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The crystal structure of *trans*-carbonyl-(diphenylcyclohexyl-phosphine- κP)iodidomethyl-(2-oxopyridin-1(2*H*)-olato- $\kappa^2 O, O'$)rhodium(III), $C_{25}H_{28}INO_3PRh$

Table 1: Data collection and handling.

Crystal:	Orange stout
Size:	0.29 × 0.15 × 0.09 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.94 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	42669, 6211, 0.060
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4321
$N(\text{param})_{\text{refined}}$:	299
Programs:	SHELX [1], Bruker [2], Diamond [3], Olex2 [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Rh1	0.39428(3)	0.63865(4)	0.66930(2)	0.03485(11)
P1	0.24271(10)	0.62125(12)	0.60246(5)	0.0307(3)
O1	0.3885(3)	0.8453(3)	0.67480(15)	0.0437(8)
O2	0.5274(3)	0.6740(4)	0.73280(16)	0.0510(9)
N1	0.4818(4)	0.8902(4)	0.70546(18)	0.0421(10)
C1	0.5516(4)	0.8015(5)	0.7350(2)	0.0361(10)
C2	0.6471(5)	0.8537(7)	0.7673(2)	0.0514(14)
H2	0.6970	0.7948	0.7875	0.062*
C3	0.6682(6)	0.9894(8)	0.7696(3)	0.0682(19)
H3	0.7318	1.0227	0.7913	0.082*
C4	0.5939(6)	1.0776(7)	0.7393(3)	0.0649(17)
H4	0.6068	1.1704	0.7412	0.078*
C5	0.5022(5)	1.0274(5)	0.7070(3)	0.0517(14)
H5	0.4533	1.0858	0.6860	0.062*
C6	0.2768(5)	0.6207(6)	0.7377(2)	0.0479(13)
H6A	0.2102	0.5672	0.7255	0.072*
H6B	0.2504	0.7090	0.7490	0.072*
H6C	0.3159	0.5778	0.7701	0.072*
C8	0.1078(4)	0.7094(5)	0.6209(2)	0.0354(10)
C9	0.1097(4)	0.8248(5)	0.6558(2)	0.0398(11)
H9	0.1812	0.8568	0.6707	0.048*
C10	0.0071(5)	0.8915(5)	0.6681(2)	0.0479(13)
H10	0.0092	0.9669	0.6923	0.057*
C11	−0.0999(5)	0.8471(6)	0.6448(3)	0.0577(15)
H11	−0.1695	0.8924	0.6531	0.069*
C12	−0.1018(5)	0.7348(7)	0.6089(3)	0.0593(16)
H12	−0.1729	0.7053	0.5925	0.071*
C13	0.0002(4)	0.6668(6)	0.5974(2)	0.0480(13)
H13	−0.0025	0.5910	0.5736	0.058*

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Abstract

$C_{25}H_{28}INO_3PRh$, monoclinic, $P2_1/c$ (no. 14), $a = 11.339(4)$ Å, $b = 9.887(5)$ Å, $c = 23.069(9)$ Å, $\beta = 91.125(5)^\circ$, $Z = 4$, $V = 2585.7(19)$ Å³, $R_{\text{gt}}(F) = 0.0463$, $wR_{\text{ref}}(F^2) = 0.1093$, $T = 293(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

[Rh(hopo)(CO)(PPh₂Cy)] (hopo = 2-oxopyridin-1(2*H*)-olate) was synthesized according to the method described previously [5]. Rhodium(III) alkyl oxidative addition product

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Table 2 (continued)

Atom	x	y	z	U _{iso} */U _{eq}
C14	0.1986(4)	0.4456(5)	0.5930(2)	0.0365(11)
C15	0.1191(5)	0.3853(5)	0.6291(2)	0.0441(12)
H15	0.0825	0.4370	0.6572	0.053*
C16	0.0924(5)	0.2495(6)	0.6244(3)	0.0542(14)
H16	0.0389	0.2104	0.6494	0.065*
C17	0.1443(7)	0.1731(6)	0.5833(3)	0.0705(19)
H17	0.1245	0.0822	0.5795	0.085*
C18	0.2274(7)	0.2301(6)	0.5466(3)	0.074(2)
H18	0.2642	0.1774	0.5189	0.089*
C19	0.2537(6)	0.3653(6)	0.5520(2)	0.0563(15)
H19	0.3093	0.4037	0.5279	0.068*
C20	0.2788(4)	0.6858(5)	0.5295(2)	0.0392(11)
H20	0.3492	0.6370	0.5171	0.047*
C21	0.1818(5)	0.6591(7)	0.4836(2)	0.0571(15)
H21A	0.1635	0.5633	0.4823	0.069*
H21B	0.1107	0.7078	0.4935	0.069*
C22	0.2250(6)	0.7064(9)	0.4244(3)	0.078(2)
H22A	0.2918	0.6515	0.4133	0.094*
H22B	0.1626	0.6936	0.3956	0.094*
C23	0.2612(7)	0.8536(8)	0.4255(3)	0.086(2)
H23A	0.2926	0.8780	0.3881	0.103*
H23B	0.1922	0.9093	0.4320	0.103*
C24	0.3518(7)	0.8817(7)	0.4718(3)	0.079(2)
H24A	0.3680	0.9779	0.4730	0.095*
H24B	0.4244	0.8354	0.4625	0.095*
C25	0.3110(6)	0.8352(5)	0.5315(2)	0.0546(15)
H25A	0.3736	0.8498	0.5601	0.066*
H25B	0.2430	0.8878	0.5428	0.066*
I1 ^a	0.57361(4)	0.64371(7)	0.59102(2)	0.06474(18)
O3 ^a	0.4217(7)	0.3319(4)	0.6760(3)	0.0794(17)
C7 ^a	0.4127(10)	0.4432(3)	0.6698(4)	0.0794(17)
I1A ^b	0.4667(2)	0.3832(2)	0.66140(12)	0.0615(6)
O3A ^b	0.5711(18)	0.688(3)	0.5692(9)	0.0794(17)
C7A ^b	0.503(2)	0.666(3)	0.6032(10)	0.0794(17)

^aOccupancy: 0.8, ^bOccupancy: 0.2.

[Rh(hopo)(CO)(CH₃)(I)(PPh₂Cy)] was prepared as follows: (0.100 g, 0.154 mmol) was dissolved in acetone (2 cm³) whereafter iodomethane (0.2186 g, 1.541 mmol) was added with stirring. The solution was stored at 25 °C for two days and yielded orange crystals (yield 68%).

IR: ν_{CO} 2056 cm⁻¹. **³¹P NMR** (162 MHz, CDCl₃) δ [ppm] 40.96 (d, ¹J_{(RhP)A} = 123.8 Hz), 37.56 (d, ¹J_{(RhP)B} = 116.3 Hz); where A = major isomer, B = minor isomer.

Experimental details

All H-atoms were positioned on geometrically idealized positions and refined using the riding model with fixed C—H distances for aromatic C—H of 0.93 Å (C—H) [*U*_{iso} (H) = 1.2 *U*_{eq}], for methyl C—H of 0.96 Å (C—H) [*U*_{iso} (H) = 1.5 *U*_{eq}], for methylene C—H of 0.97 Å (C—H) [*U*_{iso} (H) = 1.5 *U*_{eq}] and for

methine C—H of 0.98 Å (C—H) [*U*_{iso} (H) = 1.5 *U*_{eq}]. The graphics were obtained using the DIAMOND [3] program with 50% probability ellipsoids. The highest residual peak is located 0.77 Å from Rh and the deepest hole is situated 0.71 Å from Rh. The I1 and C7-O3 (carbonyl group) atoms are disordered in an approximate 80% ratio with the higher value attributed to the I1 *trans* methyl and the 20% isomer and hydrogen atoms in the figure are omitted for clarity.

Comment

The iodomethane oxidative addition reaction to Rh(I) complexes to form alkyl and acyl product is an essential and relevant reaction in catalytic processes as utilized in industry to produce acetic acid from methanol and carbon monoxide in the Monsanto process [5–7]. It is known that only one CO ligand in the precursor [Rh(BID)(CO)₂] complexes [where BID denote different monocharged bidentate ligands such as cupferrate and 2-oxopyridine *N*-oxide, etc.] can be substituted by tertiary phosphine ligands (PX₃) to form [Rh(BID)(CO)(PX₃)] complexes. These complexes have been intensively studied as possible catalysts in model catalytic reactions [8–16].

The title complex displays a distorted octahedral geometry around the Rh centre indicated by the small bite angle of 79.42(1)° of the five membered chelate ring as well as the C7—Rh—C6, C6—Rh—P1, P1—Rh—I1, P1—Rh—O2 and I1—Rh—C6 angles of 87.24(1), 91.19(8), 96.58(1), 174.32(1) and 171.08(1)°, respectively. The coordination mode in the title complex is similar to the complex reported previously [11, 17]. The Rh—O1, Rh—O2, Rh—P1, Rh—C6 and Rh—I1 bond distances are 2.0494(1), 2.1108(5), 2.2926(6), 2.0930(5) and 2.7448(7) Å, respectively. The lengthening of Rh—O2 compared to Rh—O1 is due to the strong *trans* influence of the P atom. In the figure the hydrogen atoms have been omitted for clarity.

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