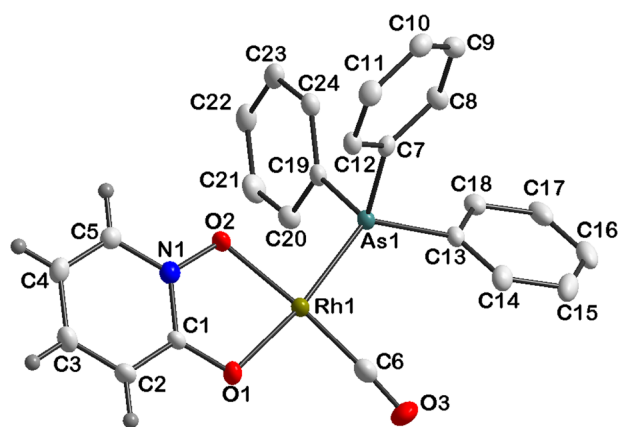


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Crystal structure of carbonyl(2-oxopyridin-1(2*H*)-olato- $\kappa^2 O, O'$)(triphenylarsine- κAs)rhodium(I), $C_{24}H_{19}AsNO_3Rh$



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Abstract

$C_{24}H_{19}AsNO_3Rh$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1358(5)$ Å, $b = 9.6478(6)$ Å, $c = 12.4509(7)$ Å, $\alpha = 92.303(2)^\circ$, $\beta = 106.281(2)^\circ$, $\gamma = 99.137(2)^\circ$, $V = 1035.89(1)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0336$, $wR_{ref}(F^2) = 0.0900$, $T = 100$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

$[Rh(hopo)(CO)_2]$ (hopo=2-oxopyridine*N*-oxide) was synthesized according to the method described previously [5]. $[Rh(opo)(CO)(AsPh_3)]$ was synthesized by dissolving

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Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.25 × 0.18 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.44 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$,	13050, 5046, 0.052
R_{int} :	
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4283
$N(param)_{refined}$:	271
Programs:	SHELX [1], Bruker [2], Diamond [3], OLEX2 [4]

$[Rh(hopo)(CO)_2]$ (0.0210 g, 0.0780 mmol) in 5 cm³ of acetone. Triphenylarsine (0.0239 g, 0.0780 mmol) was added to the aforementioned solution with stirring. Some ice water was added dropwise to precipitate the product. Yellow plate crystals were obtained from recrystallization in acetone and a few drops of water.

IR: ν_{CO} 1954 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.11 (d, $J = 6.2$ Hz, 1H), 7.77 (s, 1H), 7.67 (d, $J = 6.7$ Hz, 15H), 7.56 (d, $J = 7.5$ Hz, 1H), 7.52–7.43 (m, 15H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 8.9$ Hz, 1H), 6.76 (d, $J = 8.7$ Hz, 1H), 6.60 (s, 1H), 6.49 (t, $J = 6.3$ Hz, 1H).

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) [$U_{iso}(H) = 1.2 U_{eq}$]. The graphics were obtained using the DIAMOND [3] program with 50% probability ellipsoids.

Comment

The carbonylation of methanol using a rhodium complex as catalyst is an industrial relevant reaction to produce acetic acid. One of the carbonyl ligands in the precursor $[Rh(BID)(CO)_2]$ complexes (BID = different monocharged

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

Atom	x	y	z	U _{iso} */U _{eq}
As1	0.34390 (3)	0.29682 (3)	0.68910 (2)	0.01458 (9)
C1	-0.0073 (3)	0.2082 (3)	0.9250 (2)	0.0159 (6)
C2	-0.0990 (4)	0.1868 (4)	0.9968 (3)	0.0216 (7)
H2	-0.096246	0.106811	1.038937	0.026*
C3	-0.1927 (4)	0.2794 (4)	1.0074 (3)	0.0228 (7)
H3	-0.254851	0.264685	1.057015	0.027*
C4	-0.1972 (4)	0.3968 (4)	0.9444 (3)	0.0215 (6)
H4	-0.264618	0.460778	0.949425	0.026*
C5	-0.1043 (4)	0.4182 (3)	0.8763 (3)	0.0197 (6)
H5	-0.106210	0.497969	0.833899	0.024*
C6	0.3112 (4)	0.0396 (4)	0.8152 (3)	0.0245 (7)
C7	0.4641 (3)	0.4813 (3)	0.7527 (2)	0.0158 (6)
C8	0.5769 (4)	0.5467 (3)	0.7066 (3)	0.0195 (6)
H8	0.591718	0.503615	0.641396	0.023*
C9	0.6679 (4)	0.6757 (4)	0.7567 (3)	0.0221 (7)
H9	0.743827	0.721223	0.724948	0.027*
C10	0.6476 (4)	0.7374 (3)	0.8527 (3)	0.0225 (7)
H10	0.710298	0.824772	0.887129	0.027*
C11	0.5357 (4)	0.6713 (4)	0.8985 (3)	0.0234 (7)
H11	0.522575	0.713399	0.964706	0.028*
C12	0.4426 (4)	0.5441 (3)	0.8482 (3)	0.0187 (6)
H12	0.364669	0.500332	0.878926	0.022*
C13	0.4939 (3)	0.2123 (3)	0.6375 (3)	0.0168 (6)
C14	0.6020 (4)	0.1499 (3)	0.7128 (3)	0.0224 (7)
H14	0.598476	0.144413	0.788066	0.027*
C15	0.7154 (4)	0.0955 (4)	0.6785 (3)	0.0287 (8)
H15	0.788727	0.052146	0.729902	0.034*
C16	0.7208 (4)	0.1049 (4)	0.5689 (3)	0.0311 (8)
H16	0.799203	0.069223	0.545710	0.037*
C17	0.6133 (4)	0.1656 (4)	0.4931 (3)	0.0274 (8)
H17	0.617064	0.170712	0.417814	0.033*
C18	0.4992 (4)	0.2195 (3)	0.5275 (3)	0.0201 (6)
H18	0.424950	0.261156	0.475562	0.024*
C19	0.2027 (3)	0.3333 (3)	0.5494 (2)	0.0161 (6)
C20	0.0878 (4)	0.2215 (4)	0.4912 (3)	0.0223 (7)
H20	0.081445	0.132005	0.520383	0.027*
C21	-0.0172 (4)	0.2407 (4)	0.3907 (3)	0.0269 (7)
H21	-0.094072	0.163763	0.350405	0.032*
C22	-0.0102 (4)	0.3715 (4)	0.3490 (3)	0.0242 (7)
H22	-0.083031	0.384688	0.280597	0.029*
C23	0.1031 (4)	0.4835 (4)	0.4071 (3)	0.0218 (6)
H23	0.107648	0.573354	0.378367	0.026*
C24	0.2102 (4)	0.4645 (3)	0.5073 (3)	0.0187 (6)
H24	0.288163	0.541137	0.546844	0.022*
N1	-0.0074 (3)	0.3254 (3)	0.8681 (2)	0.0211 (6)
O1	0.0812 (3)	0.1168 (2)	0.91090 (19)	0.0209 (5)
O2	0.0869 (3)	0.3463 (2)	0.80385 (18)	0.0194 (5)
O3	0.3684 (4)	-0.0581 (3)	0.8221 (3)	0.0394 (7)
Rh1	0.21129 (3)	0.18715 (2)	0.80716 (2)	0.01565 (8)

bidentate ligands such as cupferrate and 2-oxopyridine *N*-oxide, etc.) is substituted by tertiary phosphine ligands (PX₃) to form [Rh(BID)(CO)(PX₃)] complexes. These complexes have been studied intensively for a potential

application in catalytic hydroformylation, hydrogenation, carbonylation, and decarbonylation [6–13].

The coordination mode in the title complex is similar to the complexes reported previously [14, 15]. In this 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 indicated by the small bite angle of 79.87(2)° of the five membered ring as well as the As1-Rh1-C6, As1-Rh1-O2 and C6-Rh1-O1, angles of 92.37(2), 91.89(2) and 95.89(3)°, respectively. The Rh1-O1, Rh1-O2, Rh1-As1 and Rh1-C6 bond distances are 2.0532(1), 2.0442(1), 2.3377(1) and 1.8010(1) Å, respectively. The lengthening of Rh-O1 compared to Rh-O2 is due to the strong *trans* influence of the As atom. Phenyl hydrogen atoms in the figure are omitted for clarity (see the figure).

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