxide (hopo) (0.0533 g, 0.480 mmol) was added to the aforementioned yellow

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solution followed by ice water to precipitate [Rh(hopo)$(CO)_2$]. The precipitate was filtered off and dried. [Rh(hopo)$(CO)_2$] (0.0611 g, 0.227 mmol) was dissolved in 7 cm^3 of acetone. Triphenylphosphine (PPh_3) (0.0629 g, 0.240 mmol) was added to the aforementioned solution with stirring. Ice water was added dropwise to the solution. A light yellow precipitate was filtered off and dried. Yellow cuboid crystals were obtained from recrystallization in acetone, and a few drops of water were added to enhance crystal growth. **IR**: $\nu_{CO} = 1961\ cm^{-1}$. **^{1}H NMR** (300 MHz, $CDCl_3$) $\delta = 8.07$ (d, $^1J = 6.3$ Hz, 1H), 7.91 (dd, $^2J = 20.9$, $^1J = 7.1$ Hz, 1H), 7.73–7.59 (m, 1H), 7.58–7.53 (m, 1H), 6.96 (d, $^1J = 8.4$ Hz, 1H), 6.64 (d, $^1J = 8.3$ Hz, 1H), 6.51 (t, $^1J = 5.6$ Hz, 1H), 6.43–6.34 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 0189.01 (dd, $^2J = 76.7$, $^1J = 25.3$ Hz), 163.00 (s), 162.63 (d, $^1J = 2.8$ Hz), 135.78 (d, $^1J = 4.2$ Hz), 134.74 (t, $^1J = 6.4$ Hz), 134.30 (d, $^1J = 11.8$ Hz), 133.31 (s), 133.19 (s), 132.97 (s), 132.70 (d, $^1J = 3.0$ Hz), 132.16 (s), 132.06 (s), 131.98 (d, $^1J = 2.8$ Hz), 130.48 (d, $^1J = 2.4$ Hz), 130.42 (d, $^1J = 2.5$ Hz), 130.14 (s), 128.53 (d, $^1J = 12.1$ Hz), 128.23 (d, $^1J = 10.7$ Hz), 116.36 (s), 116.28 (d, $^1J = 1.6$ Hz), 110.40 (s), 109.61 (s). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 049.26 (d, $^1J_{(PRh)} = 177.7$ Hz), 48.16 (d, $^1J_{(PRh)} = 169.6$ Hz).

Experimental details

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C_{aromatic})$. The highest peak is located 0.85 Å from O3 and the deepest hole is situated 0.80 Å from Rh1. The C5 and N1 atoms are disordered in a 57.43 % with the higher attributed to the isomer with PPh_3 *cis* to N.

Discussion

One of the CO ligands in the precursor [Rh(BID)$(CO)_2$] complexes [where (BID) represents different monoanionic bidentate ligands such as acetylacetonate [1], 2-pyridinethiolato *N*-oxide [2], cupferrate [3, 4], neocupferrate [5], 2-oxopyridine*N*-oxide [6] etc.], may be substituted by tertiary phosphine ligands (PR_3) such as PPh_3 to form [Rh(BID)(CO)(PR_3)] complexes. Generally, this substitution with asymmetrical bidentate ligands might form two isomeric

Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.4056(2)	0.6885(2)	0.4963(2)	0.0199(9)	0.024(1)	0.022(1)	0.0031(8)	0.0091(8)	0.0089(8)
C(2)	2*i*	0.3113(2)	0.7816(2)	0.5070(2)	0.0183(9)	0.031(1)	0.020(1)	0.0042(8)	0.0103(8)	0.0046(9)
C(3)	2*i*	0.3057(2)	0.8991(2)	0.4429(2)	0.0165(9)	0.024(1)	0.021(1)	0.0064(8)	0.0059(8)	0.0011(8)
C(4)	2*i*	0.3986(2)	0.9212(2)	0.3729(2)	0.0161(9)	0.018(1)	0.020(1)	0.0038(7)	0.0036(7)	0.0040(8)
C(5A)	2*i*	0.4974(2)	0.7111(2)	0.4237(2)	0.0144(8)	0.0186(9)	0.0184(9)	0.0026(7)	0.0059(7)	0.0032(7)
N(1A)	2*i*	0.4960(2)	0.8284(2)	0.3651(2)	0.0140(8)	0.0193(9)	0.0155(9)	0.0024(6)	0.0041(6)	0.0032(7)
C(5B)	2*i*	0.4960(2)	0.8284(2)	0.3651(2)	0.0140(8)	0.0193(9)	0.0155(9)	0.0024(6)	0.0041(6)	0.0032(7)
N(1B)	2*i*	0.4974(2)	0.7111(2)	0.4237(2)	0.0144(8)	0.0186(9)	0.0184(9)	0.0026(7)	0.0059(7)	0.0032(7)
C(6)	2*i*	0.8119(2)	0.5395(2)	0.3081(2)	0.023(1)	0.022(1)	0.025(1)	0.0037(8)	0.0127(8)	0.0073(9)
C(7)	2*i*	0.9853(2)	0.7155(2)	0.1396(2)	0.0131(8)	0.0125(9)	0.022(1)	−0.0005(7)	0.0069(7)	−0.0020(7)
C(8)	2*i*	1.0940(2)	0.6558(2)	0.2165(2)	0.0179(9)	0.018(1)	0.024(1)	0.0018(7)	0.0035(8)	−0.0031(8)
C(9)	2*i*	1.2081(2)	0.6022(2)	0.1821(2)	0.0153(9)	0.022(1)	0.042(1)	0.0047(8)	0.0033(9)	−0.005(1)
C(10)	2*i*	1.2154(2)	0.6090(2)	0.0722(2)	0.019(1)	0.019(1)	0.051(2)	−0.0008(8)	0.020(1)	−0.008(1)
C(11)	2*i*	1.1081(2)	0.6670(2)	−0.0049(2)	0.031(1)	0.018(1)	0.035(1)	−0.0021(8)	0.023(1)	−0.0039(9)
C(12)	2*i*	0.9928(2)	0.7195(2)	0.0289(2)	0.0215(9)	0.0147(9)	0.024(1)	0.0011(7)	0.0122(8)	0.0001(8)
C(13)	2*i*	0.9591(2)	0.9730(2)	0.2503(2)	0.0138(8)	0.0145(9)	0.0142(9)	0.0028(7)	0.0027(7)	0.0029(7)
C(14)	2*i*	0.9378(2)	1.0370(2)	0.3476(2)	0.0157(8)	0.0188(9)	0.019(1)	0.0043(7)	0.0076(7)	0.0020(8)
C(15)	2*i*	1.0295(2)	1.1657(2)	0.3989(2)	0.0215(9)	0.021(1)	0.020(1)	0.0072(8)	0.0060(8)	−0.0015(8)
C(16)	2*i*	1.1417(2)	1.2331(2)	0.3529(2)	0.0198(9)	0.0155(9)	0.023(1)	0.0025(7)	0.0020(8)	0.0001(8)
C(17)	2*i*	1.1624(2)	1.1713(2)	0.2556(2)	0.0174(9)	0.019(1)	0.024(1)	−0.0007(7)	0.0064(8)	0.0041(8)
C(18)	2*i*	1.0724(2)	1.0412(2)	0.2051(2)	0.0191(9)	0.020(1)	0.0159(9)	0.0032(7)	0.0077(7)	0.0018(8)
C(19)	2*i*	0.7109(2)	0.8307(2)	0.0585(2)	0.0136(8)	0.0203(9)	0.0133(9)	0.0042(7)	0.0060(7)	0.0017(7)
C(20)	2*i*	0.7147(2)	0.9619(2)	0.0142(2)	0.0164(9)	0.020(1)	0.0169(9)	0.0033(7)	0.0067(7)	0.0024(8)
C(21)	2*i*	0.6079(2)	0.9784(2)	−0.0862(2)	0.0210(9)	0.027(1)	0.018(1)	0.0085(8)	0.0095(8)	0.0072(8)
C(22)	2*i*	0.4978(2)	0.8635(2)	−0.1427(2)	0.0177(9)	0.041(1)	0.015(1)	0.0080(9)	0.0046(8)	0.0044(9)
C(23)	2*i*	0.4928(2)	0.7314(2)	−0.0993(2)	0.019(1)	0.033(1)	0.020(1)	−0.0044(9)	0.0020(8)	−0.0012(9)
C(24)	2*i*	0.5981(2)	0.7159(2)	0.0014(2)	0.0197(9)	0.022(1)	0.022(1)	−0.0001(8)	0.0058(8)	0.0035(8)
O(1)	2*i*	0.5858(2)	0.6198(2)	0.4086(1)	0.0213(7)	0.0198(7)	0.0240(7)	0.0075(6)	0.0132(6)	0.0089(6)
O(2)	2*i*	0.5903(2)	0.8506(1)	0.2994(1)	0.0182(6)	0.0198(7)	0.0213(7)	0.0058(5)	0.0120(6)	0.0097(6)
O(3)	2*i*	0.8626(2)	0.4375(2)	0.3126(2)	0.044(1)	0.0258(9)	0.063(1)	0.0190(8)	0.0275(9)	0.0169(8)
Rh(1)	2*i*	0.71672(2)	0.69115(2)	0.30215(1)	0.01395(8)	0.01446(8)	0.01515(8)	0.00352(5)	0.00644(6)	0.00452(6)
P(1)	2*i*	0.84533(5)	0.79792(5)	0.18922(4)	0.0128(2)	0.0137(2)	0.0132(2)	0.0022(2)	0.0054(2)	0.0019(2)

complexes where PPh_3 is *trans*-positioned with respect to the strongest donor atom of the bidentate ligand as the preferred isomer [7–12]. Various crystallographic studies on $[Rh(BID)(CO)(PPh_3)]$ complexes revealed that the reaction between $[Rh(BID)(CO)_2]$ with PPh_3 gives only one isomer that crystalizes from solution [8, 9]. The only example where both isomers crystalized in the same unit cell has been reported for $[Rh(BA)(CO)(PPh_3)]$ complex (BA = benzoylacetonato) [10]. In the title structure the ligands are coordinated to rhodium in a distorted square planar geometry. This distortion of the O1—Rh—O2 bond angle from 90° is caused by the small bite angle of 79.3 (6)° of the five membered ring of the chelate. The bite angles of all bidentate ligands of the type $[Rh(BID)(CO)(PPh_3)]$ with such five membered rings are in the range 77–80°, compared to the same type of bidentate ligands with six membered rings displaying bite angles of 86–92° [12]. In the title structure, the presence of two isomers, in a 57.43% ratio, with the principal isomer PPh_3 *cis* to the N atom, different from expected is evident from the X-ray diffraction data. Furthermore, it was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectra of the complex. The effective cone angle, θ_E, [13] of 154.52(3)° that is similar to related compounds angles [14–16]. Weak intramolecular hydrogen bond occurs between C14—H14···O2 (2.32(1) Å), as well as weak intermolecular hydrogen bond interaction between C4—H4···O1 (2.54(1) Å; $-x+1$, $-y+1$, $-z+1$).

Acknowledgements: The authors would like to thank the South African NRF, Prof. Andreas Roodt (the head of inorganic chemistry group) and the University of the Free State for financial support, while Dr. Linette Twigge is also thanked for NMR data discussion.

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