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Crystal structure of *N*-benzoyl-*N*-phenylhydroxylamino-dicarbonylrhodium(I), [Rh(BNA)CO₂]

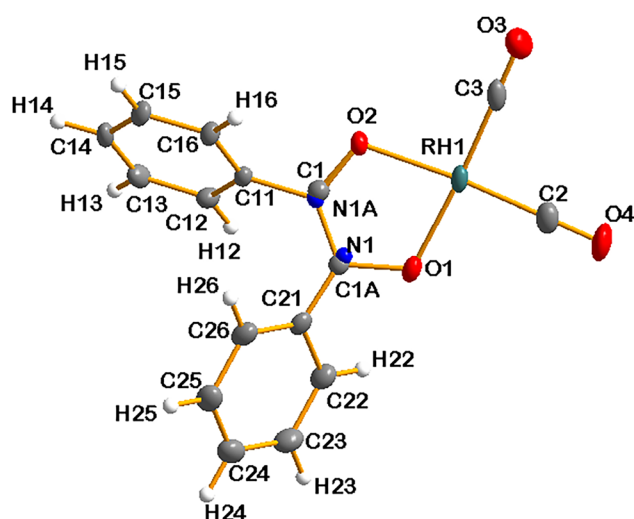


Table 1: Data collection and handling.

Crystal:	Yellow cuboid
Size:	0.34 × 0.25 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.24 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	29,933, 3438, 0.058
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3245
$N(\text{param})_{\text{refined}}$:	208
Programs:	Olex2, ^{1,2} SHELX, ^{3,4} Bruker, ⁵ Diamond ⁶

1 Source of material

[Rh(BNA)(CO)₂] was prepared *in situ* by heating RhCl₃·xH₂O (100 mg, 0.379 mmol), in 5 ml DMF under reflux for approximately 30 min. An equivalent amount of *N*-hydroxy-*N*-phenylbenzamide (BNA) bidentate ligand was then added to the cooled DMF solution of [RhCl(CO)₂]₂. The product was then precipitated by ice-water, followed by centrifuge. Yellow crystals suitable for X-ray diffraction were obtained from slow evaporation from an acetone solution (yield: 68 mg, 70.10 %). IR: CO 2061 cm⁻¹, 2001 cm⁻¹, ¹H NMR (400 MHz, chloroform-d₁): δ (ppm) 7.35–7.27 (m, 10H), 5.20 (s, 1H).

2 Experimental details

All reflections were merged and integrated with SAINT-PLUS and SADABS⁵ was used to correct absorption effects. The heavy atom method was used to solve the structures and refined through full-matrix least-squares cycles using Olex2. 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 0.98 Å (C–H) [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$]. The graphics were obtained using the DIAMOND⁶ program with 50 % probability ellipsoids. The highest peak is located 1.78 Å from Rh1 and the deepest hole is situated –3.38 Å from Rh1.

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Abstract

[Rh(BNA)(CO)₂], monoclinic, $P2_1/c$ (no. 14), $a = 12.095(3)$ Å, $b = 17.199(4)$ Å, $c = 6.778(15)$ Å, $\beta = 90.519(7)^\circ$, $V = 1398.5(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0241$, $wR_{\text{ref}}(F^2) = 0.0616$, $T = 100$ 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.

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

Atom	x	y	z	<i>U</i> _{iso} ^a / <i>U</i> _{eq}
C1 ^a	0.2274 (11)	0.6954 (6)	0.2589 (19)	0.019 (2)
C1A ^a	0.3001 (9)	0.6326 (5)	0.3418 (16)	0.018 (2)
C2	0.55711 (19)	0.78852 (13)	0.5053 (3)	0.0298 (4)
C3	0.40959 (16)	0.88815 (13)	0.3713 (3)	0.0265 (4)
C11	0.11655 (14)	0.66912 (10)	0.1677 (3)	0.0166 (3)
C12	0.10132 (16)	0.60947 (10)	0.0277 (3)	0.0212 (4)
H12	0.162962	0.579845	−0.005142	0.025*
C13	−0.00569 (17)	0.59389 (11)	−0.0635 (3)	0.0255 (4)
H13	−0.016894	0.553720	−0.160066	0.031*
C14	−0.09585 (16)	0.63668 (11)	−0.0141 (3)	0.0242 (4)
H14	−0.168692	0.624953	−0.074609	0.029*
C15	−0.07976 (15)	0.69667 (12)	0.1238 (3)	0.0230 (4)
H15	−0.141465	0.726165	0.156896	0.028*
C16	0.02645 (15)	0.71340 (10)	0.2129 (3)	0.0195 (4)
H16	0.037767	0.755126	0.304960	0.023*
C21	0.27747 (15)	0.55948 (11)	0.3952 (3)	0.0204 (4)
C22	0.35599 (17)	0.50278 (12)	0.3675 (3)	0.0258 (4)
H22	0.420243	0.515501	0.305406	0.031*
C23	0.33982 (19)	0.42729 (13)	0.4314 (3)	0.0308 (4)
H23	0.393398	0.388275	0.413535	0.037*
C24	0.24573 (19)	0.40869 (13)	0.5211 (3)	0.0310 (4)
H24	0.234230	0.356792	0.562228	0.037*
C25	0.16823 (18)	0.46598 (13)	0.5508 (3)	0.0297 (4)
H25	0.104227	0.453203	0.613530	0.036*
C26	0.18397 (17)	0.54194 (12)	0.4890 (3)	0.0256 (4)
H26	0.131572	0.581310	0.510583	0.031*
N1 ^a	0.3012 (6)	0.6441 (4)	0.3430 (12)	0.0118 (15)
N1A ^a	0.2275 (8)	0.6861 (4)	0.2646 (14)	0.0132 (19)
O1	0.40500 (10)	0.66380 (9)	0.4032 (2)	0.0231 (3)
O2	0.25383 (11)	0.76466 (8)	0.2607 (2)	0.0193 (3)
O3	0.40548 (14)	0.95477 (10)	0.3683 (2)	0.0368 (4)
O4	0.64642 (14)	0.79253 (11)	0.5788 (3)	0.0443 (4)
Rh1	0.41358 (2)	0.78105 (2)	0.38521 (2)	0.02036 (6)

^aOccupancy: 0.5.

3 Comment

The carbonylation of methanol using a rhodium complex as catalyst is an industrial reaction to produce acetic acid, and dicarbonyl complexes such as the one presented herein [Rh(BID)(CO)₂] (BID = different monocharged bidentate ligands such as cupferrate and hydroxamic acid) are precursors in the synthesis of possible catalysts.^{7–10} The title complex [Rh(BNA)(CO)₂], crystallised in the monoclinic space group *P*2₁/*c* with four molecules in the unit cell (*Z* = 4). The crystal structure is slightly distorted in a square planar geometry as it is observed from the small bite angle (O1–Rh–O2) of 80.48(6)°, and the bite angle is well within the range of similar reported structures. The structure also possesses the much larger angles of 175.74(8)° for the (C2–Rh–O2) bond angle

and 175.53(8)° for the (C3–Rh–O1) bond angle and the values are both below 180° and well within the bond angle range of similar dicarbonyl structures reported in literature.^{11,12} The C2–Rh–O1 and C3–Rh–O2 bond distances were also found to be 95.69(8)° and 95.48(9)° respectively, and they were also found to be similar to the bond angles of other similar structures reported in literature. A literature review on these rhodium dicarbonyl type of structures showed an average Rh–C bond distance of 1.848 Å, which is in good agreement with the Rh–C2 and Rh–C3 bond lengths of 1.844(3) Å and 1.838(3) Å respectfully. The C2–O01 and C3–O02 bond distances were also determined to be 1.147(3) Å and 1.136(3) Å respectively, and they were also found to be in good agreement with the bond distances of rhodium(I) dicarbonyl structures reported in literature. The Rh–O1 and Rh–O2 bond distances were also found to be 2.0396(16) Å and 2.0233(19) Å respectively, and this bond distances are also in good agreement with similar bond distances of other structures reported in literature.^{13,14} The bite distance was also found to be 2.265(4) Å and it is also in the same range of bite distances of various dicarbonyl structures reported in literature.^{15–18} However, the asymmetric unit of the reported structure shows a static positional disorder between the N1–C1 atoms of the bidentate ligand, this disorder was modelled using SIMU and ISOR shelx compatible constraints.

Molecular structure of [Rh(BNA)(CO)₂] (indicated with 50 % probability displacement ellipsoids). For the phenyl rings, the first digit indicates the ring number, while the second digit indicates the position of the carbon atom in the ring.

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