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Crystal structure of carbonyl(2-methylquinolin-8-olato- $\kappa^2 N, O$)(triphenylarsine- κAs)rhodium(I), $C_{29}H_{23}AsNO_2Rh$

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Abstract

$C_{29}H_{23}AsNO_2Rh$, triclinic, $P\bar{1}$ (no. 2), $a = 9.2778(18)$ Å, $b = 9.8274(16)$ Å, $c = 14.444(3)$ Å, $\alpha = 99.748(6)^\circ$, $\beta = 91.330(7)^\circ$, $\gamma = 114.197(6)^\circ$, $V = 1177.6(4)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0552$, $wR_{ref}(F^2) = 0.1005$, $T = 100$ 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

This complex was synthesized starting with the reduction of hydrated $RhCl_3$ in DMF which was refluxed for approximately 20 min to give a yellow solution of di- μ -chlorotetracarbonyldirhodium(I), $[RhCl(CO)_2]_2$ [5–7].

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Table 1: Data collection and handling.

Crystal:	Yellow cube
Size:	0.10 × 0.04 × 0.04 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.15 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	24079, 5879, 0.105
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3978
$N(param)_{refined}$:	308
Programs:	SHELX [1], Bruker [2], Diamond [3], OLEX2 [4]

The second step is the addition of an equivalent amount of 2-methyl-8-quinolinol ligand (2-mequinH) to the aforementioned yellow solution followed by addition of ice water to precipitate the dicarbonylrhodium(I) complex, $[Rh(2-mequin)(CO)_2]$. $[Rh(2-mequin)(CO)(AsPh_3)]$ was synthesized by dissolving $[Rh(2-mequin)(CO)_2]$ (0.0247 g, 0.0780 mmol) in 5 cm³ of acetone. Triphenylarsine, $AsPPh_3$, (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 needle-shaped crystals were obtained from recrystallization in acetone and a few drops of water.

¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.86–7.79 (m, 5H), 7.50–7.40 (m, 10H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.27 (d, $J = 7.9$ Hz, 1H), 6.89 (dd, $J = 7.9, 1.0$ Hz, 1H), 6.73 (dd, $J = 7.8, 1.1$ Hz, 1H), 3.03 (s, 3H).

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) [$U_{iso}(H) = 1.5 U_{eq}$]. The graphics were obtained using the DIAMOND [3] program with 50% probability ellipsoids. Some of the hydrogen atoms and hexyl carbon labels have been omitted for clarity.

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Rh1	0.24960 (5)	0.69631 (5)	0.19849 (3)	0.02261 (11)
As1	0.36553 (6)	0.62552 (5)	0.31787 (4)	0.02050 (13)
O1	0.0399 (4)	0.5280 (4)	0.2174 (3)	0.0332 (9)
O2	0.5611 (5)	0.9441 (5)	0.1880 (3)	0.0550 (13)
N1	0.0957 (6)	0.7155 (5)	0.0960 (3)	0.0298 (10)
C1	−0.0786 (7)	0.5043 (6)	0.1556 (4)	0.0309 (13)
C2	−0.2291 (7)	0.3905 (7)	0.1535 (5)	0.0410 (15)
H2	−0.248801	0.323930	0.197003	0.049*
C3	−0.3525 (8)	0.3717 (8)	0.0886 (5)	0.0481 (17)
H3	−0.455064	0.292999	0.089057	0.058*
C4	−0.3294 (8)	0.4627 (8)	0.0251 (4)	0.0484 (18)
H4	−0.414204	0.445224	−0.020111	0.058*
C5	−0.1797 (7)	0.5837 (7)	0.0256 (4)	0.0364 (14)
C6	−0.0541 (7)	0.6032 (6)	0.0903 (4)	0.0306 (13)
C7	−0.1439 (9)	0.6868 (9)	−0.0355 (4)	0.0515 (19)
H7	−0.224077	0.676139	−0.081852	0.062*
C8	0.0042 (9)	0.8028 (8)	−0.0298 (4)	0.0437 (16)
H8	0.025638	0.874419	−0.070091	0.052*
C9	0.1255 (8)	0.8145 (7)	0.0371 (4)	0.0374 (14)
C10	0.2865 (8)	0.9405 (7)	0.0394 (4)	0.0464 (16)
H10A	0.318792	1.003979	0.102864	0.070*
H10B	0.283186	1.002740	−0.006292	0.070*
H10C	0.363170	0.897533	0.022996	0.070*
C11	0.4393 (7)	0.8470 (6)	0.1900 (4)	0.0360 (14)
C12	0.5934 (6)	0.7119 (5)	0.3481 (3)	0.0223 (10)
C13	0.6902 (6)	0.7255 (5)	0.2759 (4)	0.0275 (12)
H13	0.645494	0.698478	0.212034	0.033*
C14	0.8534 (7)	0.7790 (6)	0.2970 (4)	0.0333 (13)
H14	0.919786	0.788502	0.247169	0.040*
C15	0.9194 (6)	0.8181 (6)	0.3886 (4)	0.0348 (13)
H15	1.031004	0.855036	0.402668	0.042*
C16	0.8220 (6)	0.8031 (6)	0.4599 (4)	0.0308 (12)
H16	0.867261	0.829268	0.523585	0.037*
C17	0.6598 (6)	0.7509 (5)	0.4409 (4)	0.0277 (12)
H17	0.594162	0.741652	0.491130	0.033*
C18	0.3154 (6)	0.4086 (5)	0.3011 (3)	0.0211 (10)
C19	0.4320 (6)	0.3592 (6)	0.3139 (4)	0.0311 (12)
H19	0.539454	0.430909	0.330156	0.037*
C20	0.3934 (7)	0.2057 (6)	0.3032 (4)	0.0342 (13)
H20	0.474551	0.172790	0.313294	0.041*
C21	0.2386 (6)	0.0991 (6)	0.2779 (4)	0.0283 (12)
H21	0.212590	−0.006595	0.269704	0.034*
C22	0.1214 (6)	0.1504 (6)	0.2648 (4)	0.0295 (12)
H22	0.013961	0.078841	0.248159	0.035*
C23	0.1599 (6)	0.3053 (6)	0.2758 (4)	0.0275 (11)
H23	0.079580	0.339322	0.266003	0.033*
C24	0.2934 (6)	0.6701 (5)	0.4395 (3)	0.0226 (11)
C25	0.2276 (6)	0.5625 (6)	0.4944 (4)	0.0292 (12)
H25	0.214827	0.461025	0.472537	0.035*
C26	0.1801 (6)	0.6015 (6)	0.5812 (4)	0.0320 (13)
H26	0.133876	0.526985	0.618758	0.038*
C27	0.2003 (6)	0.7489 (6)	0.6128 (4)	0.0313 (12)
H27	0.169009	0.776127	0.672772	0.038*
C28	0.2649 (7)	0.8567 (6)	0.5589 (4)	0.0348 (13)

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
H28	0.277994	0.958107	0.581389	0.042*
C29	0.3116 (6)	0.8180 (6)	0.4707 (4)	0.0293 (12)
H29	0.355369	0.892203	0.432594	0.035*

Comment

The precursor [Rh(I)₂(CO)₂][−] in the Monsanto process is relatively unstable and by modifying this precursor by introducing different bidentate ligands forming [Rh(BID)(CO)₂] complexes [where BID denote different monocharged bidentate ligands such as 2-oxypyridine *N*-oxide, 8-hydroxyquinoline, 2-methyl-8-quinolinol, etc.]. Then one of the CO ligands in this precursor may be substituted by monophosphine or arsine or stibine ligands to form [Rh(BID)(CO)(AX~3~)] complexes [where *A* = *P* or *As* or *Sb* and *X*₃ = Ph₃, Ph₂Cy, PhCy₂, Cy₃, etc.] and in most cases, these modified complexes are found to be more stable i.e. altering the electronic and steric properties of the ligand resulting in significant changes in the outcome of the catalytic process. These complexes have been studied intensively for potential application in catalytic hydroformylation, hydrogenation, carbonylation, and decarbonylation [8–19].

The coordination mode in the title complex is similar to the complexes reported previously [20]. In this structure, the ligands are coordinated to rhodium in a distorted square planar geometry. This distortion of the O1–Rh1–N1 bond angle from 90° is indicated by the small bite angle of 79.80 (7)° of the five membered ring as well as the As1–Rh1–O1, As1–Rh1–C11 and C11–Rh1–N1, angles of 86.54(8), 90.17(8) and 103.51 (10)°, respectively. The Rh1–O1, Rh1–N1, Rh1–As1 and Rh1–C11 bond distances are 2.0336(3), 2.1172(1), 2.3554(3) and 1.7998(3) Å, respectively. The lengthening of Rh1–N1 compared to Rh1–O1 is due to the *trans* influence of the As atom.

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